United States
Environmental Protection
Agency

EPA-600-R-16-236Fa
December 2016
www.epa.gov/hfstudy

Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States

Office of Research and Development
Washington, DC

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U.S. Environmental Protection Agency
Washington, DC 20460

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Preferred citation: USEPA (U.S. Environmental Protection Agency). 2016. Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States. Office of Research and Development, Washington, DC. EPA-600-R-16-236Fa.

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List of Acronyms/Abbreviations

Acronym	Definition
2BE	2-butoxyethanol
ACToR	Aggregated Computational Toxicology Resource database
AME	Acton Mickelson Environmental, Inc.
AMEC	AMEC Environment & Infrastructure, Inc.
ANRC	Arkansas Natural Resources Commission
AO	administrative order
AOGC	Arkansas Oil and Gas Commission
API	American Petroleum Institute
ATSDR	Agency for Toxic Substance and Disease Registry
AWWA	American Water Works Association
BLM	Bureau of Land Management
BTEX	benzene, toluene, ethylbenzene, and xylenes
CARES	Casella Altela Regional Environmental Services
CASRN	chemical abstract services registration number
CBI	confidential business information
CBM	coalbed methane
CCST	California Council on Science and Technology
CDC	Centers for Disease Control and Prevention
CDWR	Colorado Division of Water Resources
CFR	Code of Federal Regulations
CICAD	Concise International Chemical Assessment Document
CM	chemical mixing
CMV	commercial motor vehicle
COGCC	Colorado Oil and Gas Conservation Commission
COWDF	Commercial Oil Field Waste Disposal Facilities
CWA	Clean Water Act
CWCB	Colorado Water Conservation Board
CWT	centralized waste treatment
CWTF	centralized water treatment facility
DBNM	dibromochloronitromethane
DBP	disinfection byproduct
DecaBDE	decabromodipheyl ether
DfE	Design for the Environment
DI	Drilling Info, Inc.
DMA	dimethylamine
DMR	Discharge Monitoring Report
DNR	Department of Natural Resources
DO	dissolved oxygen
DOC	dissolved organic carbon

DOE	U.S. Department of Energy
DOGGR	California Department of Conservation's Division of Oil, Gas & Geothermal Resources
DOI	U.S. Department of the Interior
DOJ	U.S. Department of Justice
DOT	U.S. Department of Transportation
DRB	Delaware River Basin
DRO	diesel range organics
DWSHA	Drinking Water Standards and Health Advisories
ECHA	European Chemicals Agency
EERC	Energy and Environmental Research Center, University of North Dakota
EIA	U.S. Energy Information Administration
EPA	U.S. Environmental Protection Agency
EPA OW	U.S. Environmental Protection Agency, Office of Water
EPI	estimation programs interface
EPWU	El Paso Water Utility
ERCB	Energy Resource Conservation Board
ERG	Eastern Research Group
ESN	Environmental Services Network
ESOD	erythrocyte Cu, Zn-superoxide dismutase
EWI	Energy Water Initiative
FDA	U.S. Food and Drug Administration
FOIA	Freedom of Information Act
FRS	fluids recovery services
GES	Groundwater & Environmental Services, Inc.
GHGRP	Greenhouse Gas Reporting Program
GNB	Government of New Brunswick
GRAS	generally recognized as safe
GRO	gasoline range organics
GTI	Gas Technology Institute
GWPC	Ground Water Protection Council
HBCD	hexabromocyclododecane
HDPE	high-density polyethylene
HF	hydraulic fracturing
HHBP	Human Health Benchmarks for Pesticides
HISA	Highly Influential Scientific Assessment
HPG	hydroxypropylguar
HTS	high throughput screening
HUC	hydrological unit code
IAEA	International Atomic Energy Agency
IARC	International Agency for Research on Cancer
IHS	Information Handling Services
IOGCC	Interstate Oil and Gas Compact Commission

IPCC	Intergovernmental Panel on Climate Change
IPCS	International Programme on Chemical Safety
IRIS	Integrated Risk Information System
IUPAC	International Union of Pure and Applied Chemistry
KWO	Kansas Water Office
LDEQ	Louisiana Department of Environmental Quality
LOAEL	lowest observed adverse effect level
MCDA	multicriteria decision analysis
MCL	maximum contaminant level
MCLG	maximum containment level goal
MCOR	Marcellus Center for Outreach and Research
MGD	million gallons per day
MIT	mechanical integrity test
MMCF	million cubic feet
MRL	minimum risk level
MSC	Marcellus Shale Coalition
MT GWIC	Montana Ground Water Information Center
MTBE	methyl tert-butyl ether
MVR	mechanical vapor recompression
NAS	National Academy of Sciences
NDDMR	North Dakota Department of Mineral Resources
NDDOH	North Dakota Department of Health
NDMA	N-nitrosodimethylamine
NDPES	National Pollution Discharge Elimination System
NDSWC	North Dakota State Water Commission
NETL	National Energy Technology Laboratory
NGO	non-governmental organization
NIH	National Institutes of Health
NM OCD	New Mexico Oil Conservation Division
NM OSE	New Mexico Office of the State Engineer
NOAEL	no observed adverse effect level
NORM	naturally occurring radioactive material
NPC	National Petroleum Council
NPDES	National Pollution Discharge Elimination System
NPDWR	National Primary Drinking Water Regulations
NRC	National Resource Council
NTP	U.S. National Toxicology Program
NYSDEC	New York State Department of Environmental Conservation
O&G	oil and gas
ODNR	Ohio Department of Natural Resources
DMRM	Division of Mineral Resources Management
OECD	The Organisation for Economic Co-operation and Development

OEPA	Ohio Environmental Protection Agency
OMB	Office of Management and Budget
ORB	Ohio River Basin
ORD	Office of Research and Development
OSF	oral slope factor
OSHA	Occupational Safety & Health Administration
OSWER	Office of Solid Water and Emergency Response
OWRB	Oklahoma Water Resources Board
PA DCNR	Pennsylvania Department of Conservation and Natural Resources
PA DEP	Pennsylvania Department of Environmental Protection
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PFBC	Pennsylvania Fish and Boat Commission
PDL	positive determination letter
PMF	Positive Matrix Factorization
PMN	pre-manufacturing notices
POD	point-of-departure
POTW	publicly owned treatment work
PPRTV	provisional peer-reviewed toxicity value
PVC	polyvinyl chloride
PWS	public water system
PWSA	Pittsburgh Water and Sewer Authority
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
QSAR	Quantitative Structure Activity Relationship
RAHC	reasonably anticipated to be a human carcinogen
RBC	red blood cells
RfD	reference dose
RfV	reference value
RO	reverse osmosis
SAB	Science Advisory Board
SAIC	Science Applications International Corporation
SAR	sodium adsorption ratio
SCN	thiocyanates
SDWA	Safe Drinking Water Act
SDWIS	Safe Drinking Water Information System
SEECO	Southern Electrical Equipment Company
SGEIS	supplemented generic environmental impact statement
SHS MSC	statewide health standards for medium-specific concentrations
SMCL	secondary maximum contaminant level
SPE	Society of Petroleum Engineers

SRB	Susquehanna River basin
SRBC	Susquehanna River Basin Commission
STO	Statoil
STRONGER	State review of oil and natural gas environmental regulations
SVOC	semi-volatile organic compounds
SWE	Southwestern Energy
TARM	TerrAqua Resource Management
TBA	tert-butyl alcohol
TDI	tolerable daily intake
TDS	total dissolved solids
TENORM	technologically enhanced naturally occurring radioactive material
THM	trihalomethane
TIPRO	Texas Independent Producers and Royalty Owners Association
TMDL	total maximum daily load
TOC	total organic carbon
TOPKAT	Toxicity Prediction by Komputer Assisted Technology
TPH	total petroleum hydrocarbons
TPHWG	Total Petroleum Hydrocarbon Criteria Working Group
TSS	total suspended solids
TTC	Threshold of Toxicological Concern
TTHM	total trihalomethane
TWDB	Texas Water Development Board
TXRRC	Texas Railroad Commission
UCRB	Upper Colorado River basin
UIC	underground injection control
UOG	unconventional oil and gas
USGAO	U.S. Government Accountability Office
USGS	U.S. Geological Survey
UWS	Universal Well Services
VES	viscoelastic surfactant
VOC	volatile organic compounds
WAWSA	Western Area Water Supply Authority
WFR	Well File Review
WHO	World Health Organization
WOE	weight of evidence
WRF	Water Research Foundation
WVDEP	West Virginia Department of Environmental Protection
WWTP	wastewater treatment plant
WYOGCC	Wyoming Oil and Gas Conservation Commission

Preface

Hydraulic fracturing is a technique used to increase oil and gas production from underground oil- or gas-bearing rock formations. Since the mid-2000s, the combination of hydraulic fracturing and directional drilling has become widespread, raising concerns about the potential impacts of hydraulic fracturing on drinking water resources. This concern is the focus of this report.

In 2010, the U.S. Environmental Protection Agency (EPA) initiated a study of the potential impacts of hydraulic fracturing activities on drinking water resources. The EPA defined the scope of its study to focus on the acquisition, use, disposal, and reuse of water used for hydraulic fracturing—what we call the hydraulic fracturing water cycle. This was done in recognition that concerns raised about potential impacts were not limited to the relatively short-term act of fracturing rock, but can include impacts related to other activities associated with hydraulic fracturing.

The EPA's study included the development of multiple research projects using the following research approaches: the analysis of existing data, scenario and modeling evaluations, laboratory studies, toxicological assessments, and five case studies. Throughout the study, the EPA engaged with stakeholders, including industry, the states, tribal nations, academia, and others, for input on the scope, approach, and initial results. To date, the study has resulted in the publication of multiple peer-reviewed scientific products, including 13 EPA technical reports and 14 journal articles.

This report represents the capstone product of the EPA's hydraulic fracturing drinking water study. It captures the state-of-the-science concerning drinking water impacts from activities in the hydraulic fracturing activities water cycle and integrates the results of the EPA's study of the subject with approximately 1,200 other publications and sources of information. The goals of this report were to assess the potential for activities in the hydraulic fracturing water cycle to impact the quality or quantity of drinking water resources and to identify factors that affect the frequency or severity of those impacts.

This report is a science document and does not present or evaluate policy options or make policy recommendations. A draft of this report was reviewed by the EPA's independent Science Advisory Board (SAB). Reflecting the complexity of the subject, the expert ad hoc panel formed by the SAB was the largest ever convened for the review of a scientific product. Combined with over 100,000 comments submitted by members of the public, SAB comments helped the EPA to refine, clarify, and better support the final conclusions presented in this report.

The release of this final assessment report marks the completion of the EPA's hydraulic fracturing drinking water study. The study has already prompted increased dialogue among industry, the states, tribal nations, the public, and others concerning how drinking water resources can be better protected in areas where hydraulic fracturing is occurring or being considered. However, there are data gaps and uncertainties limiting our understanding of the impacts of hydraulic fracturing activities on drinking water resources. As additional data become available, and with continued dialogue among stakeholders, our understanding of the potential impacts of hydraulic fracturing on drinking water resources will improve.

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The development of this assessment involved individuals from across the Agency, many of which have been listed as authors, contributors or reviewers, or acknowledged below. We want to specifically highlight and acknowledge Jeanne Briskin for her role with making the EPA's Hydraulic Fracturing Drinking Water Study a success. Jeanne was responsible for the development of the 2011 Study Plan and for coordinating the implementation of the projects outlined in that Study Plan. Jeanne also played a large role with reaching out to stakeholders for input that informed the development of the reports and publications resulting from Study Plan projects, and the development of this assessment.

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Contract support was provided by The Cadmus Group, Inc. under contracts EP-C-08-015 and EP-C-15-022 and by Neptune & Co., Inc. under contract EP-C-13-022. Authors and contributors included student service contractors to USEPA: Kevin Blackwood (Contract EP-13-C-000133); Maryam Cluff (Contract EP-13-H-000438); Ashley McElmury (Contract EP-12-C-000025); Claudia Meza-Cuadra (Contract EP-13-H-000054); Alison Singer (Contract EP-13-H-000474); Sarah Solomon (Contract EP-D-15-003); Jessica Wilhelm (Contract EP-D-15-003); Jie Xu (Contract EP-13-C-00120); Liabeth Yohannes (Contract EP-14-H-000455). Kay Pinley was supported under the Senior Environmental Employment Program under agreement CQ-835363 with NCCBA.

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Executive Summary

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Executive Summary

People rely on clean and plentiful water resources to meet their basic needs, including drinking, bathing, and cooking. In the early 2000s, members of the public began to raise concerns about potential impacts on their drinking water from hydraulic fracturing at nearby oil and gas production wells. In response to these concerns, Congress urged the U.S. Environmental Protection Agency (EPA) to study the relationship between hydraulic fracturing for oil and gas and drinking water in the United States.

The goals of the study were to assess the potential for activities in the hydraulic fracturing water cycle to impact the quality or quantity of drinking water resources and to identify factors that affect the frequency or severity of those impacts. To achieve these goals, the EPA conducted independent research, engaged stakeholders through technical workshops and roundtables, and reviewed approximately 1,200 cited sources of data and information. The data and information gathered through these efforts served as the basis for this report, which represents the culmination of the EPA's study of the potential impacts of hydraulic fracturing for oil and gas on drinking water resources.

The hydraulic fracturing water cycle describes the use of water in hydraulic fracturing, from water withdrawals to make hydraulic fracturing fluids, through the mixing and injection of hydraulic fracturing fluids in oil and gas production wells, to the collection and disposal or reuse of produced water. These activities can impact drinking water resources under some circumstances. Impacts can range in frequency and severity, depending on the combination of hydraulic fracturing water cycle activities and local- or regional-scale factors. The following combinations of activities and factors are more likely than others to result in more frequent or more severe impacts:

- Water withdrawals for hydraulic fracturing in times or areas of low water availability, particularly in areas with limited or declining groundwater resources;
- Spills during the management of hydraulic fracturing fluids and chemicals or produced water that result in large volumes or high concentrations of chemicals reaching groundwater resources;
- Injection of hydraulic fracturing fluids into wells with inadequate mechanical integrity, allowing gases or liquids to move to groundwater resources;
- Injection of hydraulic fracturing fluids directly into groundwater resources;
- Discharge of inadequately treated hydraulic fracturing wastewater to surface water resources; and
- Disposal or storage of hydraulic fracturing wastewater in unlined pits, resulting in contamination of groundwater resources.

The above conclusions are based on cases of identified impacts and other data, information, and analyses presented in this report. Cases of impacts were identified for all stages of the hydraulic fracturing water cycle. Identified impacts generally occurred near hydraulically fractured oil and gas production wells and ranged in severity, from temporary changes in water quality to contamination that made private drinking water wells unusable.

The available data and information allowed us to qualitatively describe factors that affect the frequency or severity of impacts at the local level. However, significant data gaps and uncertainties in the available data prevented us from calculating or estimating the national frequency of impacts on drinking water resources from activities in the hydraulic fracturing water cycle. The data gaps and uncertainties described in this report also precluded a full characterization of the severity of impacts.

The scientific information in this report can help inform decisions by federal, state, tribal, and local officials; industry; and communities. In the short-term, attention could be focused on the combinations of activities and factors outlined above. In the longer-term, attention could be focused on reducing the data gaps and uncertainties identified in this report. Through these efforts, current and future drinking water resources can be better protected in areas where hydraulic fracturing is occurring or being considered.

Drinking Water Resources in the United States

In this report, drinking water resources are defined as any water that now serves, or in the future could serve, as a source of drinking water for public or private use. This includes both surface water resources and groundwater resources (Text Box ES-1). In 2010, approximately 58% of the total volume of water withdrawn for public and non-public water supplies came from surface water resources and approximately 42% came from groundwater resources (Maupin et al., 2014).[1] Most people (86% of the population) in the United States relied on public water supplies for their drinking water in 2010, and approximately 14% of the population obtained drinking water from non-public water supplies. Non-public water supplies are often private water wells that supply drinking water to a residence.

Future access to high-quality drinking water in the United States will likely be affected by changes in climate and water use. Since 2000, about 30% of the total area of the contiguous United States has experienced moderate drought conditions and about 20% has experienced severe drought conditions. Declines in surface water resources have led to increased withdrawals and net depletions of groundwater in some areas. As a result, non-fresh water resources (e.g., wastewater from sewage treatment plants, brackish groundwater and surface water, and seawater) are increasingly treated and used to meet drinking water demand.

Natural processes and human activities can affect the quality and quantity of current and future drinking water resources. This report focuses on the potential for activities in the hydraulic fracturing water cycle to impact drinking water resources; other processes or activities are not discussed.

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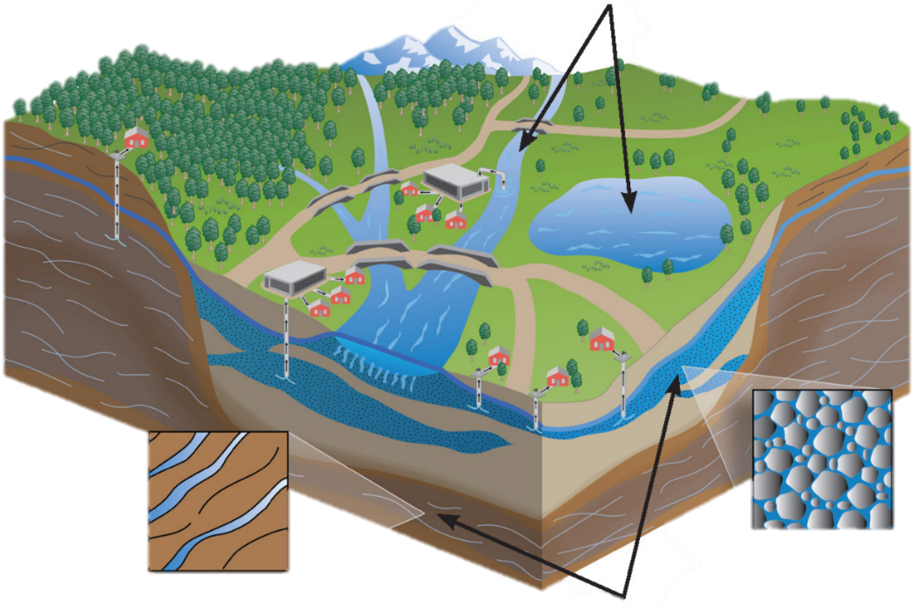
[1] Public water systems provide water for human consumption from surface or groundwater through pipes or other infrastructure to at least 15 service connections or serve an average of at least 25 people for at least 60 days a year. Non-public water systems have fewer than 15 service connections and serve fewer than 25 individuals.

Text Box ES-1. Drinking Water Resources.

In this report, drinking water resources are considered to be any water that now serves, or in the future could serve, as a source of drinking water for public or private use. This includes both surface water bodies and underground rock formations that contain water.

Surface water resources include water bodies located on the surface of the Earth. Rivers, springs, lakes, and reservoirs are examples of surface water resources. Water quality and quantity are often considered when determining whether a surface water resource could be used as a drinking water resource.



Groundwater resources are underground rock formations that contain water. Groundwater resources are found at different depths nearly everywhere in the United States. Resource depth, water quality, and water yield are often considered when determining whether a groundwater resource could be used as a drinking water resource.

Hydraulic Fracturing for Oil and Gas in the United States

Hydraulic fracturing is frequently used to enhance oil and gas production from underground rock formations and is one of many activities that occur during the life of an oil and gas production well (Figure ES-1). During hydraulic fracturing, hydraulic fracturing fluid is injected down an oil or gas production well and into the targeted rock formation under pressures great enough to fracture the oil- and gas-bearing rock.[1] The hydraulic fracturing fluid usually carries proppant (typically sand) into the newly-created fractures to keep the fractures "propped" open. After hydraulic fracturing, oil, gas, and other fluids flow through the fractures and up the production well to the surface, where they are collected and managed.

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[1] The targeted rock formation (sometimes called the "target zone" or "production zone") is the portion of a subsurface rock formation that contains the oil or gas to be extracted.

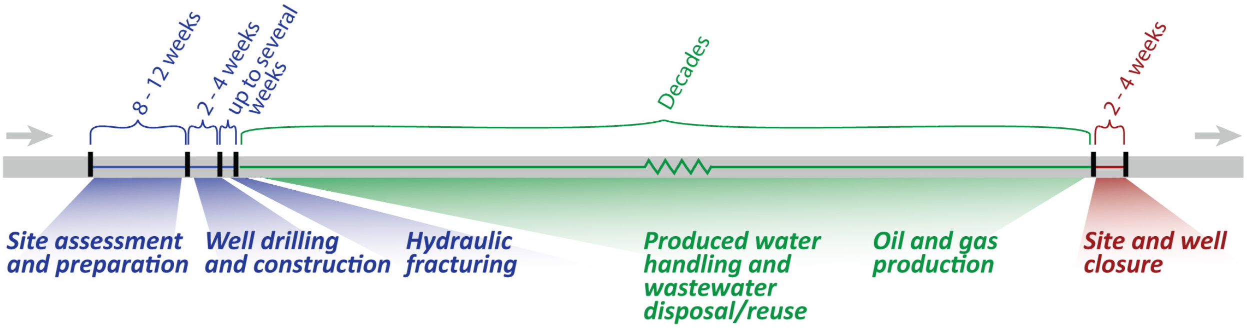

Figure ES-1. General timeline and summary of activities at a hydraulically fractured oil or gas production well.

Hydraulically fractured oil and gas production wells have significantly contributed to the surge in domestic oil and gas production, accounting for slightly more than 50% of oil production and nearly 70% of gas production in 2015 (EIA, 2016c, d). The surge occurred when hydraulic fracturing was combined with directional drilling technologies around 2000. Directional drilling allows oil and gas production wells to be drilled horizontally or directionally along the targeted rock formation, exposing more of the oil- or gas-bearing rock formation to the production well. When combined with directional drilling technologies, hydraulic fracturing expanded oil and gas production to oil- and gas-bearing rock formations previously considered uneconomical. Although hydraulic fracturing is commonly associated with oil and gas production from deep, horizontal wells drilled into shale (e.g., the Marcellus Shale in Pennsylvania or the Bakken Shale in North Dakota), it has been used in a variety of oil and gas production wells (Text Box ES-2) and other types of oil- or gas-bearing rock (e.g., sandstone, carbonate, and coal).

Approximately 1 million wells have been hydraulically fractured since the technique was first developed in the late 1940s (Gallegos and Varela, 2015; IOGCC, 2002). Roughly one third of those wells were hydraulically fractured between 2000 and approximately 2014. Wells hydraulically fractured between 2000 and 2013 were located in pockets of activity across the United States (Figure ES-2). Based on several different data compilations, we estimate that 25,000 to 30,000 new wells were drilled and hydraulically fractured in the United States each year between 2011 and 2014, in addition to existing wells that were hydraulically fractured to increase production.[1] Following the decline in oil and gas prices, the number of new wells drilled and hydraulically fractured appears to have decreased, with about 20,000 new wells drilled and hydraulically fractured in 2015.

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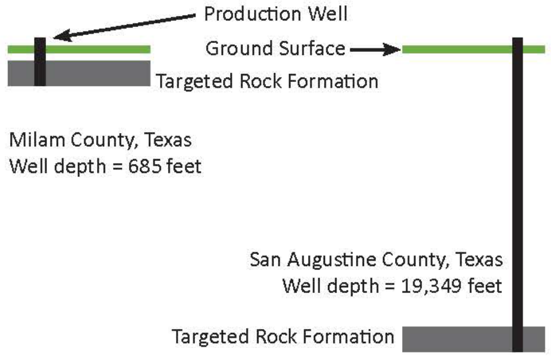
[1] See Table 3-1 in Chapter 3.

Text Box ES-2. Hydraulically Fractured Oil and Gas Production Wells.

Hydraulically fractured oil and gas production wells come in different shapes and sizes. They can have different depths, orientations, and construction characteristics. They can include new wells (i.e., wells that are hydraulically fractured soon after construction) and old wells (i.e., wells that are hydraulically fractured after producing oil and gas for some time).

Well Depth

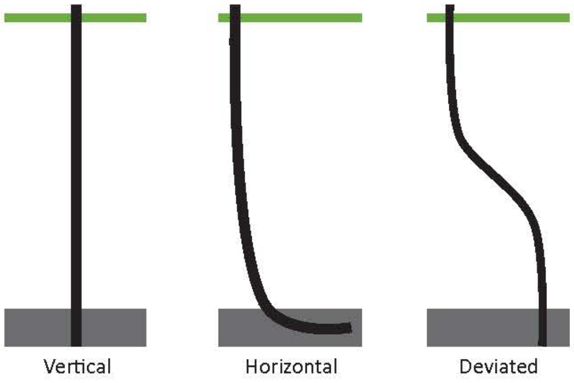
Wells can be relatively shallow or relatively deep, depending on the depth of the targeted rock formation.



Well depths and locations from FracFocus.org.

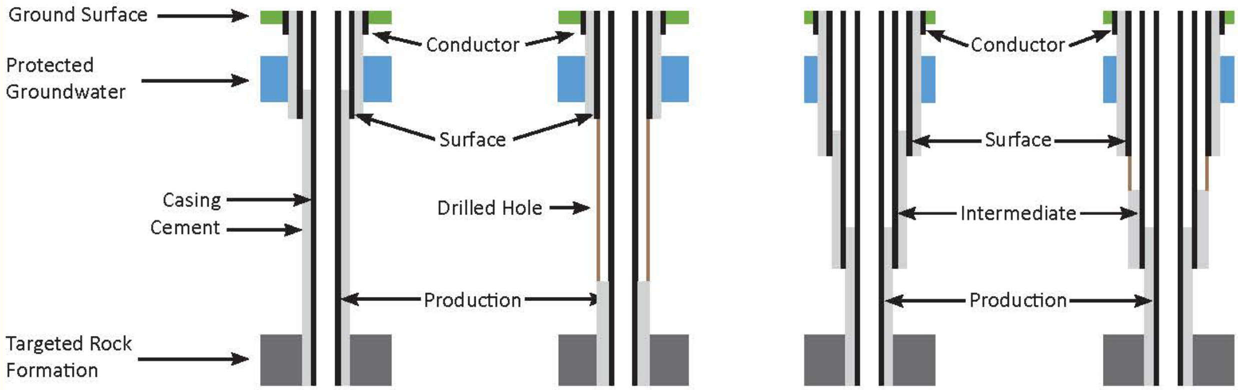
Well Orientation

Wells can be vertical, horizontal, or deviated.



Well Construction Characteristics

Wells are typically constructed using multiple layers of casing and cement. The subsurface environment, state and federal regulations, and industry experience and practices influence the number and placement of casing and cement.



Conductor, surface, and production casings

Conductor, surface, intermediate, and production casings

Well diagrams are not to scale.

Oil and Gas Production Well Dictionary

Casing	Steel pipe that extends from the ground surface to the bottom of the drilled hole
Cement	A slurry that hardens around the outside of the casing; cement fills the space between casings or between a casing and the drilled hole and provides support for the casing
Conductor casing	Casing that prevents the in-fill of dirt and rock in the uppermost few feet of drilled hole
Intermediate casing	Casing that seals off intermediate rock formations that may have different pressures than deeper or shallower rock formations
Production casing	Casing that transports fluids up and down the well
Surface casing	Casing that seals off groundwater resources that are identified as drinking water or useable
Targeted rock formation	The part of a rock formation that contains the oil and/or gas to be extracted

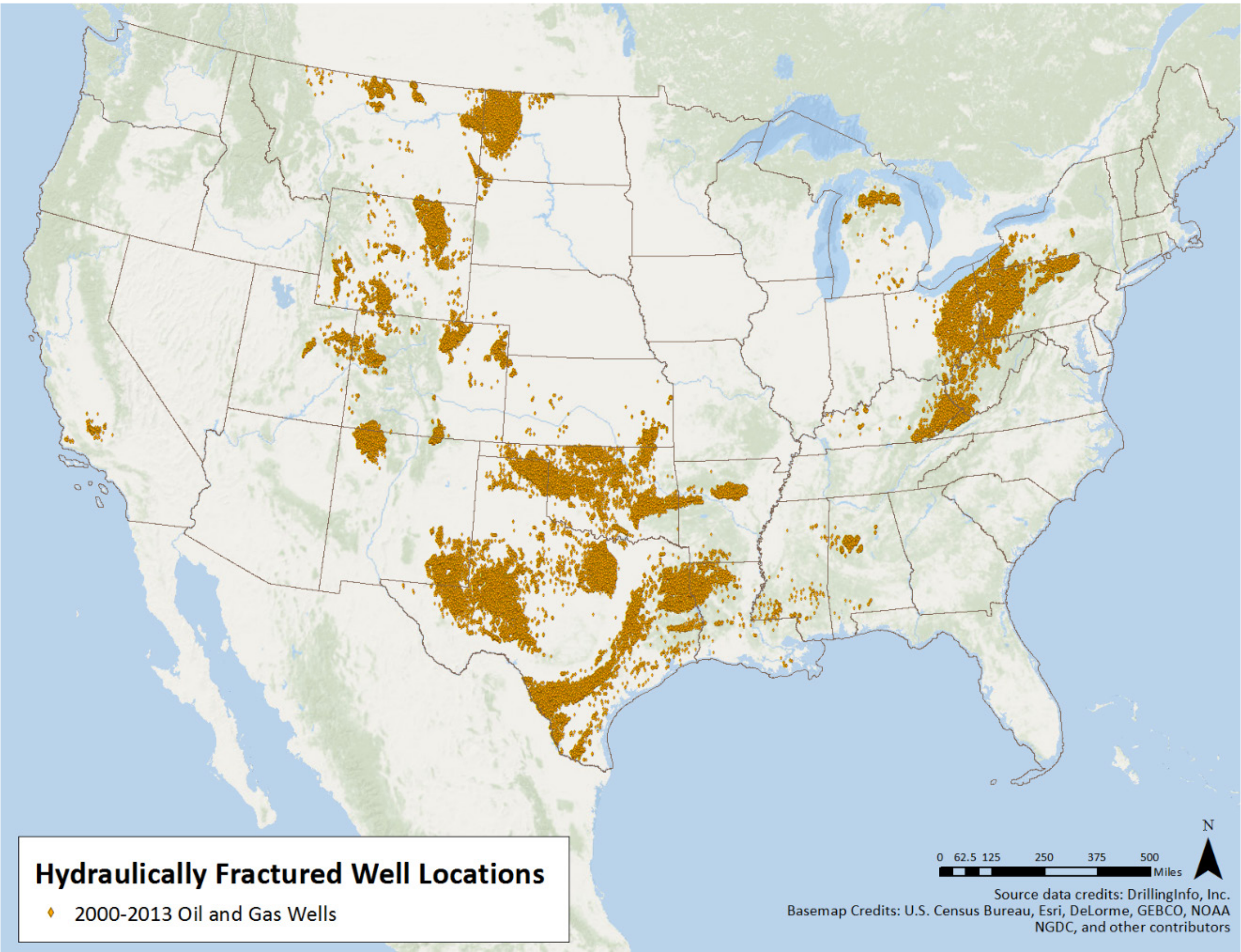


Figure ES-2. Locations of approximately 275,000 wells that were drilled and likely hydraulically fractured between 2000 and 2013.
Data from DrillingInfo (2014a).

Hydraulically fractured oil and gas production wells can be located near or within sources of drinking water. Between 2000 and 2013, approximately 3,900 public water systems were estimated to have had at least one hydraulically fractured well within 1 mile of their water source; these public water systems served more than 8.6 million people year-round in 2013. An additional 3.6 million people were estimated to have obtained drinking water from non-public water supplies in counties with at least one hydraulically fractured well.[1] Underground, hydraulic fracturing can occur in close vertical proximity to drinking water resources. In some parts of the United States (e.g., the Powder River Basin in Montana and Wyoming), there is no vertical distance between the top of the hydraulically fractured oil- or gas-bearing rock formation and the bottom of treatable water, as determined by data from state oil and gas agencies and state geological survey data.[2] In other parts of the country (e.g., the Eagle Ford Shale in Texas), there can be thousands of feet of

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[1] This estimate only includes counties in which 30% or more of the population (i.e., two or more times the national average) relied on non-public water supplies in 2010. See Section 2.5 in Chapter 2.

[2] In these cases, water that is naturally found in the oil- and gas-bearing rock formation meets the definition of drinking water in some parts of the basin. See Section 6.3.2 in Chapter 6.

rock that separate treatable water from the hydraulically fractured oil- or gas-bearing rock formation. When hydraulically fractured oil and gas production wells are located near or within drinking water resources, there is a greater potential for activities in the hydraulic fracturing water cycle to impact those resources.

Approach: The Hydraulic Fracturing Water Cycle

The EPA studied the relationship between hydraulic fracturing for oil and gas and drinking water resources using the hydraulic fracturing water cycle (Figure ES-3). The hydraulic fracturing water cycle has five stages; each stage is defined by an activity involving water that supports hydraulic fracturing. The stages and activities of the hydraulic fracturing water cycle include:

- **Water Acquisition:** the withdrawal of groundwater or surface water to make hydraulic fracturing fluids;
- **Chemical Mixing:** the mixing of a base fluid (typically water), proppant, and additives at the well site to create hydraulic fracturing fluids;[1]
- **Well Injection:** the injection and movement of hydraulic fracturing fluids through the oil and gas production well and in the targeted rock formation;
- **Produced Water Handling:** the on-site collection and handling of water that returns to the surface after hydraulic fracturing and the transportation of that water for disposal or reuse;[2] and
- **Wastewater Disposal and Reuse:** the disposal and reuse of hydraulic fracturing wastewater.[3]

Potential impacts on drinking water resources from the above activities are considered in this report. We do not address other concerns that have been raised by stakeholders about hydraulic fracturing (e.g., potential air quality impacts or induced seismicity) or other oil and gas exploration and production activities (e.g., environmental impacts from site selection and development), as these were not included in the scope of the study. Additionally, this report is not a human health risk assessment; it does not identify populations exposed to hydraulic fracturing-related chemicals, and it does not estimate the extent of exposure or estimate the incidence of human health impacts.

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[1] A base fluid is the fluid into which proppants and additives are mixed to make a hydraulic fracturing fluid; water is an example of a base fluid. Additives are chemicals or mixtures of chemicals that are added to the base fluid to change its properties.

[2] “Produced water” is defined in this report as water that flows from and through oil and gas wells to the surface as a by-product of oil and gas production.

[3] “Hydraulic fracturing wastewater” is defined in this report as produced water from hydraulically fractured oil and gas wells that is being managed using practices that include, but are not limited to, injection in Class II wells, reuse in other hydraulic fracturing operations, and various aboveground disposal practices. The term “wastewater” is being used as a general description of certain waters and is not intended to constitute a term of art for legal or regulatory purposes. Class II wells are used to inject wastewater associated with oil and gas production underground and are regulated under the Underground Injection Control Program of the Safe Drinking Water Act.

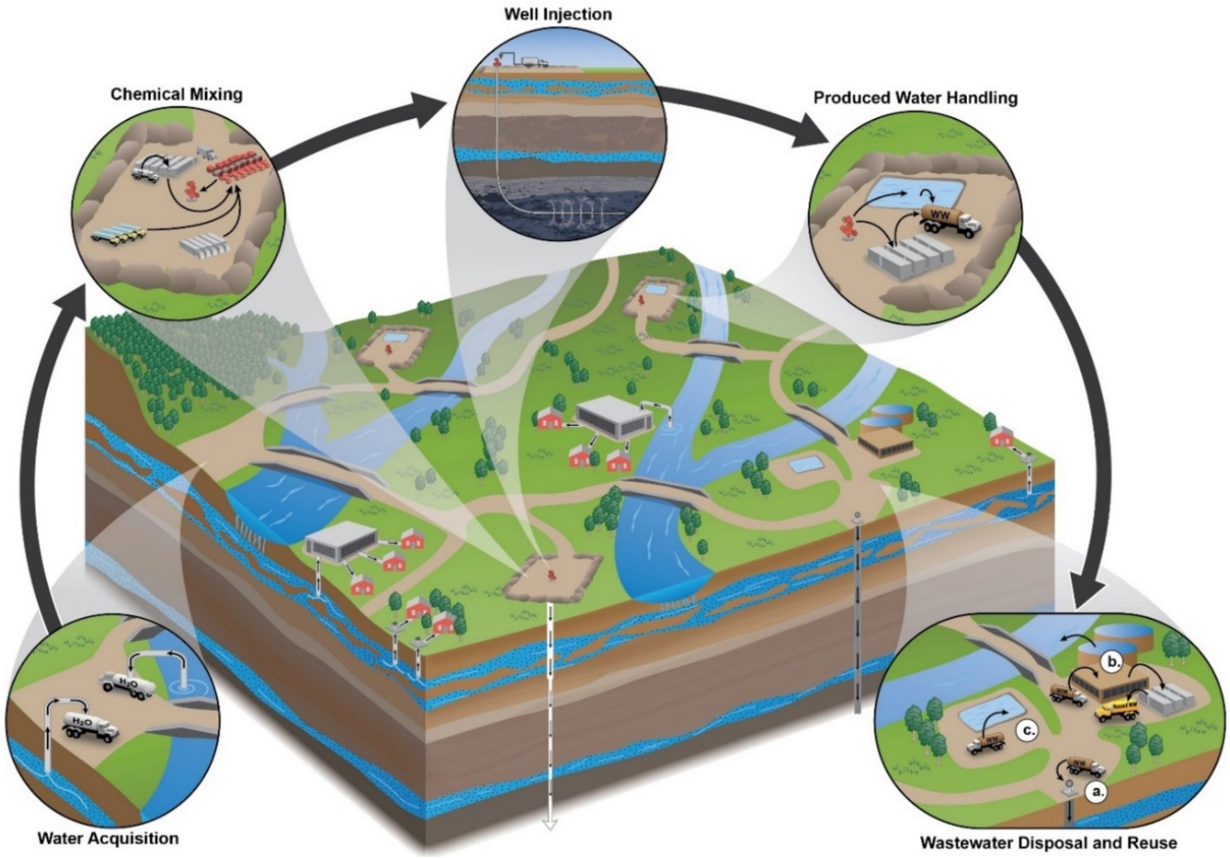


Figure ES-3. The five stages of the hydraulic fracturing water cycle.
The stages (shown in the insets) identify activities involving water that support hydraulic fracturing for oil and gas. Activities may take place in the same watershed or different watersheds and close to or far from drinking water resources. Thin arrows in the insets depict the movement of water and chemicals. Specific activities in the "Wastewater Disposal and Reuse" inset include (a) disposal of wastewater through underground injection, (b) wastewater treatment followed by reuse in other hydraulic fracturing operations or discharge to surface waters, and (c) disposal through evaporation or percolation pits.

Each stage of the hydraulic fracturing water cycle was assessed to identify (1) the potential for impacts on drinking water resources and (2) factors that affect the frequency or severity of impacts. Specific definitions used in this report are provided below:

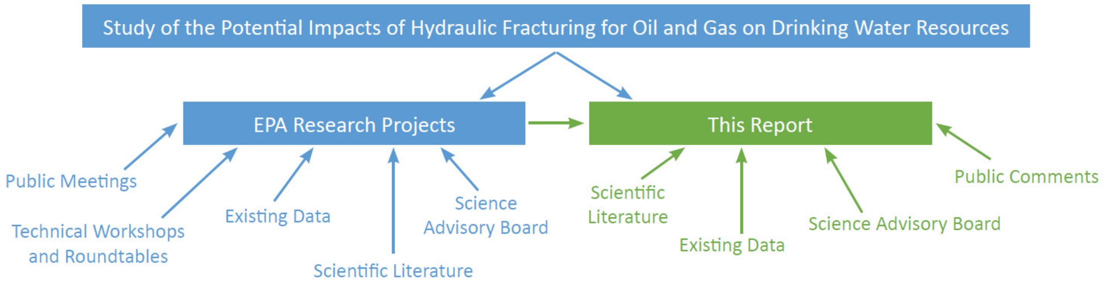
- An **impact** is any change in the quality or quantity of drinking water resources, regardless of severity, that results from an activity in the hydraulic fracturing water cycle.
- A **factor** is a feature of hydraulic fracturing operations or an environmental condition that affects the frequency or severity of impacts.
- **Frequency** is the number of impacts per a given unit (e.g., geographic area, unit of time, number of hydraulically fractured wells, or number of water bodies).
- **Severity** is the magnitude of change in the quality or quantity of a drinking water resource as measured by a given metric (e.g., duration, spatial extent, or contaminant concentration).

Factors affecting the frequency or severity of impacts were identified because they describe conditions under which impacts are more or less likely to occur and because they could inform the development of future strategies and actions to prevent or reduce impacts. Although no attempt was made to identify or evaluate best practices, ways to reduce the frequency or severity of impacts from activities in the hydraulic fracturing water cycle are described in this report when they were reported in the scientific literature. Laws, regulations, and policies also exist to protect drinking water resources, but a comprehensive summary and broad evaluation of current or proposed regulations and policies was beyond the scope of this report.

Relevant scientific literature and data were evaluated for each stage of the hydraulic fracturing water cycle. Literature included articles published in science and engineering journals, federal and state government reports, non-governmental organization reports, and industry publications. Data sources included federal- and state-collected data sets, databases maintained by federal and state government agencies, other publicly available data, and industry data provided to the EPA.[1] The relevant literature and data complement research conducted by the EPA under its *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (Text Box ES-3).

Text Box ES-3. The EPA's *Study of the Potential Impacts of Hydraulic Fracturing for Oil and Gas on Drinking Water Resources*.

The EPA's study is the first national study of the potential impacts of hydraulic fracturing for oil and gas on drinking water resources. It included independent research projects conducted by EPA scientists and contractors and a state-of-the-science assessment of available data and information on the relationship between hydraulic fracturing and drinking water resources (i.e., this report).



Throughout the study, the EPA consulted with the Agency's independent Science Advisory Board (SAB) on the scope of the study and the progress made on the research projects. The SAB also conducted a peer review of both the *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (U.S. EPA, 2011d; referred to as the Study Plan in this report) and a draft of this report.

Stakeholder engagement also played an important role in the development and implementation of the study. While developing the scope of the study, the EPA held public meetings to get input from stakeholders on the study scope and design. While conducting the study, the EPA requested information from the public and engaged with technical, subject-matter experts on topics relevant to the study in a series of technical workshops and roundtables. For more information on the EPA's study, including the role of the SAB and stakeholders, visit www.epa.gov/hfstudy.

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[1] Industry data was provided to the EPA in response to two separate information requests to oil and gas service companies and oil and gas production well operators. Some of these data were claimed as confidential business information under the Toxic Substances Control Act and were treated as such in this report.

A draft of this report underwent peer review by the EPA's Science Advisory Board (SAB). The SAB is an independent federal advisory committee that often conducts peer reviews of high-profile scientific matters relevant to the EPA. Members of the SAB and ad hoc panels formed under the auspices of the SAB are nominated by the public and selected based on factors such as technical expertise, knowledge, experience, and absence of any real or perceived conflicts of interest. Peer review comments provided by the SAB and public comments submitted to the SAB during their peer review, including comments on major conclusions and technical content, were carefully considered in the development of this final document.

A summary of the activities in the hydraulic fracturing water cycle and their potential to impact drinking water resources is provided below, including what is known about human health hazards associated with chemicals identified across all stages of the hydraulic fracturing water cycle. Additional details are available in the full report.

Water Acquisition

Activity: The withdrawal of groundwater or surface water to make hydraulic fracturing fluids.

Relationship to Drinking Water Resources: Groundwater and surface water resources that provide water for hydraulic fracturing fluids can also provide drinking water for public or non-public water supplies.

Water is the major component of nearly all hydraulic fracturing fluids, typically making up 90–97% of the total fluid volume injected into a well. The median volume of water used, per well, for hydraulic fracturing was approximately 1.5 million gallons (5.7 million liters) between January 2011 and February 2013, as reported in FracFocus 1.0 (Text Box ES-4). There was wide variation in the water volumes reported per well, with 10th and 90th percentiles of 74,000 gallons (280,000 liters) and 6 million gallons (23 million liters) per well, respectively. There was also variation in water use per well within and among states (Table ES-1). This variation likely results from several factors, including the type of well, the fracture design, and the type of hydraulic fracturing fluid used. An analysis of hydraulic fracturing fluid data from Gallegos et al. (2015) indicates that water volumes used per well have increased over time as more horizontal wells have been drilled.

Water used for hydraulic fracturing is typically fresh water taken from available groundwater and/or surface water resources located near hydraulically fractured oil and gas production wells. Water sources can vary across the United States, depending on regional or local water availability; laws, regulations, and policies; and water management practices. Hydraulic fracturing operations in the humid eastern United States generally rely on surface water resources, whereas operations in the arid and semi-arid western United States generally rely on groundwater or surface water. Geographic differences in water use for hydraulic fracturing are illustrated in Figure ES-4, which shows that most of the water used for hydraulic fracturing in the Marcellus Shale region of the Susquehanna River Basin came from surface water resources between approximately 2008 and 2013. In comparison, less than half of the water used for hydraulic fracturing in the Barnett Shale region of Texas came from surface water resources between approximately 2011 and 2013.

Text Box ES-4. FracFocus Chemical Disclosure Registry.

The FracFocus Chemical Disclosure Registry is a publicly-accessible website (www.fracfocus.org) managed by the Ground Water Protection Council (GWPC) and the Interstate Oil and Gas Compact Commission (IOGCC). Oil and gas production well operators can disclose information at this website about water and chemicals used in hydraulic fracturing fluids at individual wells. In many states where oil and gas production occurs, well operators are required to disclose to FracFocus well-specific information on water and chemical use during hydraulic fracturing.

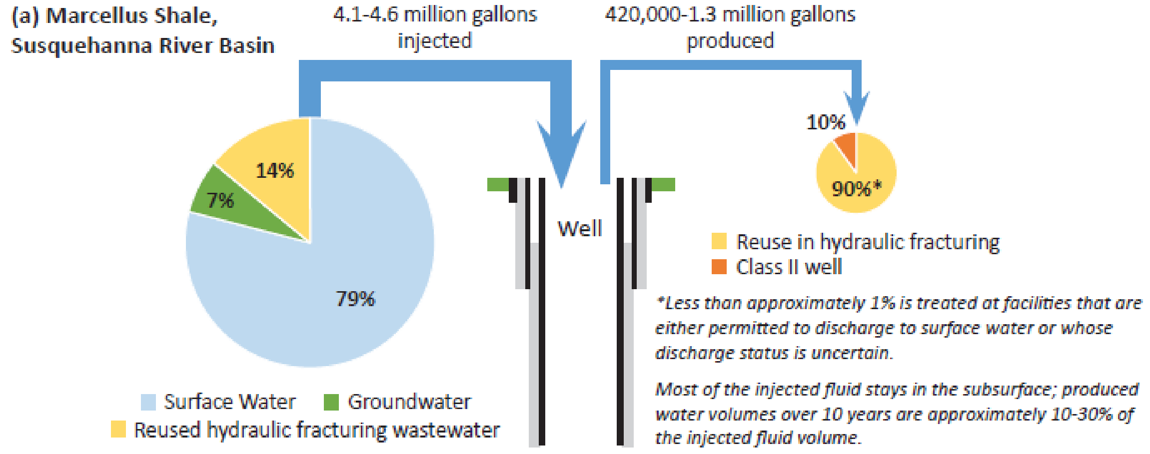
The GWPC and the IOGCC provided the EPA with over 39,000 PDF disclosures submitted by well operators to FracFocus (version 1.0) before March 1, 2013. Data in the disclosures were extracted and compiled in a project database, which was used to conduct analyses on water and chemical use for hydraulic fracturing. Analyses were conducted on over 38,000 unique disclosures for wells located in 20 states that were hydraulically fractured between January 1, 2011, and February 28, 2013.

Despite the challenge of adapting a dataset originally created for local use and single-PDF viewing to answer broader questions, the project database created by the EPA provided substantial insight into water and chemical use for hydraulic fracturing. The project database represents the data reported to FracFocus 1.0 rather than all hydraulic fracturing that occurred in the United States during the study time period. The project database is an incomplete picture of all hydraulic fracturing due to voluntary reporting in some states for certain time periods (in the absence of state reporting requirements), the omission of information on confidential chemicals from disclosures, and invalid or erroneous information in the original disclosures or created during the development of the database. The development of FracFocus 2.0, which became the exclusive reporting mechanism in June 2013, was intended to increase the quality, completeness, and consistency of the data submitted by providing dropdown menus, warning and error messages during submission, and automatic formatting of certain fields. The GWPC has announced additional changes and upgrades for FracFocus 3.0 to enhance data searchability, increase system security, provide greater data accuracy, and further increase data transparency.

Table ES-1. Water use per hydraulically fractured well between January 2011 and February 2013.
Medians and percentiles were calculated from data submitted to FracFocus 1.0 (Appendix B).

State	Number of FracFocus 1.0 disclosures	Median volume per well (gallons)	10th percentile (gallons)	90th percentile (gallons)
Arkansas	1,423	5,259,965	3,234,963	7,121,249
California	711	76,818	21,462	285,306
Colorado	4,898	463,462	147,353	3,092,024
Kansas	121	1,453,788	10,836	2,227,926
Louisiana	966	5,077,863	1,812,099	7,945,630
Montana	207	1,455,757	367,326	2,997,552
New Mexico	1,145	175,241	35,638	1,871,666
North Dakota	2,109	2,022,380	969,380	3,313,482
Ohio	146	3,887,499	2,885,568	5,571,027
Oklahoma	1,783	2,591,778	1,260,906	7,402,230
Pennsylvania	2,445	4,184,936	2,313,649	6,615,981
Texas	16,882	1,420,613	58,709	6,115,195
Utah	1,406	302,075	76,286	769,360
West Virginia	273	5,012,238	3,170,210	7,297,080
Wyoming	1,405	322,793	5,727	1,837,602

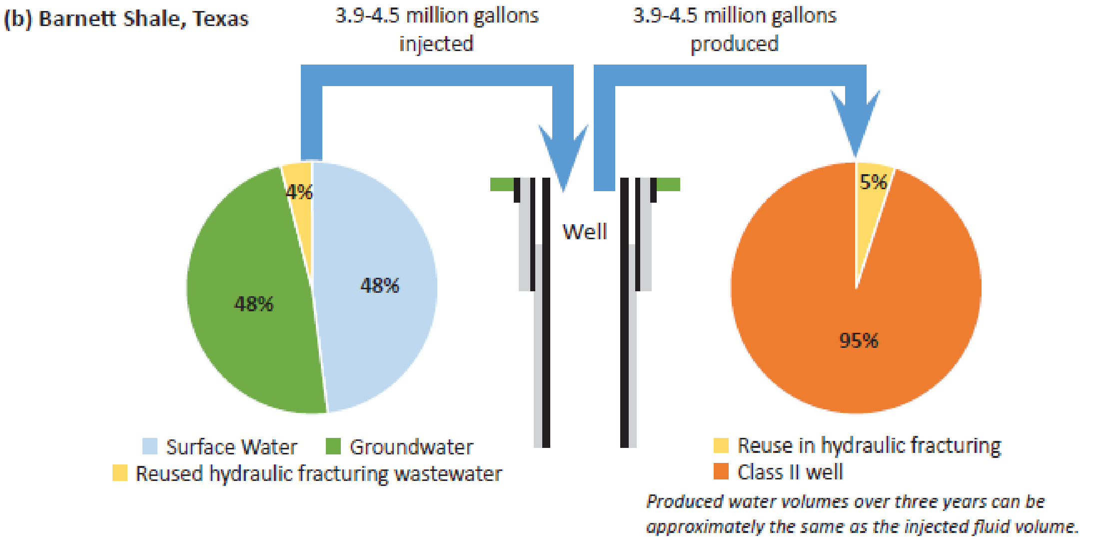
Hydraulic fracturing wastewater and other lower-quality water can also be used in hydraulic fracturing fluids to offset the need for fresh water, although the proportion of injected fluid that is reused hydraulic fracturing wastewater varies by location (Figure ES-4).[1] Overall, the proportion of



(a) Marcellus Shale, Susquehanna River Basin

**Less than approximately 1% is treated at facilities that are either permitted to discharge to surface water or whose discharge status is uncertain.*

Most of the injected fluid stays in the subsurface; produced water volumes over 10 years are approximately 10-30% of the injected fluid volume.



(b) Barnett Shale, Texas

Produced water volumes over three years can be approximately the same as the injected fluid volume.

Figure ES-4. Water budgets illustrative of hydraulic fracturing water management practices in the Marcellus Shale in the Susquehanna River Basin between approximately 2008 and 2013 and the Barnett Shale in Texas between approximately 2011 and 2013.
Class II wells are used to inject wastewater associated with oil and gas production underground and are regulated under the Underground Injection Control Program of the Safe Drinking Water Act. Data sources are described in Figure 10-1 in Chapter 10.

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[1] Reused hydraulic fracturing wastewater as a percentage of injected fluid differs from the percentage of produced water that is managed through reuse in other hydraulic fracturing operations. For example, in the Marcellus Shale region of the Susquehanna River Basin, approximately 14% of injected fluid was reused hydraulic fracturing wastewater, while approximately 90% of produced water was managed through reuse in other hydraulic fracturing operations (Figure ES-4a).

water used in hydraulic fracturing that comes from reused hydraulic fracturing wastewater appears to be low. In a survey of literature values from 10 states, basins, or plays, the median percentage of the injected fluid volume that came from reused hydraulic fracturing wastewater was 5% between approximately 2008 and 2014.[1] There was an increase in the reuse of hydraulic fracturing wastewater as a percentage of the injected hydraulic fracturing fluid in both Pennsylvania and West Virginia between approximately 2008 and 2014. This increase is likely due to the limited availability of Class II wells, which are commonly used to dispose of oil and gas wastewater, and the costs of trucking wastewater to Ohio, where Class II wells are more prevalent.[2] Class II wells are also prevalent in Texas, and the reuse of wastewater in hydraulic fracturing fluids in the Barnett Shale appears to be lower than in the Marcellus Shale (Figure ES-4).

Because the same water resource can be used to support hydraulic fracturing and to provide drinking water, withdrawals for hydraulic fracturing can directly impact drinking water resources by changing the quantity or quality of the remaining water. Although every water withdrawal affects water quantity, we focused on water withdrawals that have the potential to significantly impact drinking water resources by limiting the availability of drinking water or altering its quality. Water withdrawals for a single hydraulically fractured oil and gas production well are not expected to significantly impact drinking water resources, because the volume of water needed to hydraulically fracture a single well is unlikely to limit the availability of drinking water or alter its quality. If, however, multiple oil and gas production wells are located within an area, the total volume of water needed to hydraulically fracture all of the wells has the potential to be a significant portion of the water available and impacts on drinking water resources can occur.

To assess whether hydraulic fracturing operations are a relatively large or small user of water, we compared water use for hydraulic fracturing to total water use at the county level (Text Box ES-5). In most counties studied, the average annual water volumes reported in FracFocus 1.0 were generally less than 1% of total water use. This suggests that hydraulic fracturing operations represented a relatively small user of water in most counties. There were exceptions, however. Average annual water volumes reported in FracFocus 1.0 were 10% or more of total water use in 26 of the 401 counties studied, 30% or more in nine counties, and 50% or more in four counties.[3] In these counties, hydraulic fracturing operations represented a relatively large user of water.

The above results suggest that hydraulic fracturing operations can significantly increase the volume of water withdrawn in particular areas. Increased water withdrawals can result in significant impacts on drinking water resources if there is insufficient water available in the area to accommodate all users. To assess the potential for these impacts, we compared hydraulic fracturing water use to estimates of water availability at the county level.[4] In most counties studied, average

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[1] See Section 4.2 in Chapter 4.

[2] See Chapter 8 for additional information on Class II wells.

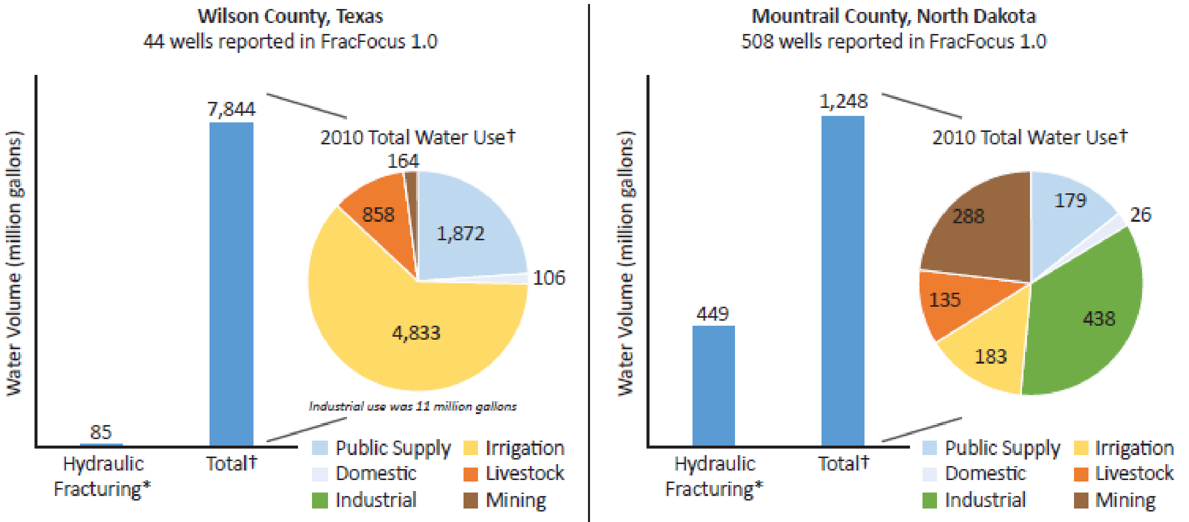
[3] Hydraulic fracturing water consumption estimates followed the same general pattern as the water use estimates presented here, but with slightly larger percentages in each category (Section 4.4 in Chapter 4).

[4] County-level water availability estimates were derived from the Tidwell et al. (2013) estimates of water availability for siting new thermoelectric power plants (see Text Box 4-2 in Chapter 4 for details). The county-level water availability estimates used in this report represent the portion of water available to new users within a county.

Text Box ES-5. County-Level Water Use for Hydraulic Fracturing.

To assess whether hydraulic fracturing operations are a relatively large or small user of water, the average annual water use for hydraulic fracturing in 2011 and 2012 was compared, at the county-level, to total water use in 2010. For most counties studied, average annual water volumes reported for individual counties in FracFocus 1.0 were less than 1% of total water use in those counties. But in some counties, hydraulic fracturing operations reported in FracFocus 1.0 represented a relatively large user of water.

Examples of Water Use in Two Counties: Wilson County, Texas, and Mountrail County, North Dakota



Depending on local water availability, hydraulic fracturing water withdrawals may be **less likely** to significantly impact drinking water resources under this kind of scenario.

Depending on local water availability, hydraulic fracturing water withdrawals may be **more likely** to significantly impact drinking water resources under this kind of scenario.

*Hydraulic fracturing water use is a function of the water use per well and the total number of wells hydraulically fractured within a county. Average annual water use for hydraulic fracturing was calculated at the county-level using data reported in FracFocus 1.0 in 2011 and 2012 (Appendix B).

†The U.S. Geological Survey compiles national water use estimates every five years in the National Water Census. Total water use at the county-level was obtained from the most recent census, which was conducted in 2010 (Maupin et al., 2014).

2010 Total Water Use Categories

Public supply	Water withdrawn by public and private water suppliers that provide water to at least 25 people or have a minimum of 15 connections
Domestic	Self-supplied water withdrawals for indoor household purposes such as drinking, food preparation, bathing, washing clothes and dishes, flushing toilets, and outdoor purposes such as watering lawns and gardens
Industrial	Water used for fabrication, processing, washing, and cooling
Irrigation	Water that is applied by an irrigation system to assist crop and pasture growth or to maintain vegetation on recreational lands (e.g., parks and golf courses)
Livestock	Water used for livestock watering, feedlots, dairy operations, and other on-farm needs
Mining	Water used for the extraction of naturally-occurring minerals, including solids (e.g., coal, sand, gravel, and other ores), liquids (e.g., crude petroleum), and gases (e.g., natural gas)

annual water volumes reported for hydraulic fracturing were less than 1% of the estimated annual volume of readily-available fresh water. However, average annual water volumes reported for hydraulic fracturing were greater than the estimated annual volume of readily-available fresh water in 17 counties in Texas. This analysis suggests that there was enough water available annually to support the level of hydraulic fracturing reported to FracFocus 1.0 in most, but not all, areas of the country. This observation does not preclude the possibility of local impacts in other areas of the country, nor does it indicate that local impacts have occurred or will occur in the 17 counties in Texas. To better understand whether local impacts have occurred, and the factors that affect those impacts, local-level studies, such as the ones described below, are needed.

Local impacts on drinking water quantity have occurred in areas with increased hydraulic fracturing activity. In 2011, for example, drinking water wells in an area overlying the Haynesville Shale ran out of water due to higher than normal groundwater withdrawals and drought (LA Ground Water Resources Commission, 2012). Water withdrawals for hydraulic fracturing contributed to these conditions, along with other water users and the lack of precipitation. Groundwater impacts have also been reported in Texas. In a detailed case study, Scanlon et al. (2014b) estimated that groundwater levels in approximately 6% of the area studied dropped by 100 feet (31 meters) to 200 feet (61 meters) or more after hydraulic fracturing activity increased in 2009.

In contrast, studies in the Upper Colorado and Susquehanna River basins found minimal impacts on drinking water resources from hydraulic fracturing. In the Upper Colorado River Basin, the EPA found that high-quality water produced from oil and gas wells in the Piceance tight sands provided nearly all of the water for hydraulic fracturing in the study area (U.S. EPA, 2015e). Due to this high reuse rate, the EPA did not identify any locations in the study area where hydraulic fracturing contributed to locally high water use. In the Susquehanna River Basin, multiple studies and state reports have identified the potential for hydraulic fracturing water withdrawals in the Marcellus Shale to impact surface water resources. Evidence suggests, however, that current water management strategies, including passby flows and reuse of hydraulic fracturing wastewater, help protect streams from depletion by hydraulic fracturing water withdrawals. A passby flow is a prescribed, low-streamflow threshold below which water withdrawals are not allowed.

The above examples highlight factors that can affect the frequency or severity of impacts on drinking water resources from hydraulic fracturing water withdrawals. In particular, areas of the United States that rely on declining groundwater resources are vulnerable to more frequent and more severe impacts from all water withdrawals, including withdrawals for hydraulic fracturing. Extensive groundwater withdrawals can limit the availability of belowground drinking water resources and can also change the quality of the water remaining in the resource. Because groundwater recharge rates can be low, impacts can last for many years. Seasonal or long-term drought can also make impacts more frequent and more severe for groundwater and surface water resources. Hot, dry weather reduces or prevents groundwater recharge and depletes surface water bodies, while water demand often increases simultaneously (e.g., for irrigation). This combination of factors—high hydraulic fracturing water use and relatively low water availability due to declining groundwater resources and/or frequent drought—was found to be present in southern and western Texas.

Water management strategies can also affect the frequency and severity of impacts on drinking water resources from hydraulic fracturing water withdrawals. These strategies include using hydraulic fracturing wastewater or brackish groundwater for hydraulic fracturing, transitioning from limited groundwater resources to more abundant surface water resources, and using passby flows to control water withdrawals from surface water resources. Examples of these water management strategies can be found throughout the United States. In western and southern Texas, for example, the use of brackish water is currently reducing impacts on fresh water sources, and could, if increased, reduce future impacts. Louisiana and North Dakota have encouraged well operators to withdraw water from surface water resources instead of high-quality groundwater resources. And, as described above, the Susquehanna River Basin Commission limits surface water withdrawals during periods of low stream flow.

Water Acquisition Conclusions

With notable exceptions, hydraulic fracturing uses a relatively small percentage of water when compared to total water use and availability at large geographic scales. Despite this, hydraulic fracturing water withdrawals can affect the quantity and quality of drinking water resources by changing the balance between the demand on local water resources and the availability of those resources. Changes that have the potential to limit the availability of drinking water or alter its quality are more likely to occur in areas with relatively high hydraulic fracturing water withdrawals and low water availability, particularly due to limited or declining groundwater resources. Water management strategies (e.g., encouragement of alternative water sources or water withdrawal restrictions) can reduce the frequency or severity of impacts on drinking water resources from hydraulic fracturing water withdrawals.

Chemical Mixing

Activity: The mixing of a base fluid, proppant, and additives at the well site to create hydraulic fracturing fluids.

Relationship to Drinking Water Resources: Spills of additives and hydraulic fracturing fluids can reach groundwater and surface water resources.

Hydraulic fracturing fluids are engineered to create and grow fractures in the targeted rock formation and to carry proppant through the oil and gas production well into the newly-created fractures. Hydraulic fracturing fluids are typically made up of base fluids, proppant, and additives. Base fluids make up the largest proportion of hydraulic fracturing fluids by volume. As illustrated in Text Box ES-6, base fluids can be a single substance (e.g., water in the slickwater example) or can be a mixture of substances (e.g., water and nitrogen in the energized fluid example). The EPA's analysis of hydraulic fracturing fluid data reported to FracFocus 1.0 suggests that water was the most commonly used base fluid between January 2011 and February 2013 (U.S. EPA, 2015a). Non-water substances, such as gases and hydrocarbon liquids, were reported to be used alone or blended with water to form a base fluid in fewer than 3% of wells in FracFocus 1.0.

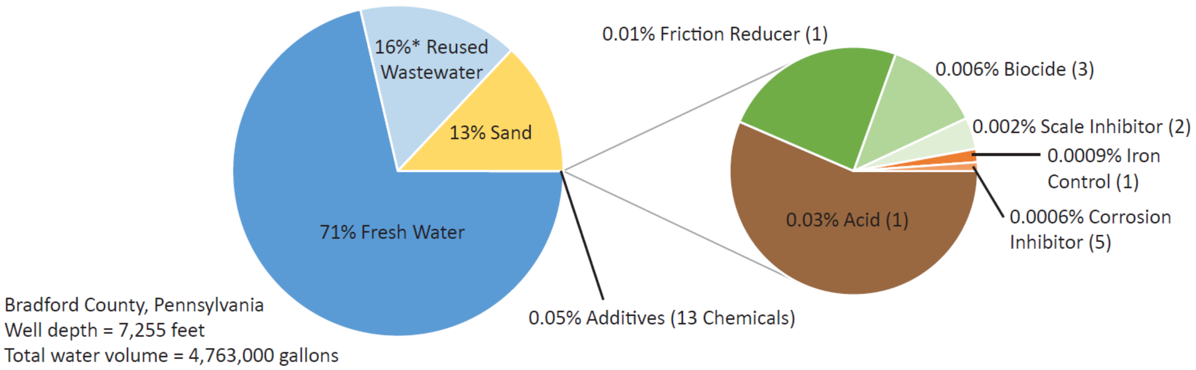
Proppant makes up the second largest proportion of hydraulic fracturing fluids (Text Box ES-6). Sand (i.e., quartz) was the most commonly reported proppant between January 2011 and February 2013, with 98% of wells in FracFocus 1.0 reporting sand as the proppant (U.S. EPA, 2015a). Other

Text Box ES-6. Examples of Hydraulic Fracturing Fluids.

Hydraulic fracturing fluids are engineered to create and extend fractures in the targeted rock formation and to carry proppant through the production well into the newly-created fractures. While there is no universal hydraulic fracturing fluid, there are general types of hydraulic fracturing fluids. Two types of hydraulic fracturing fluids are described below.

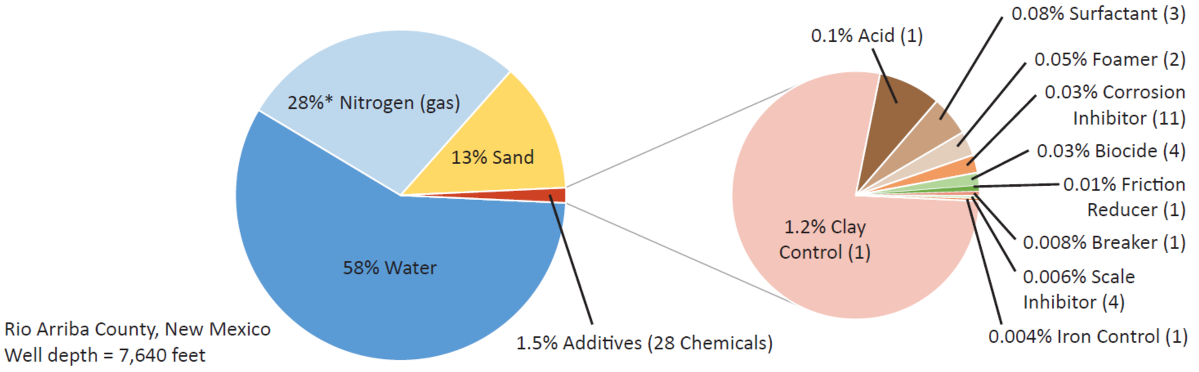
Slickwater

Slickwater hydraulic fracturing fluids are water-based fluids that generally contain a friction reducer. The friction reducer makes it easier for the fluid to be pumped down the oil and gas production well at high rates. Slickwater is commonly used to hydraulically fracture shale formations.



Energized Fluid

Energized fluids are mixtures of liquids and gases. They can be used for hydraulic fracturing in under-pressured gas formations.



Maximum percent by mass of the total hydraulic fracturing fluid. Data obtained from FracFocus.org

Additive Dictionary

Acid	Dissolves minerals and creates pre-fractures in the rock
Biocide	Controls or eliminates bacteria in the hydraulic fracturing fluid
Breaker	Reduces the thickness of the hydraulic fracturing fluid
Clay control	Prevents swelling and migration of formation clays
Corrosion inhibitor	Protects iron and steel equipment from rusting
Foamer	Creates a foam hydraulic fracturing fluid
Friction reducer	Reduces friction between the hydraulic fracturing fluid and pipes during pumping
Iron control	Prevents the precipitation of iron-containing chemicals
Scale inhibitor	Prevents the formation of scale buildup within the well
Surfactant	Reduces the surface tension of the hydraulic fracturing fluid

proppants can include man-made or specially engineered particles, such as high-strength ceramic materials or sintered bauxite.[1]

Additives generally make up the smallest proportion of the overall composition of hydraulic fracturing fluids (Text Box ES-6), yet have the greatest potential to impact the quality of drinking water resources compared to proppant and base fluids. Additives, which can be a single chemical or a mixture of chemicals, are added to the base fluid to change its properties (e.g., adjust pH, increase fluid thickness, or limit bacterial growth). The choice of which additives to use depends on the characteristics of the targeted rock formation (e.g., rock type, temperature, and pressure), the economics and availability of desired additives, and well operator or service company preferences and experience.

The variability of additives, both in their purpose and chemical composition, suggests that a large number of different chemicals may be used in hydraulic fracturing fluids across the United States. The EPA identified 1,084 chemicals that were reported to have been used in hydraulic fracturing fluids between 2005 and 2013.[2,3] The EPA's analysis of FracFocus 1.0 data indicates that between 4 and 28 chemicals were used per well between January 2011 and February 2013 and that no single chemical was used in all wells (U.S. EPA, 2015a). Three chemicals—methanol, hydrotreated light petroleum distillates, and hydrochloric acid—were reported in 65% or more of the wells in FracFocus 1.0; 35 chemicals were reported in at least 10% of the wells (Table ES-2).

Table ES-2. Chemicals reported in 10% or more of disclosures in FracFocus 1.0.
Disclosures provided information on chemicals used at individual well sites between January 1, 2011, and February 28, 2013.

Chemical Name (CASRN)[a]	Percent of FracFocus 1.0 disclosures[b]
Methanol (67-56-1)	72
Hydrotreated light petroleum distillates (64742-47-8)	65
Hydrochloric acid (7647-01-0)	65
Water (7732-18-5)[c]	48
Isopropanol (67-63-0)	47
Ethylene glycol (107-21-1)	46
Peroxydisulfuric acid, diammonium salt (7727-54-0)	44
Sodium hydroxide (1310-73-2)	39
Guar gum (9000-30-0)	37

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[1] Sintered bauxite is crushed and powdered bauxite that is fused into spherical beads at high temperatures.

[2] This list includes 1,084 unique Chemical Abstracts Service Registration Numbers (CASRNs), which can be assigned to a single chemical (e.g., hydrochloric acid) or a mixture of chemicals (e.g., hydrotreated light petroleum distillates). Throughout this report, we refer to the substances identified by unique CASRNs as "chemicals."

[3] Dayalu and Konschnik (2016) identified 995 unique CASRNs from data submitted to FracFocus between March 9, 2011, and April 13, 2015. Two hundred sixty-three of these CASRNs are not on the list of unique CASRNs identified by the EPA (Appendix H). Only one of the 263 chemicals was reported at greater than 1% of wells, which suggests that these chemicals were used at only a few sites.

Chemical Name (CASRN)[a]	Percent of FracFocus 1.0 disclosures[b]
Quartz (14808-60-7)[c]	36
Glutaraldehyde (111-30-8)	34
Propargyl alcohol (107-19-7)	33
Potassium hydroxide (1310-58-3)	29
Ethanol (64-17-5)	29
Acetic acid (64-19-7)	24
Citric acid (77-92-9)	24
2-Butoxyethanol (111-76-2)	21
Sodium chloride (7647-14-5)	21
Solvent naphtha, petroleum, heavy aromatic (64742-94-5)	21
Naphthalene (91-20-3)	19
2,2-Dibromo-3-nitrilopropionamide (10222-01-2)	16
Phenolic resin (9003-35-4)	14
Choline chloride (67-48-1)	14
Methenamine (100-97-0)	14
Carbonic acid, dipotassium salt (584-08-7)	13
1,2,4-Trimethylbenzene (95-63-6)	13
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides (68424-85-1)	12
Poly(oxy-1,2-ethanediyl)-nonylphenyl- hydroxy (mixture) (127087-87-0)	12
Formic acid (64-18-6)	12
Sodium chlorite (7758-19-2)	11
Nonyl phenol ethoxylate (9016-45-9)	11
Tetrakis(hydroxymethyl)phosphonium sulfate (55566-30-8)	11
Polyethylene glycol (25322-68-3)	11
Ammonium chloride (12125-02-9)	10
Sodium persulfate (7775-27-1)	10

[a] "Chemical" refers to chemical substances with a single CASRN; these may be pure chemicals (e.g., methanol) or chemical mixtures (e.g., hydrotreated light petroleum distillates).

[b] Analysis considered 34,675 disclosures that met selected quality assurance criteria. See Table 5-2 in Chapter 5.

[c] Quartz and water were reported as ingredients in additives, in addition to proppants and base fluids.

Concentrated additives are delivered to the well site and stored until they are mixed with the base fluid and proppant and pumped down the oil and gas production well (Text Box ES-7). While the overall concentration of additives in hydraulic fracturing fluids is generally small (typically 2% or less of the total volume of the injected fluid), the total volume of additives delivered to the well site can be large. Because over 1 million gallons (3.8 million liters) of hydraulic fracturing fluid are generally injected per well, thousands of gallons of additives can be stored on site and used during hydraulic fracturing.

As illustrated in Text Box ES-7, additives are often stored in multiple, closed containers [typically 200 gallons (760 liters) to 375 gallons (1,420 liters) per container] and moved around the site in hoses and tubing. This equipment is designed to contain additives and blended hydraulic fracturing fluid, but spills can occur. Changes in drinking water quality can occur if spilled fluids reach groundwater or surface water resources.

Several studies have documented spills of hydraulic fracturing fluids or additives. Nearly all of these studies identified spills from state-managed spill databases. Data gathered for these studies suggest that spills of hydraulic fracturing fluids or additives were primarily caused by equipment failure or human error. For example, an EPA analysis of spill reports from nine state agencies, nine oil and gas well operators, and nine hydraulic fracturing service companies characterized 151 spills of hydraulic fracturing fluids or additives on or near well sites in 11 states between January 2006 and April 2012 (U.S. EPA, 2015m). These spills were primarily caused by equipment failure (34% of the spills) or human error (25%), and more than 30% of the spills were from fluid storage units (e.g., tanks, totes, and trailers). Similarly, a study of spills reported to the Colorado Oil and Gas Conservation Commission identified 125 spills during well stimulation (i.e., a part of the life of an oil and gas well that often, but not always, includes hydraulic fracturing) between January 2010 and August 2013 (COGCC, 2014). Of these spills, 51% were caused by human error and 46% were due to equipment failure.

Studies of spills of hydraulic fracturing fluids or additives provide insights on spill volumes, but little information on chemical-specific spill composition. Among the 151 spills characterized by the EPA, the median volume of fluid spilled was 420 gallons (1,600 liters), although the volumes spilled ranged from 5 gallons (19 liters) to 19,320 gallons (73,130 liters). Spilled fluids were often described as acids, biocides, friction reducers, crosslinkers, gels, and blended hydraulic fracturing fluid, but few specific chemicals were mentioned.[1] Considine et al. (2012) identified spills related to oil and gas development in the Marcellus Shale that occurred between January 2008 and August 2011 from Notices of Violations issued by the Pennsylvania Department of Environmental Protection. The authors identified spills greater than 400 gallons (1,500 liters) and spills less than 400 gallons (1,500 liters).

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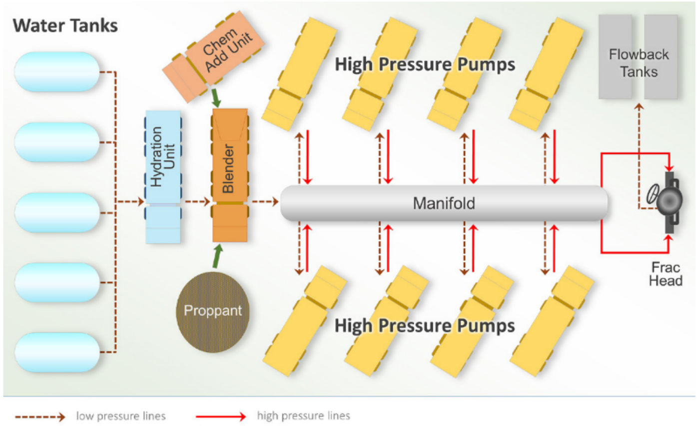
[1] A crosslinker is an additive that increases the thickness of gelled fluids by connecting polymer molecules in the gelled fluid.

Text Box ES-7. Chemical Mixing Equipment.



Source: Adapted from Olson (2011) and BJ Services Company (2009)

Typical Layout of Chemical Mixing Equipment

This illustration shows how the different pieces of equipment fit together to contain, mix, and inject hydraulic fracturing fluid into a production well.

Water, proppant, and additives are blended together and pumped to the manifold, where high pressure pumps transfer the fluid to the frac head.

Additives and proppant can be blended with water at different times and in different amounts during hydraulic fracturing. Thus, the composition of hydraulic fracturing fluids can vary during the hydraulic fracturing job.

Well Pad During Hydraulic Fracturing

Equipment set up for hydraulic fracturing.

Source: Schlumberger

Chemical Mixing Equipment Dictionary

Blender	Blends water, proppant, and additives
Chemical additive unit	Transports additives to the site and stores additives onsite
Flowback tanks	Stores liquid that returns to the surface after hydraulic fracturing
Frac head	Connects hydraulic fracturing equipment to the production well
High pressure pumps	Pressurize mixed fluids before injection into the production well
Hydration unit	Creates and stores gels used in some hydraulic fracturing fluids
Manifold	Transfers fluids from the blender to the frac head
Proppant	Stores proppant (often sand)
Water tanks	Stores water

Spills of hydraulic fracturing fluids or additives have reached, and therefore impacted, surface water resources. Thirteen of the 151 spills characterized by the EPA were reported to have reached a surface water body (often creeks or streams). Among the 13 spills, reported spill volumes ranged from 28 gallons (105 liters) to 7,350 gallons (27,800 liters). Additionally, Brantley et al. (2014) and Considine et al. (2012) identified fewer than 10 total instances of spills of additives and/or hydraulic fracturing fluids greater than 400 gallons (1,500 liters) that reached surface waters in

Pennsylvania between January 2008 and June 2013. Reported spill volumes for these spills ranged from 3,400 gallons (13,000 liters) to 227,000 gallons (859,000 liters).

Although impacts on surface water resources have been documented, site-specific studies that could be used to describe factors that affect the frequency or severity of impacts were not available. In the absence of such studies, we relied on fundamental scientific principles to identify factors that affect how hydraulic fracturing fluids and chemicals can move through the environment to drinking water resources. Because these factors influence whether spilled fluids reach groundwater and surface water resources, they affect the frequency and severity of impacts on drinking water resources from spills during the chemical mixing stage of the hydraulic fracturing water cycle.

The potential for spilled fluids to impact groundwater or surface water resources depends on the characteristics of the spill, the environmental fate and transport of the spilled fluid, and spill response activities (Figure ES-5). Site-specific characteristics affect how spilled liquids move through soil into the subsurface or over the land surface. Generally, highly permeable soils or fractured rock can allow spilled liquids to move quickly into and through the subsurface, limiting the opportunity for spilled liquids to move over land to surface water resources. In low permeability soils, spilled liquids are less able to move into the subsurface and are more likely to move over the land surface. In either case, the volume spilled and the distance between the location of the spill and nearby water resources affects whether spilled liquids reach drinking water resources. Large-volume spills are generally more likely to reach drinking water resources because they are more likely to be able to travel the distance between the location of the spill and nearby water resources.

In general, chemical and physical properties, which depend on the identity and structure of a chemical, control whether spilled chemicals evaporate, stick to soil particles, or move with water. The EPA identified measured or estimated chemical and physical properties for 455 of the 1,084 chemicals used in hydraulic fracturing fluids between 2005 and 2013.[1] The properties of these chemicals varied widely, from chemicals that are more likely to move quickly through the environment with a spilled liquid to chemicals that are more likely to move slowly through the environment because they stick to soil particles.[2] Chemicals that move slowly through the environment may act as longer-term sources of contamination if spilled.

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[1] Chemical and physical properties were identified using EPI Suite™. EPI Suite™ is a collection of chemical and physical property and environmental fate estimation programs developed by the EPA and Syracuse Research Corporation. It can be used to estimate chemical and physical properties of individual organic compounds. Of the 1,084 hydraulic fracturing fluid chemicals identified by the EPA, 629 were not individual organic compounds, and thus EPI Suite™ could not be used to estimate their chemical and physical properties.

[2] These results describe how some hydraulic fracturing chemicals behave in infinitely dilute aqueous solutions, which is a simplified approximation of the real-world mixtures found in hydraulic fracturing fluids. The presence of other chemicals in a mixture can affect the fate and transport of a chemical.

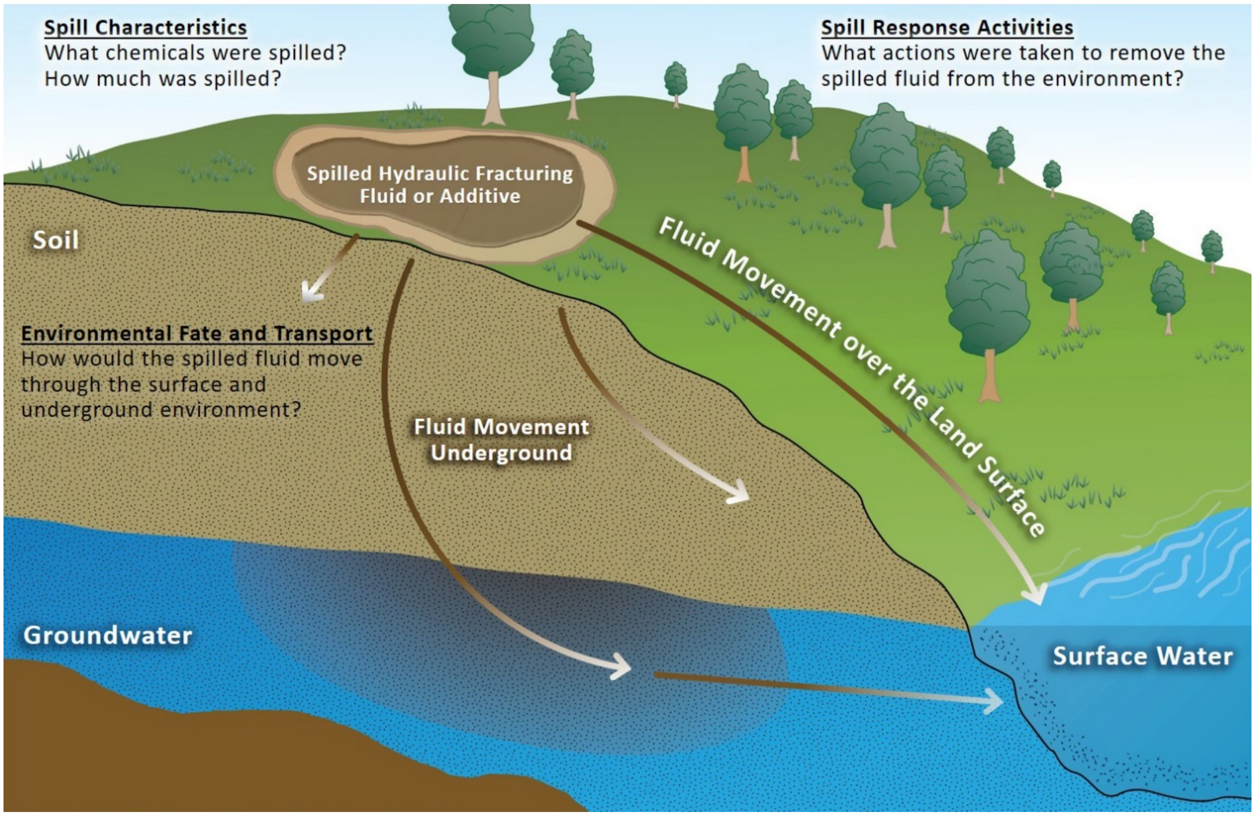

Figure ES-5. Generalized depiction of factors that influence whether spilled hydraulic fracturing fluids or additives reach drinking water resources, including spill characteristics, environmental fate and transport, and spill response activities.

Spill prevention practices and spill response activities are designed to prevent spilled fluids from reaching groundwater or surface water resources and minimize impacts from spilled fluids. Spill prevention and response activities are influenced by federal, state, and local regulations and company practices. Spill prevention practices include secondary containment systems (e.g., liners and berms), which are designed to contain spilled fluids and prevent them from reaching soil, groundwater, or surface water. Spill response activities include activities taken to stop the spill, contain spilled fluids (e.g., the deployment of emergency containment systems), and clean up spilled fluids (e.g., removal of contaminated soil). It was beyond the scope of this report to evaluate the implementation and efficacy of spill prevention practices and spill response activities.

The severity of impacts on water quality from spills of hydraulic fracturing fluids or additives depends on the identity and amount of chemicals that reach groundwater or surface water resources, the toxicity of the chemicals, and the characteristics of the receiving water resource.[1] Characteristics of the receiving groundwater or surface water resource (e.g., water resource size and flow rate) can affect the magnitude and duration of impacts by reducing the concentration of spilled chemicals in a drinking water resource. Impacts on groundwater resources have the

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[1] Human health hazards associated with hydraulic fracturing fluid chemicals are discussed in Chapter 9 and summarized in the "Chemicals in the Hydraulic Fracturing Water Cycle" section below.

potential to be more severe than impacts on surface water resources because it takes longer to naturally reduce the concentration of chemicals in groundwater and because it is generally difficult to remove chemicals from groundwater resources. Due to a lack of data, particularly in terms of groundwater monitoring after spill events, little is publicly known about the severity of drinking water impacts from spills of hydraulic fracturing fluids or additives.

Chemical Mixing Conclusions

Spills of hydraulic fracturing fluids and additives during the chemical mixing stage of the hydraulic fracturing water cycle have reached surface water resources in some cases and have the potential to reach groundwater resources. Although the available data indicate that spills of various volumes can reach surface water resources, large volume spills are more likely to travel longer distances to nearby groundwater or surface water resources. Consequently, large volume spills likely increase the frequency of impacts on drinking water resources. Large volume spills, particularly of concentrated additives, are also likely to result in more severe impacts on drinking water resources than small volume spills because they can deliver a large quantity of potentially hazardous chemicals to groundwater or surface water resources. Impacts on groundwater resources are likely to be more severe than impacts on surface water resources because of the inherent characteristics of groundwater. Spill prevention and response activities are designed to prevent spilled fluids from reaching groundwater or surface water resources and minimize impacts from spilled fluids.

Well Injection

Activity: The injection and movement of hydraulic fracturing fluids through the oil and gas production well and in the targeted rock formation.

Relationship to Drinking Water Resources: Belowground pathways, including the production well itself and newly-created fractures, can allow hydraulic fracturing fluids or other fluids to reach underground drinking water resources.

Hydraulic fracturing fluids primarily move along two pathways during the well injection stage: the oil and gas production well and the newly-created fracture network. Oil and gas production wells are designed and constructed to move fluids to and from the targeted rock formation without leaking and to prevent fluid movement along the outside of the well. This is generally accomplished by installing multiple layers of casing and cement within the drilled hole (Text Box ES-2), particularly where the well intersects oil-, gas-, and/or water-bearing rock formations. Casing and cement, in addition to other well components (e.g., packers), can control hydraulic fracturing fluid movement by creating a preferred flow pathway (i.e., inside the casing) and preventing unintentional fluid movement (e.g., from the inside of the casing to the surrounding environment or vertically along the well from the targeted rock formation to shallower formations).[1] An EPA survey of oil and gas production wells hydraulically fractured between approximately September 2009 and September 2010 suggests that hydraulically fractured wells are often, but not always, constructed

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[1] Packers are mechanical devices installed with casing. Once the casing is set in the drilled hole, packers swell to fill the space between the outside of the casing and the surrounding rock or casing.

with multiple casings that have varying amounts of cement surrounding each casing (U.S. EPA, 2015n). Among the wells surveyed, the most common number of casings per well was two: surface casing and production casing (Text Box ES-2). The presence of multiple cemented casings that extend from the ground surface to below the designated drinking water resource is one of the primary well construction features that protects underground drinking water resources.

During hydraulic fracturing, a well is subjected to greater pressure and temperature changes than during any other activity in the life of the well. As hydraulic fracturing fluid is injected into the well, the pressure applied to the well increases until the targeted rock formation fractures; then pressure decreases. Maximum pressures applied to wells during hydraulic fracturing have been reported to range from less than 2,000 pounds per square inch (psi) [14 megapascals (MPa)] to approximately 12,000 psi (83 MPa).[1] A well can also experience temperature changes as cooler hydraulic fracturing fluid enters the warmer well. In some cases, casing temperatures have been observed to drop from 212°F (100°C) to 64°F (18°C). A well can experience multiple pressure and temperature cycles if hydraulic fracturing is done in multiple stages or if a well is re-fractured.[2] Casing, cement, and other well components need to be able to withstand these changes in pressure and temperature, so that hydraulic fracturing fluids can flow to the targeted rock formation without leaking.

The fracture network created during hydraulic fracturing is the other primary pathway along which hydraulic fracturing fluids move. Fracture growth during hydraulic fracturing is complex and depends on the characteristics of the targeted rock formation and the characteristics of the hydraulic fracturing operation. In general, rock characteristics, particularly the natural stresses placed on the targeted rock formation due to the weight of the rock above, affect how the rock fractures, including whether newly-created fractures grow vertically (i.e., perpendicular to the ground surface) or horizontally (i.e., parallel to the ground surface) (Text Box ES-8). Because hydraulic fracturing fluids are used to create and grow fractures, fracture growth during hydraulic fracturing can be controlled by limiting the rate and volume of hydraulic fracturing fluid injected into the well.

Publicly available data on fracture growth are currently limited to microseismic and tiltmeter data collected during hydraulic fracturing operations in five shale plays in the United States. Analyses of these data by Fisher and Warpinski (2012) and Davies et al. (2012) indicate that the direction of fracture growth generally varied with depth and that upward vertical fracture growth was often on the order of tens to hundreds of feet in the shale formations studied (Text Box ES-8). One percent of the fractures had a fracture height greater than 1,148 feet (350 meters), and the maximum fracture height among all of the data reported was 1,929 feet (588 meters). These reported fracture heights suggest that some fractures can grow out of the targeted rock formation and into an overlying formation. It is unknown whether these observations apply to other hydraulically fractured rock formations because similar data from hydraulic fracturing operations in other rock formations are not currently available to the public.

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[1] For comparison, average atmospheric pressure is approximately 15 psi.

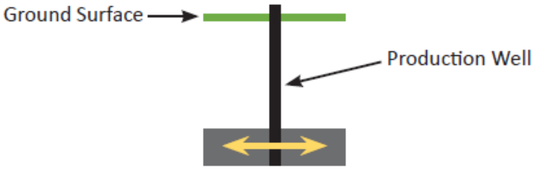
[2] In a multi-stage hydraulic fracturing operation, specific parts of the well are isolated and hydraulically fractured until the total desired length of the well has been hydraulically fractured.

Text Box ES-8. Fracture Growth.

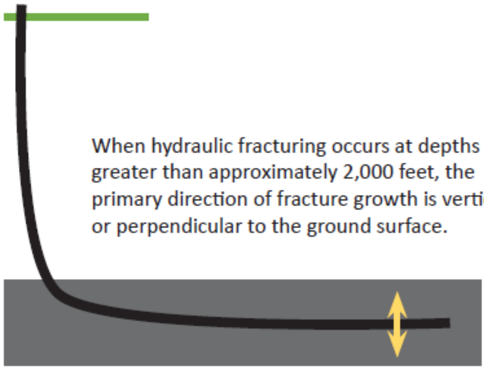
Fracture growth during hydraulic fracturing is complex and depends on the characteristics of the targeted rock formation and the characteristics of the hydraulic fracturing operation.

Primary Direction of Fracture Growth

In general, the weight of the rock above the point of hydraulic fracturing affects the primary direction of fracture growth. Therefore, the depth at which hydraulic fracturing occurs affects whether fractures grow vertically or horizontally.



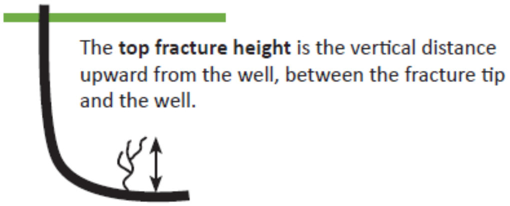
When hydraulic fracturing occurs at depths less than approximately 2,000 feet, the primary direction of fracture growth is horizontal, or parallel to the ground surface.



When hydraulic fracturing occurs at depths greater than approximately 2,000 feet, the primary direction of fracture growth is vertical, or perpendicular to the ground surface.

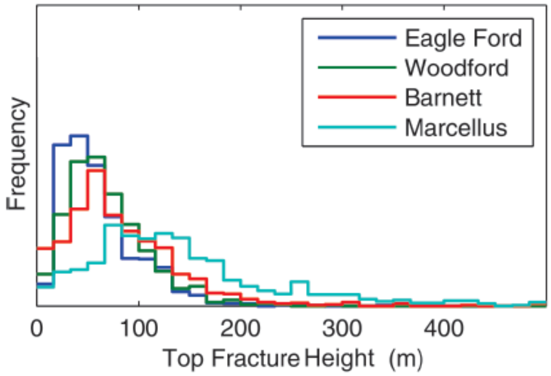
Fracture Height

Fisher and Warpinski (2012) and Davies et al. (2012) analyzed microseismic and tiltmeter data collected during thousands of hydraulic fracturing operations in the Barnett, Eagle Ford, Marcellus, Niobrara, and Woodford shale plays. Their data provide information on fracture heights in shale. Top fracture heights varied between shale plays and within individual shale plays.



The **top fracture height** is the vertical distance upward from the well, between the fracture tip and the well.

SHALE PLAY	APPROXIMATE MEDIAN TOP FRACTURE HEIGHT [FEET (METERS)]
Eagle Ford	130 (40)
Woodford	160 (50)
Barnett	200 (60)
Marcellus	400 (120)
Niobrara	160 (50)



Source: Davies et. (2012)

The potential for hydraulic fracturing fluids to reach, and therefore impact, underground drinking water resources is related to the pathways along which hydraulic fracturing fluids primarily move during hydraulic fracturing: the oil and gas production well itself and the fracture network created during hydraulic fracturing. Because the well can be a pathway for fluid movement, the mechanical integrity of the well is an important factor that affects the frequency and severity of impacts from the well injection stage of the hydraulic fracturing water cycle.[1] A well with insufficient mechanical integrity can allow unintended fluid movement, either from the inside to the outside of the well (pathway 1 in Figure ES-6) or vertically along the outside of the well (pathways 2-5). The existence of one or more of these pathways can result in impacts on drinking water resources if hydraulic fracturing fluids reach groundwater resources. Impacts on drinking water resources can also occur if gases or liquids released from the targeted rock formation or other formations during hydraulic fracturing travel along these pathways to groundwater resources.

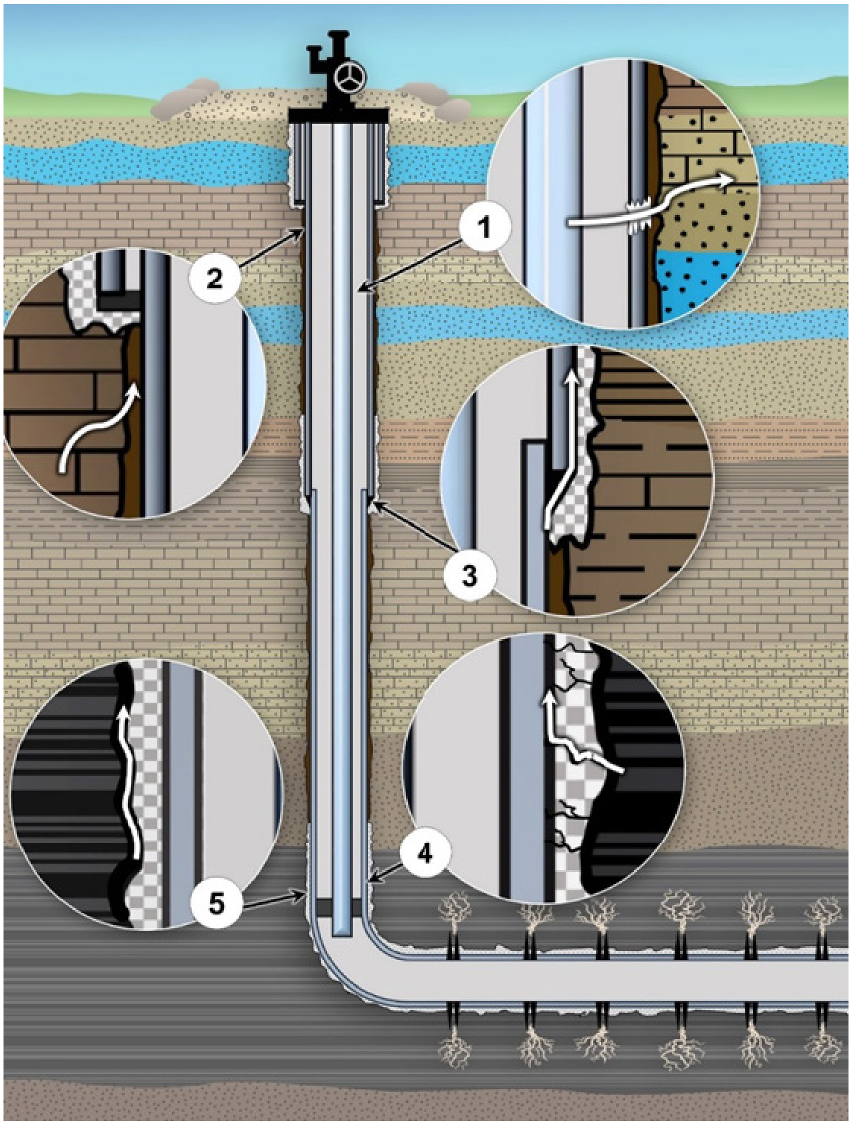


Figure ES-6. Potential pathways for fluid movement in a cemented well.

These pathways (represented by the white arrows) include: (1) a casing and tubing leak into the surrounding rock, (2) an uncemented annulus (i.e., the space behind the casing), (3) microannuli between the casing and cement, (4) gaps in cement due to poor cement quality, and (5) microannuli between the cement and the surrounding rock. This figure is intended to provide a conceptual illustration of pathways that can be present in a well and is not to scale.

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[1] Mechanical integrity is the absence of significant leakage within or outside of the well components.

The pathways shown in Figure ES-6 can exist because of inadequate well design or construction (e.g., incomplete cement around the casing where the well intersects with water-, oil-, or gas-bearing formations) or can develop over the well's lifetime, including during hydraulic fracturing. In particular, casing and cement can degrade over the life of the well because of exposure to corrosive chemicals, formation stresses, and operational stresses (e.g., pressure and temperature changes during hydraulic fracturing). As a result, some hydraulically fractured oil and gas production wells may develop one or more of the pathways shown in Figure ES-6. Changes in mechanical integrity over time have implications for older wells that are hydraulically fractured because these wells may not be able to withstand the stresses applied during hydraulic fracturing. Older wells may also be hydraulically fractured at shallower depths, where cement around the casing may be inadequate or missing.

Examples of mechanical integrity problems have been documented in hydraulically fractured oil and gas production wells. In one case, hydraulic fracturing of an inadequately cemented gas well in Bainbridge Township, Ohio, contributed to the movement of methane into local drinking water resources.[1] In another case, an inner string of casing burst during hydraulic fracturing of an oil well near Killdeer, North Dakota, resulting in a release of hydraulic fracturing fluids and formation fluids that impacted a groundwater resource.

The potential for hydraulic fracturing fluids or other fluids to reach underground drinking water resources is also related to the fracture network created during hydraulic fracturing. Because fluids travel through the newly-created fractures, the location of these fractures relative to underground drinking water resources is an important factor affecting the frequency and severity of potential impacts on drinking water resources. Data on the relative location of induced fractures to underground drinking water resources are generally not available, because fracture networks are infrequently mapped and because there can be uncertainty in the depth of the bottom of the underground drinking water resource at a specific location.

Without these data, we were often unable to determine with certainty whether fractures created during hydraulic fracturing have reached underground drinking water resources. Instead, we considered the vertical separation distance between hydraulically fractured rock formations and the bottom of underground drinking water resources. Based on computer modeling studies, Birdsell et al. (2015a) concluded that it is less likely that hydraulic fracturing fluids would reach an overlying drinking water resource if (1) the vertical separation distance between the targeted rock formation and the drinking water resource is large and (2) there are no open pathways (e.g., natural faults or fractures, or leaky wells). As the vertical separation distance between the targeted rock formation and the underground drinking water resource decreases, the likelihood of upward migration of hydraulic fracturing fluids to the drinking water resource increases (Birdsell et al., 2015a).

Figure ES-7 illustrates how the vertical separation distance between the targeted rock formation and underground drinking water resources can vary across the United States. The two example

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[1] Although ingestion of methane is not considered to be toxic, methane can pose a physical hazard. Methane can accumulate to explosive levels when allowed to exsolve (degas) from groundwater in closed environments.

environments depicted in panels a and b represent the range of separation distances shown in panel c. In Figure ES-7a, there are thousands of feet between the bottom of the underground drinking water resource and the hydraulically fractured rock formation. These conditions are generally reflective of deep shale formations (e.g., Haynesville Shale), where oil and gas production wells are first drilled vertically and then horizontally along the targeted rock formation. Microseismic data and modeling studies suggest that, under these conditions, fractures created during hydraulic fracturing are unlikely to grow through thousands of feet of rock into underground drinking water resources.

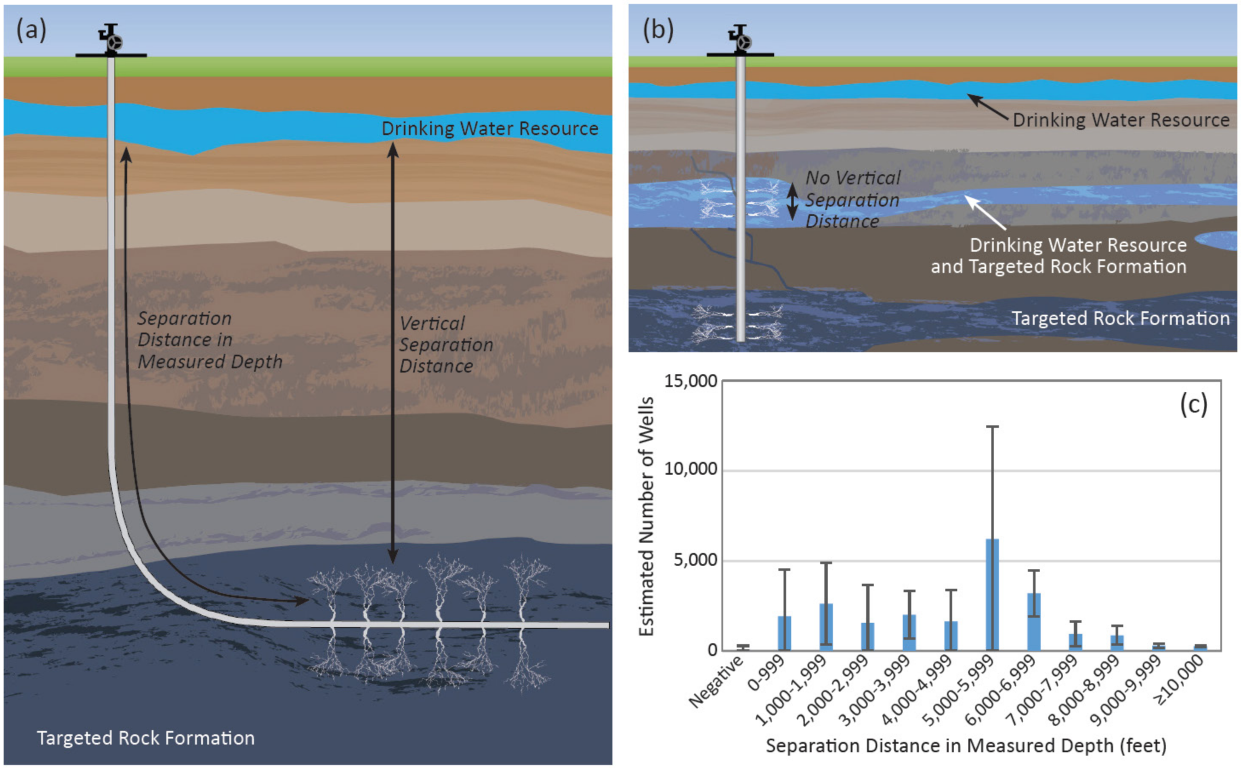

Figure ES-7. Examples of different subsurface environments in which hydraulic fracturing takes place.

In panel a, there are thousands of feet between the base of the underground drinking water resource and the part of the well that is hydraulically fractured. Panel b illustrates the co-location of groundwater and oil and gas resources. In these types of situations, there is no separation between the shallowest point of hydraulic fracturing within the well and the bottom of the underground drinking water resource. Panel c shows the estimated distribution of separation distances for approximately 23,000 oil and gas production wells hydraulically fractured by nine service companies between 2009 and 2019 (U.S. EPA, 2015n). The separation distance is the distance along the well between the point of shallowest hydraulic fracturing in the well and the base of the protected groundwater resource (illustrated in panel a). The error bars in panel c display 95% confidence intervals.

When drinking water resources are co-located with oil and gas resources and there is no vertical separation between the hydraulically fractured rock formation and the bottom of the underground drinking water resource (Figure ES-7b), the injection of hydraulic fracturing fluids impacts the quality of the drinking water resource. According to the information examined in this report, the overall occurrence of hydraulic fracturing within a drinking water resource appears to be low, with the activity generally concentrated in some areas in the western United States (e.g., the Wind River Basin near Pavillion, Wyoming, and the Powder River Basin of Montana and Wyoming).[1] Hydraulic fracturing within drinking water resources introduces hydraulic fracturing fluid into formations that may currently serve, or in the future could serve, as a drinking water source for public or private use. This is of concern in the short-term if people are currently using these formations as a drinking water supply. It is also of concern in the long-term, because drought or other conditions may necessitate the future use of these formations for drinking water.

Regardless of the vertical separation between the targeted rock formation and the underground drinking water resource, the presence of other wells near hydraulic fracturing operations can increase the potential for hydraulic fracturing fluids or other subsurface fluids to move to drinking water resources. There have been cases in which hydraulic fracturing at one well has affected a nearby oil and gas well or its fracture network, resulting in unexpected pressure increases at the nearby well, damage to the nearby well, or spills at the surface of the nearby well. These well communication events, or “frac hits,” have been reported in New Mexico, Oklahoma, and other locations. Based on the available information, frac hits most commonly occur when multiple wells are drilled from the same surface location and when wells are spaced less than 1,100 feet (335 meters) apart. Frac hits have also been observed at wells up to 8,422 feet (2,567 meters) away from a well undergoing hydraulic fracturing.

Abandoned wells near a well undergoing hydraulic fracturing can provide a pathway for vertical fluid movement to drinking water resources if those wells were not properly plugged or if the plugs and cement have degraded over time. For example, an abandoned well in Pennsylvania produced a 30-foot (9-meter) geyser of brine and gas for more than a week after hydraulic fracturing of a nearby gas well. The potential for fluid movement along abandoned wells may be a significant issue in areas with historic oil and gas exploration and production. Various studies estimate the number of abandoned wells in the United States to be significant. For instance, the Interstate Oil and Gas Compact Commission estimates that over 1 million wells were drilled in the United States prior to the enactment of state oil and gas regulations (IOGCC, 2008). The location and condition of many of these wells are unknown, and some states have programs to find and plug abandoned wells.

Well Injection Conclusions

Impacts on drinking water resources associated with the well injection stage of the hydraulic fracturing water cycle have occurred in some instances. In particular, mechanical integrity failures have allowed gases or liquids to move to underground drinking water resources. Additionally, hydraulic fracturing has occurred within underground drinking water resources in parts of the United States. This practice introduces hydraulic fracturing fluids into underground drinking water resources. Consequently, the mechanical integrity of the well and the vertical separation distance between the targeted rock formation and underground drinking water resources are important factors that affect the frequency and severity of impacts on drinking water resources. The presence of multiple layers of cemented casing and thousands of feet of rock between hydraulically fractured

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[1] Section 6.3.2 in Chapter 6.

rock formations and underground drinking water resources can reduce the frequency of impacts on drinking water resources during the well injection stage of the hydraulic fracturing water cycle.

Produced Water Handling

Activity: The on-site collection and handling of water that returns to the surface after hydraulic fracturing and the transportation of that water for disposal or reuse.

Relationship to Drinking Water Resources: Spills of produced water can reach groundwater and surface water resources.

After hydraulic fracturing, the injection pressure applied to the oil or gas production well is released, and the direction of fluid flow reverses, causing fluid to flow out of the well. The fluid that initially returns to the surface after hydraulic fracturing is mostly hydraulic fracturing fluid and is sometimes called "flowback" (Text Box ES-9). As time goes on, the fluid that returns to the surface contains water and economic quantities of oil and/or gas that are separated and collected. Water that returns to the surface during oil and gas production is similar in composition to the fluid naturally found in the targeted rock formation and is typically called "produced water." The term "produced water" is also used to refer to any water, including flowback, that returns to the surface through the production well as a by-product of oil and gas production. This latter definition of "produced water" is used in this report.

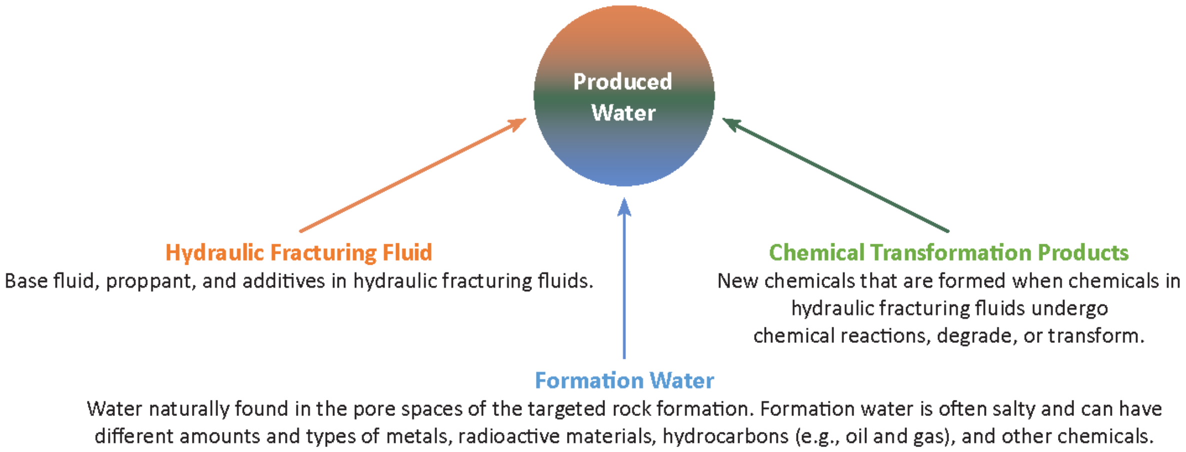
Produced water can contain many constituents, depending on the composition of the injected hydraulic fracturing fluid and the type of rock hydraulically fractured. Knowledge of the chemical composition of produced water comes from the collection and analysis of produced water samples, which often requires advanced laboratory equipment and techniques that can detect and quantify chemicals in produced water. In general, produced water has been found to contain:

- Salts, including those composed from chloride, bromide, sulfate, sodium, magnesium, and calcium;
- Metals, including barium, manganese, iron, and strontium;
- Naturally-occurring organic compounds, including benzene, toluene, ethylbenzene, xylenes (BTEX), and oil and grease;
- Radioactive materials, including radium; and
- Hydraulic fracturing chemicals and their chemical transformation products.

The amount of these constituents in produced water varies across the United States, both within and among different rock formations. Produced water from shale and tight gas formations is typically very salty compared to produced water from coalbed methane formations. For example, the salinity of produced water from the Marcellus Shale has been reported to range from less than 1,500 milligrams per liter (mg/L) of total dissolved solids to over 300,000 mg/L, while produced water from coalbed methane formations has been reported to range from 170 mg/L of total

Text Box ES-9. Produced Water from Hydraulically Fractured Oil and Gas Production Wells.

Water of varying quality is a byproduct of oil and gas production. The composition and volume of produced water varies by well, rock formation, and time after hydraulic fracturing. Produced water can contain hydraulic fracturing fluid, formation water, and chemical transformation products.



Hydraulic Fracturing Fluid
Base fluid, proppant, and additives in hydraulic fracturing fluids.

Chemical Transformation Products
New chemicals that are formed when chemicals in hydraulic fracturing fluids undergo chemical reactions, degrade, or transform.

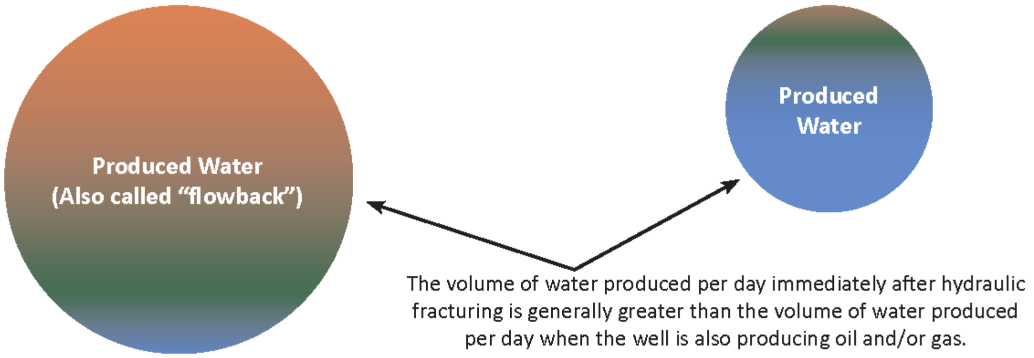
Formation Water
Water naturally found in the pore spaces of the targeted rock formation. Formation water is often salty and can have different amounts and types of metals, radioactive materials, hydrocarbons (e.g., oil and gas), and other chemicals.

Water Produced Immediately After Hydraulic Fracturing

Generally, the fluid that initially returns to the surface is mostly a mixture of the injected hydraulic fracturing fluid and its reaction and degradation products.

Water Produced During Oil or Gas Production

The fluid that returns to the surface when oil and/or gas is produced generally resembles the formation water.



The volume of water produced per day immediately after hydraulic fracturing is generally greater than the volume of water produced per day when the well is also producing oil and/or gas.

dissolved solids to nearly 43,000 mg/L.[1] Shale and sandstone formations also commonly contain radioactive materials, including uranium, thorium, and radium. As a result, radioactive materials have been detected in produced water from these formations.

Produced water volumes can vary by well, rock formation, and time after hydraulic fracturing. Volumes are often described in terms of the volume of hydraulic fracturing fluid used to fracture the well. For example, Figure ES-4 shows that wells in the Marcellus Shale typically produce 10-30% of the volume injected in the first 10 years after hydraulic fracturing. In comparison, some wells in the Barnett Shale have produced 100% of the volume injected in the first three years.

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[1] For comparison, the average salinity of seawater is approximately 35,000 mg/L of total dissolved solids.

Because of the large volumes used for hydraulic fracturing [about 4 million gallons (15 million liters) per well in the Marcellus Shale and the Barnett Shale], hundreds of thousands to millions of gallons of produced water need to be collected and handled at the well site. The volume of water produced per day generally decreases with time, so the volumes handled on site immediately after hydraulic fracturing can be much larger than the volumes handled when the well is producing oil and/or gas (Text Box ES-9).

Produced water flows from the well to on-site tanks or pits through a series of pipes or flowlines (Text Box ES-10) before being transported offsite via trucks or pipelines for disposal or reuse. While produced water collection, storage, and transportation systems are designed to contain produced water, spills can occur. Changes in drinking water quality can occur if produced water spills reach groundwater or surface water resources.

Produced water spills have been reported across the United States. Median spill volumes among the datasets reviewed for this report ranged from approximately 340 gallons (1,300 liters) to 1,000 gallons (3,800 liters) per spill.[1] There were, however, a small number of large volume spills. In North Dakota, for example, there were 12 spills greater than 21,000 gallons (79,500 liters), five spills greater than 42,000 gallons (160,000 liters), and one spill of 2.9 million gallons (11 million liters) in 2015. Common causes of produced water spills included human error and equipment leaks or failures. Common sources of produced water spills included hoses or lines and storage equipment.

Spills of produced water have reached groundwater and surface water resources. In U.S. EPA (2015m), 30 of the 225 (13%) produced water spills characterized were reported to have reached surface water (e.g., creeks, ponds, or wetlands), and one was reported to have reached groundwater. Of the spills that were reported to have reached surface water, reported spill volumes ranged from less than 170 gallons (640 liters) to almost 74,000 gallons (280,000 liters). A separate assessment of produced water spills reported to the California Office of Emergency Services between January 2009 and December 2014 reported that 18% of the spills impacted waterways (CCST, 2015a).

Documented cases of water resource impacts from produced water spills provide insights into the types of impacts that can occur. In most of the cases reviewed for this report, documented impacts included elevated levels of salinity in groundwater and/or surface water resources.[2] For example, the largest produced water spill reported in this report occurred in North Dakota in 2015, when approximately 2.9 million gallons (11 million liters) of produced water spilled from a broken pipeline. The spilled fluid flowed into Blacktail Creek and increased the concentration of chloride and the electrical conductivity of the creek; these observations are consistent with an increase in water salinity. Elevated levels of electrical conductivity and chloride were also found downstream in the Little Muddy River and the Missouri River. In another example, pits holding flowback fluids overflowed in Kentucky in 2007. The spilled fluid reached the Acorn Fork Creek, decreasing the pH of the creek and increasing the electrical conductivity.

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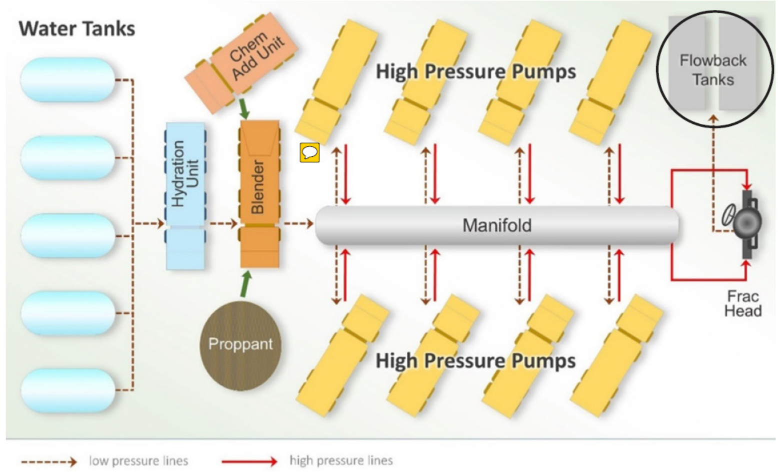
[1] See Section 7.4 in Chapter 7.

[2] Groundwater impacts from produced water management practices are described in Chapter 8 and summarized in the "Wastewater Disposal and Reuse" section below.

Text Box ES-10. On-Site Storage of Produced Water.

Water that returns to the surface after hydraulic fracturing is collected and stored on site in pits or tanks.

Above: Flowback pit. (Source: US DOE/NETL)
Right: Flowback tanks. (Source: US EPA)



Produced Water Storage Immediately after Hydraulic Fracturing

After hydraulic fracturing, water is returned to the surface. Water initially produced from the well after hydraulic fracturing is sometimes called "flowback." This water can be stored onsite in tanks or pits before being taken offsite for injection in Class II wells, reuse in other hydraulic fracturing operations, or aboveground disposal.

Source: Adapted from Olson (2011) and BJ Services Company (2009)

Produced Water Storage During Oil or Gas Production

Water is generally produced throughout the life of an oil and gas production well. During oil and gas production, the equipment on the well pad often includes the wellhead and storage tanks or pits for gas, oil, and produced water.

Above: Produced water storage pit. (Source: US EPA)
Left: Produced water storage tanks. (Source: US EPA)

Site-specific studies of historical produced water releases highlight the role of local geology in the movement of produced water through the environment. Whittemore (2007) described a site in Kansas where low permeability soils and rock caused produced water to primarily flow over the land surface to nearby surface water resources, reducing the amount of produced water that infiltrated soil. In contrast, Otton et al. (2007) explored the release of produced water and oil from two pits in Oklahoma. In this case, produced water from the pits flowed through thin soil and into the underlying, permeable rock. Produced water was also identified in deeper, less permeable rock. The authors suggest that produced water moved into the deeper, less permeable rock through natural fractures. Together, these studies highlight the role of preferential flow paths (i.e., paths of least resistance) in the movement of produced water through the environment.

Spill response activities likely reduce the severity of impacts on groundwater and surface water resources from produced water spills. For example, in the North Dakota example noted above, absorbent booms were placed in the affected creek and contaminated soil and oil-coated ice were removed from the site. In another example, a pipeline leak in Pennsylvania spilled approximately 11,000 gallons (42,000 liters) of produced water, which flowed into a nearby stream. In response, the pipeline was shut off, a dam was constructed to contain the spilled produced water, water was removed from the stream, and the stream was flushed with fresh water. In both examples, it was not possible to quantify how spill response activities reduced the severity of impacts on groundwater or surface water resources. However, actions taken after the spills were designed to stop produced water from entering the environment (e.g., shutting off a pipeline), remove produced water from the environment (e.g., using absorbent booms), and reduce the concentration of produced water constituents introduced into water resources (e.g., flushing a stream with fresh water).

The severity of impacts on water quality from spills of produced water depends on the identity and amount of produced water constituents that reach groundwater or surface water resources, the toxicity of those constituents, and the characteristics of the receiving water resource.[1] In particular, spills of produced water can have high levels of total dissolved solids, which affects how the spilled fluid moves through the environment. When a spilled fluid has greater levels of total dissolved solids than groundwater, the higher-density fluid can move downward through groundwater resources. Depending on the flow rate and other properties of the groundwater resource, impacts from produced water spills can last for years.

Produced Water Handling Conclusions

Spills of produced water during the produced water handling stage of the hydraulic fracturing water cycle have reached groundwater and surface water resources in some cases. Several cases of water resource impacts from produced water spills suggest that impacts are characterized by increases in the salinity of the affected groundwater or surface water resource. In the absence of direct pathways to groundwater resources (e.g., fractured rock), large volume spills are more likely to travel further from the site of the spill, potentially to groundwater or surface water resources.

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[1] Human health hazards associated with chemicals detected in produced water are discussed in Chapter 9 and summarized in the “Chemicals in the Hydraulic Fracturing Water Cycle” section below.

Additionally, saline produced water can migrate downward through soil and into groundwater resources, leading to longer-term groundwater contamination. Spill prevention and response activities can prevent spilled fluids from reaching groundwater or surface water resources and minimize impacts from spilled fluids.

Wastewater Disposal and Reuse

Activity: The disposal and reuse of hydraulic fracturing wastewater.

Relationship to Drinking Water Resources: Disposal practices can release inadequately treated or untreated hydraulic fracturing wastewater to groundwater and surface water resources.

In general, produced water from hydraulically fractured oil and gas production wells is managed through injection in Class II wells, reuse in other hydraulic fracturing operations, or various aboveground disposal practices (Text Box ES-11). In this report, produced water from hydraulically fractured oil and gas wells that is being managed through one of the above management strategies is referred to as "hydraulic fracturing wastewater." Wastewater management choices are affected by cost and other factors, including: the local availability of disposal methods; the quality of produced water; the volume, duration, and flow rate of produced water; federal, state, and local regulations; and well operator preferences.

Available information suggests that hydraulic fracturing wastewater is mostly managed through injection in Class II wells. Veil (2015) estimated that 93% of produced water from the oil and gas industry was injected in Class II wells in 2012. Although this estimate included produced water from oil and gas wells in general, it is likely indicative of nationwide management practices for hydraulic fracturing wastewater. Disposal of hydraulic fracturing wastewater in Class II wells is often cost-effective, especially when a Class II disposal well is located within a reasonable distance from a hydraulically fractured oil or gas production well. In particular, large numbers of active Class II disposal wells are found in Texas (7,876), Kansas (5,516), Oklahoma (3,837), Louisiana (2,448), and Illinois (1,054) (U.S. EPA, 2016d). Disposal of hydraulic fracturing wastewater in Class II wells has been associated with earthquakes in several states, which may reduce the availability of injection in Class II wells as a wastewater disposal option in these states.

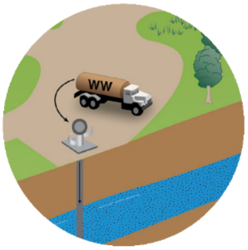
Nationwide, aboveground disposal and reuse of hydraulic fracturing wastewater are currently practiced to a much lesser extent compared to injection in Class II wells, and these management strategies appear to be concentrated in certain parts of the United States. For example, approximately 90% of hydraulic fracturing wastewater from Marcellus Shale gas wells in Pennsylvania was reused in other hydraulic fracturing operations in 2013 (Figure ES-4a). Reuse in hydraulic fracturing operations is practiced in some other areas of the United States as well, but at lower rates (approximately 5-20%). Evaporation ponds and percolation pits have historically been used in the western United States to manage produced water from the oil and gas industry and have likely been used to manage hydraulic fracturing wastewater. Percolation pits, in particular, were commonly reported to have been used to manage produced water from stimulated wells in Kern

Text Box ES-11. Hydraulic Fracturing Wastewater Management.

Produced water from hydraulically fractured oil and gas production wells is often, but not always, considered a waste product to be managed. Hydraulic fracturing wastewater (i.e., produced water from hydraulically fractured wells) is generally managed through injection in Class II wells, reuse in other hydraulic fracturing operations, and various aboveground disposal practices.

Injection in Class II Wells

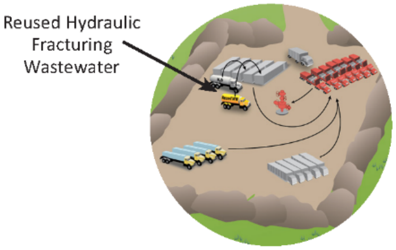
Most oil and gas wastewater—including hydraulic fracturing wastewater—is injected in Class II wells, which are regulated under the Underground Injection Control Program of the Safe Drinking Water Act.



Class II wells are used to inject wastewater associated with oil and gas production underground. Fluids can be injected for disposal or to enhance oil or gas production from nearby oil and gas production wells.

Reuse in Other Hydraulic Fracturing Operations

Hydraulic fracturing wastewater can be used, in combination with fresh water, to make up hydraulic fracturing fluids at nearby hydraulic fracturing operations.

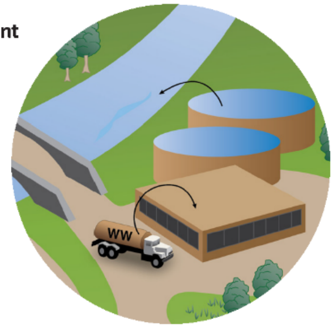


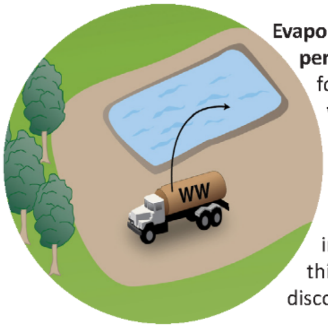
Reuse in other hydraulic fracturing operations depends on the quality and quantity of the available wastewater, the cost associated with treatment and transportation of the wastewater, and local water demand for hydraulic fracturing.

Aboveground Disposal Practices

Aboveground disposal of treated and untreated hydraulic fracturing wastewater can take many forms, including release to surface water resources and land application.

Some **wastewater treatment facilities** treat hydraulic fracturing wastewater and release the treated wastewater to surface water. Solid or liquid by-products of the treatment process can be sent to landfills or injected underground.





Evaporation ponds and **percolation pits** can be used for hydraulic fracturing wastewater disposal. Evaporation ponds allow liquid waste to naturally evaporate. Percolation pits allow wastewater to move into the ground, although this practice has been discontinued in most states.

Federal and state regulations affect aboveground disposal management options. For example, existing federal regulations generally prevent the direct release of wastewater pollutants to waters of the United States from onshore oil and gas extraction facilities east of the 98th meridian. However, in the arid western portion of the continental United States (west of the 98th meridian), direct discharges of wastewater from onshore oil and gas extraction facilities to waters of the United States may be permitted if the produced water has a use in agriculture or wildlife propagation and meets established water quality criteria when discharged.

County, California, between 2011 and 2014.[1] Beneficial uses (e.g., livestock watering and irrigation) are also practiced in the western United States if the water quality is considered acceptable, although available data on the use of these practices are incomplete.

Aboveground disposal practices generally release treated or, under certain conditions, untreated wastewater directly to surface water or the land surface (e.g., wastewater treatment facilities, evaporation pits, or irrigation). If released to the land surface, treated or untreated wastewater can move through soil to groundwater resources. Because the ultimate fate of the wastewater can be groundwater or surface water resources, the aboveground disposal of hydraulic fracturing wastewater, in particular, can impact drinking water resources.

Impacts on drinking water resources from the aboveground disposal of hydraulic fracturing wastewater have been documented. For example, early wastewater management practices in the Marcellus Shale region in Pennsylvania included the use of wastewater treatment facilities that released (i.e., discharged) treated wastewater to surface waters (Figure ES-8). The wastewater treatment facilities were unable to adequately remove the high levels of total dissolved solids found in produced water from Marcellus Shale gas wells, and the discharges contributed to elevated levels of total dissolved solids (particularly bromide) in the Monongahela River Basin. In the Allegheny River Basin, elevated bromide levels were linked to increases in the concentration of hazardous disinfection byproducts in at least one downstream drinking water facility and a shift to more toxic brominated disinfection byproducts.[2] In response, the Pennsylvania Department of Environmental Protection revised existing regulations to prevent these discharges and also requested that oil and gas operators voluntarily stop bringing certain kinds of hydraulic fracturing wastewater to facilities that discharge inadequately treated wastewater to surface waters.[3]

The scientific literature and recent data from the Pennsylvania Department of Environmental Protection suggest that other produced water constituents (e.g., barium, strontium, and radium) may have been introduced to surface waters through the release of inadequately treated hydraulic fracturing wastewater. In particular, radium has been detected in stream sediments at or near wastewater treatment facilities that discharged inadequately treated hydraulic fracturing wastewater. Such sediments can migrate if they are disturbed during dredging or flood events. Additionally, residuals from the treatment of hydraulic fracturing wastewater (i.e., the solids or liquids that remain after treatment) are concentrated in the constituents removed during treatment, and these residuals can impact groundwater or surface water resources if they are not managed properly.

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[1] Hydraulic fracturing was the predominant stimulation practice. Other stimulation practices included acid fracturing and matrix acidizing. California updated its regulations in 2015 to prohibit the use of percolation pits for the disposal of fluids produced from stimulated wells.

[2] Disinfection byproducts form through chemical reactions between organic material and disinfectants, which are used in drinking water treatment. Human health hazards associated with disinfection byproducts are described in Section 9.5.6 in Chapter 9.

[3] See Text Box 8-1 in Chapter 8.

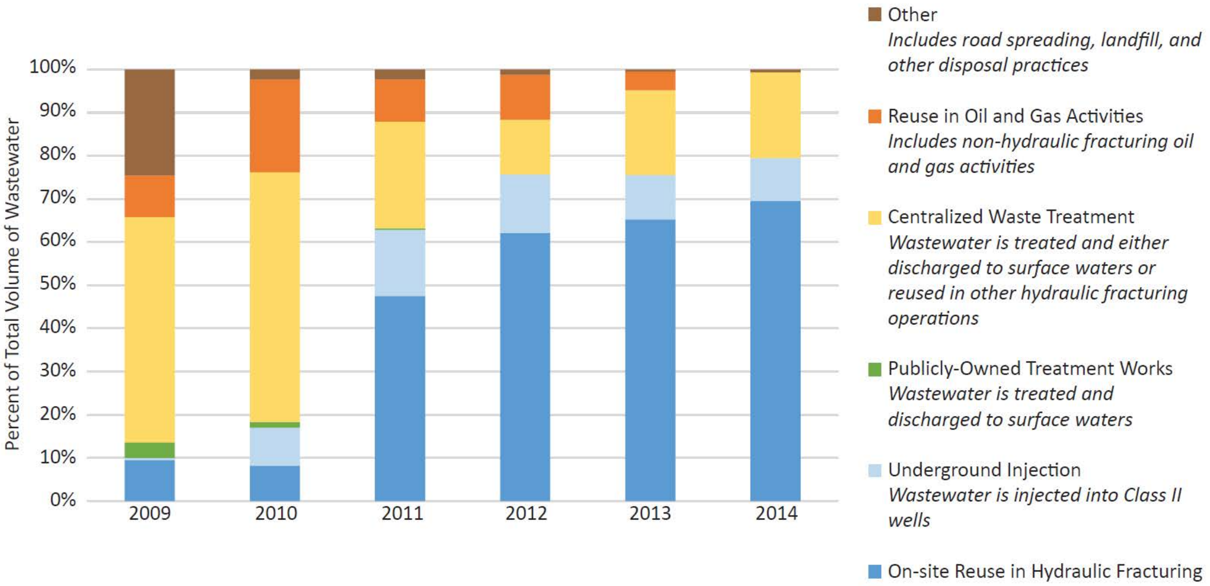

Figure ES-8. Changes in wastewater management practices over time in the Marcellus Shale area of Pennsylvania.

Data from PA DEP (2015a).

Impacts on groundwater and surface water resources from current and historic uses of lined and unlined pits, including percolation pits, in the oil and gas industry have been documented. For example, Kell (2011) reported 63 incidents of non-public water supply contamination from unlined or inadequately constructed pits in Ohio between 1983 and 2007, and 57 incidents of groundwater contamination from unlined produced water disposal pits in Texas prior to 1984. Other cases of impacts have been identified in several states, including New Mexico, Oklahoma, Pennsylvania, and Wyoming.[1] Impacts among these cases included the detection of volatile organic compounds in groundwater resources, wastewater reaching surface water resources from pit overflows, and wastewater reaching groundwater resources through liner failures. Based on documented impacts on groundwater resources from unlined pits, many states have implemented regulations that prohibit percolation pits or unlined storage pits for either hydraulic fracturing wastewater or oil and gas wastewater in general.

The severity of impacts on drinking water resources from the aboveground disposal of hydraulic fracturing wastewater depends on the volume and quality of the discharged wastewater and the characteristics of the receiving water resource. In general, large surface water resources with high flow rates can reduce the severity of impacts through dilution, although impacts may not be eliminated. In contrast, groundwater is generally slow moving, which can lead to an accumulation of hydraulic fracturing wastewater contaminants in groundwater from continuous or repeated discharges to the land surface; the resulting contamination can be long-lasting. The severity of

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[1] See Section 8.4.5 in Chapter 8.

impacts on groundwater resources will also be influenced by soil and sediment properties and other factors that control the movement or degradation of wastewater constituents.

Wastewater Disposal and Reuse Conclusions

The aboveground disposal of hydraulic fracturing wastewater has impacted the quality of groundwater and surface water resources in some instances. In particular, discharges of inadequately treated hydraulic fracturing wastewater to surface water resources have contributed to elevated levels of hazardous disinfection byproducts in at least one downstream drinking water system. Additionally, the use of lined and unlined pits for the storage or disposal of oil and gas wastewater has impacted surface and groundwater resources. Unlined pits, in particular, provide a direct pathway for contaminants to reach groundwater. Wastewater management is dynamic, and recent changes in state regulations and practices have been made to limit impacts on groundwater and surface water resources from the aboveground disposal of hydraulic fracturing wastewater.

Chemicals in the Hydraulic Fracturing Water Cycle

Chemicals are present in the hydraulic fracturing water cycle. During the chemical mixing stage of the hydraulic fracturing water cycle, chemicals are intentionally added to water to alter its properties for hydraulic fracturing (Text Box ES-6). Produced water, which is collected, handled, and managed in the last two stages of the hydraulic fracturing water cycle, contains chemicals added to hydraulic fracturing fluids, naturally occurring chemicals found in hydraulically fractured rock formations, and any chemical transformation products (Text Box ES-9). By evaluating available data sources, we compiled a list of 1,606 chemicals that are associated with the hydraulic fracturing water cycle, including 1,084 chemicals reported to have been used in hydraulic fracturing fluids and 599 chemicals detected in produced water. This list represents a national analysis; an individual well would likely have a fraction of the chemicals on this list and may have other chemicals that were not included on this list.

In many stages of the hydraulic fracturing water cycle, the severity of impacts on drinking water resources depends, in part, on the identity and amount of chemicals that enter the environment. The properties of a chemical influence how it moves and transforms in the environment and how it interacts with the human body. Therefore, some chemicals in the hydraulic fracturing water cycle are of more concern than others because they are more likely to move with water (e.g., spilled hydraulic fracturing fluid) to drinking water resources, persist in the environment (e.g., chemicals that do not degrade), and/or affect human health.

Evaluating potential hazards from chemicals in the hydraulic fracturing water cycle is most useful at local and/or regional scales because chemical use for hydraulic fracturing can vary from well to well and because the characteristics of produced water are influenced by the geochemistry of hydraulically fractured rock formations. Additionally, site-specific characteristics (e.g., the local landscape, and soil and subsurface permeability) can affect whether and how chemicals enter drinking water resources, which influences how long people may be exposed to specific chemicals and at what concentrations. As a first step for informing site-specific risk assessments, the EPA compiled toxicity values for chemicals in the hydraulic fracturing water cycle from federal, state, and international sources that met the EPA's criteria for inclusion in this report.[1,2]

The EPA was able to identify chronic oral toxicity values from the selected data sources for 98 of the 1,084 chemicals that were reported to have been used in hydraulic fracturing fluids between 2005 and 2013. Potential human health hazards associated with chronic oral exposure to these chemicals include cancer, immune system effects, changes in body weight, changes in blood chemistry, cardiotoxicity, neurotoxicity, liver and kidney toxicity, and reproductive and developmental toxicity. Of the chemicals most frequently reported to FracFocus 1.0, nine had toxicity values from the selected data sources (Table ES-3). Critical effects for these chemicals include kidney/renal toxicity, hepatotoxicity, developmental toxicity (extra cervical ribs), reproductive toxicity, and decreased terminal body weight.

Table ES-3. Available chronic oral reference values for hydraulic fracturing chemicals reported in 10% or more of disclosures in FracFocus 1.0.

Chemical name (CASRN)[a]	Chronic oral reference value (mg/kg/day)	Critical effect	Percent of FracFocus 1.0 disclosures[b]
Propargyl alcohol (107-19-7)	0.002[c]	Renal and hepatotoxicity	33
1,2,4-Trimethylbenzene (95-63-6)	0.01[c]	Decreased pain sensitivity	13
Naphthalene (91-20-3)	0.02[c]	Decreased terminal body weight	19
Sodium chlorite (7758-19-2)	0.03[c]	Neuro-developmental effects	11
2-Butoxyethanol (111-76-2)	0.1[c]	Hemosiderin deposition in the liver	23
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides (68424-85-1)	0.44[d]	Decreased body weight and weight gain	12
Formic acid (64-18-6)	0.9[e]	Reproductive toxicity	11
Ethylene glycol (107-21-1)	2[c]	Kidney toxicity	47
Methanol (67-56-1)	2[c]	Extra cervical ribs	73

[a] "Chemical" refers to chemical substances with a single CASRN; these may be pure chemicals (e.g., methanol) or chemical mixtures (e.g., hydrotreated light petroleum distillates).

[b] Analysis considered 35,957 disclosures that met selected quality assurance criteria. See Table 9-2 in Chapter 9.

[c] From the EPA Integrated Risk Information System database.

[d] From the EPA Human Health Benchmarks for Pesticides database.

[e] From the EPA Provisional Peer-Reviewed Toxicity Value database.

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[1] Specifically, the EPA compiled noncancer oral reference values and cancer oral slope factors (Chapter 9). A reference value describes the dose of a chemical that is likely to be without an appreciable risk of adverse health effects. In the context of this report, the term "reference value" generally refers to reference values for noncancer effects occurring via the oral route of exposure and for chronic durations. An oral slope factor is an upper-bound estimate on the increased cancer risk from a lifetime oral exposure to an agent.

[2] The EPA's criteria for inclusion in this report are described in Section 9.4.1 in Chapter 9. Sources of information that met these criteria are listed in Table 9-1 of Chapter 9.

Chronic oral toxicity values from the selected data sources were identified for 120 of the 599 chemicals detected in produced water. Potential human health hazards associated with chronic oral exposure to these chemicals include liver toxicity, kidney toxicity, neurotoxicity, reproductive and developmental toxicity, and carcinogenesis. Chemical-specific toxicity values are included in Chapter 9.

Chemicals in the Hydraulic Fracturing Water Cycle Conclusions

Some of the chemicals in the hydraulic fracturing water cycle are known to be hazardous to human health. Of the 1,606 chemicals identified by the EPA, 173 had chronic oral toxicity values from federal, state, and international sources that met the EPA's criteria for inclusion in this report. These data alone, however, are insufficient to determine which chemicals have the greatest potential to impact drinking water resources and human health. To understand whether specific chemicals can affect human health through their presence in drinking water, data on chemical concentrations in drinking water would be needed. In the absence of these data, relative hazard potential assessments could be conducted at local and/or regional scales using the multi-criteria decision analysis approach outlined in Chapter 9. This approach combines available chemical occurrence data with selected chemical, physical, and toxicological properties to place the severity of potential impacts (i.e., the toxicity of specific chemicals) into the context of factors that affect the likelihood of impacts (i.e., frequency of use, and chemical and physical properties relevant to environmental fate and transport).

Data Gaps and Uncertainties

The information reviewed for this report included cases of impacts on drinking water resources from activities in the hydraulic fracturing water cycle. Using these cases and other data, information, and analyses, we were able to identify factors that likely result in more frequent or more severe impacts on drinking water resources. However, there were instances in which we were unable to form conclusions about the potential for activities in the hydraulic fracturing water cycle to impact drinking water resources and/or the factors that influence the frequency or severity of impacts. Below, we provide perspective on the data gaps and uncertainties that prevented us from drawing additional conclusions about the potential for impacts on drinking water resources and/or the factors that affect the frequency and severity of impacts.

In general, comprehensive information on the location of activities in the hydraulic fracturing water cycle is lacking, either because it is not collected, not publicly available, or prohibitively difficult to aggregate. This includes information on the:

- Above- and belowground locations of water withdrawals for hydraulic fracturing;
- Surface locations of hydraulically fractured oil and gas production wells, where the chemical mixing, well injection, and produced water handling stages of the hydraulic fracturing water cycle take place;
- Belowground locations of hydraulic fracturing, including data on fracture growth; and
- Locations of hydraulic fracturing wastewater management practices, including the disposal of treatment residuals.

There can also be uncertainty in the location of drinking water resources. In particular, depths of groundwater resources that are, or in the future could be, used for drinking water are not always known. If comprehensive data about the locations of both drinking water resources and activities in the hydraulic fracturing water cycle were available, it would have been possible to more completely identify areas in the United States in which hydraulic fracturing-related activities either directly interact with drinking water resources or have the potential to interact with drinking water resources.

In places where we know activities in the hydraulic fracturing water cycle have occurred or are occurring, data that could be used to characterize the presence, migration, or transformation of hydraulic fracturing-related chemicals in the environment before, during, and after hydraulic fracturing were scarce. Specifically, local water quality data needed to compare pre- and post-hydraulic fracturing conditions are not usually collected or readily available. The limited amount of data collected before, during, and after activities in the hydraulic fracturing water cycle reduces the ability to determine whether these activities affected drinking water resources.

Site-specific cases of alleged impacts on underground drinking water resources during the well injection stage of the hydraulic fracturing water cycle are particularly challenging to understand (e.g., methane migration in Dimock, Pennsylvania; the Raton Basin of Colorado; and Parker County, Texas[1]). This is because the subsurface environment is complex and below ground fluid movement is not directly observable. In cases of alleged impacts, activities in the hydraulic fracturing water cycle may be one of several causes of impacts, including other oil and gas activities, other industries, and natural processes. Thorough scientific investigations are often necessary to narrow down the list of potential causes to a single source at site-specific cases of alleged impacts.

Additionally, information on chemicals in the hydraulic fracturing water cycle (e.g., chemical identity; frequency of use or occurrence; and physical, chemical, and toxicological properties) is not complete. Well operators claimed at least one chemical as confidential at more than 70% of wells reported to FracFocus 1.0 (U.S. EPA, 2015a).[2] The identity and concentration of these chemicals, their transformation products, and chemicals in produced water would be needed to characterize how chemicals associated with hydraulic fracturing activities move through the environment and interact with the human body. Identifying chemicals in the hydraulic fracturing water cycle also informs decisions about which chemicals would be appropriate to test for when establishing pre-hydraulic fracturing baseline conditions and in the event of a suspected drinking water impact.

Of the 1,606 chemicals identified by the EPA in hydraulic fracturing fluid and/or produced water, 173 had toxicity values from sources that met the EPA's criteria for inclusion in this report. Toxicity values from these selected data sources were not available for 1,433 (89%) of the chemicals, although many of these chemicals have toxicity data available from other data sources.[3] Given the

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[1] See Text Boxes 6-2 (Dimock, Pennsylvania), 6-3 (Raton Basin), and 6-4 (Parker County, Texas) in Chapter 6.

[2] Chemical withholding rates in FracFocus have increased over time. Konschnik and Dayalu (2016) reported that 92% of wells reported in FracFocus 2.0 between approximately March 2011 and April 2015 used at least one chemical that was claimed as confidential.

[3] Chapter 9 describes the availability of data in other data sources. The quality of these data sources was not evaluated as part of this report.

large number of chemicals identified in the hydraulic fracturing water cycle, this missing information represents a significant data gap that makes it difficult to fully understand the severity of potential impacts on drinking water resources.

Because of the significant data gaps and uncertainties in the available data, it was not possible to fully characterize the severity of impacts, nor was it possible to calculate or estimate the national frequency of impacts on drinking water resources from activities in the hydraulic fracturing water cycle. We were, however, able to estimate impact frequencies in some, limited cases (i.e., spills of hydraulic fracturing fluids or produced water and mechanical integrity failures).[1] The data used to develop these estimates were often limited in geographic scope or otherwise incomplete. Consequently, national estimates of impact frequencies for any stage of the hydraulic fracturing water cycle have a high degree of uncertainty. Our inability to quantitatively determine a national impact frequency or to characterize the severity of impacts, however, did not prevent us from qualitatively describing factors that affect the frequency or severity of impacts at the local level.

Report Conclusions

This report describes how activities in the hydraulic fracturing water cycle can impact—and have impacted—drinking water resources and the factors that influence the frequency and severity of those impacts. It also describes data gaps and uncertainties that limited our ability to draw additional conclusions about impacts on drinking water resources from activities in the hydraulic fracturing water cycle. Both types of information—what we know and what we do not know—provide stakeholders with scientific information to support future efforts.

The uncertainties and data gaps identified throughout this report can be used to identify future efforts to further our understanding of the potential for activities in the hydraulic fracturing water cycle to impact drinking water resources and the factors that affect the frequency and severity of those impacts. Future efforts could include, for example, groundwater and surface water monitoring in areas with hydraulically fractured oil and gas production wells or targeted research programs to better characterize the environmental fate and transport and human health hazards associated with chemicals in the hydraulic fracturing water cycle. Future efforts could identify additional vulnerabilities or other factors that affect the frequency and/or severity of impacts.

In the near term, decision-makers could focus their attention on the combinations of hydraulic fracturing water cycle activities and local- or regional-scale factors that are more likely than others to result in more frequent or more severe impacts. These include:

- Water withdrawals for hydraulic fracturing in times or areas of low water availability, particularly in areas with limited or declining groundwater resources;
- Spills during the management of hydraulic fracturing fluids and chemicals or produced water that result in large volumes or high concentrations of chemicals reaching groundwater resources;

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[1] See Chapter 10.

- Injection of hydraulic fracturing fluids into wells with inadequate mechanical integrity, allowing gases or liquids to move to groundwater resources;
- Injection of hydraulic fracturing fluids directly into groundwater resources;
- Discharge of inadequately treated hydraulic fracturing wastewater to surface water resources; and
- Disposal or storage of hydraulic fracturing wastewater in unlined pits, resulting in contamination of groundwater resources.

The above combinations of activities and factors highlight, in particular, the vulnerability of groundwater resources to activities in the hydraulic fracturing water cycle. By focusing attention on the situations described above, impacts on drinking water resources from activities in the hydraulic fracturing water cycle could be prevented or reduced.

Overall, hydraulic fracturing for oil and gas is a practice that continues to evolve. Evaluating the potential for activities in the hydraulic fracturing water cycle to impact drinking water resources will need to keep pace with emerging technologies and new scientific studies. This report provides a foundation for these efforts, while helping to reduce current vulnerabilities to drinking water resources.

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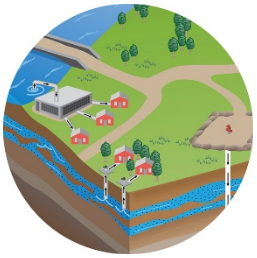
Chapter 1. Introduction



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1. Introduction

1.1 Background

People rely on clean and plentiful water resources to meet their basic needs. In the early 2000s, members of the public began to raise concerns about the use of hydraulic fracturing for oil and gas production and its potential impacts on drinking water resources. Hydraulic fracturing involves the injection of fluids into a well under pressures great enough to fracture oil- and gas-bearing formations. While hydraulic fracturing has been used to enhance oil and gas production from conventional rock formations, the combination of hydraulic fracturing and directional drilling has made it economical to produce oil and gas from previously unused unconventional rock formations.[1] This has led to increases in oil and gas production and expanded activity throughout the United States.

Concerns about the impacts of hydraulic fracturing activities on both the quality and quantity of drinking water resources have been raised by the public. Some residents living close to oil and gas production wells report changes in the quality of groundwater resources used for drinking water and assert that hydraulic fracturing is responsible for these changes. Other concerns include impacts on water availability due to water use in hydraulic fracturing, especially in areas of the country experiencing drought, and impacts on water quality from the disposal of wastewater generated after hydraulic fracturing.

In response to public concerns, the U.S. Congress urged the U.S. Environmental Protection Agency (EPA) to study the relationship between hydraulic fracturing and drinking water (H.R. Rep. 111-316, 2009). In 2011, the EPA published its *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (U.S. EPA, 2011d; hereafter Study Plan), which described the research the Agency would be conducting on activities involving water that support hydraulic fracturing (referred to as the "hydraulic fracturing water cycle"). The research described in the Study Plan began the same year. In 2012, the EPA issued *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources: Progress Report* (U.S. EPA, 2012h; hereafter Progress Report) to update the public on the status of EPA's research. Since its initiation, the EPA's hydraulic fracturing study has directly resulted in the publication of 27 separate government reports and scientific journal articles. This assessment integrates results from those reports and scientific journal articles with publicly available data and information. It represents the culmination of the EPA's hydraulic fracturing study focused on characterizing the relationship between hydraulic fracturing and drinking water.

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[1] Conventional oil- and gas-bearing rock formations are often described as "permeable" and tend to have many large, well-connected pore spaces that allow fluids to move within the rock formation. Unconventional oil- and gas-bearing rock formations do not exhibit these characteristics. See Chapter 3 for more information on uses of the terms conventional and unconventional.

1.2 Goals

The goals of this assessment are to assess the potential for activities in the hydraulic fracturing water cycle to impact the quality or quantity of drinking water resources and to identify factors that affect the frequency or severity of those impacts.

1.3 Scope

The hydraulic fracturing water cycle defines the activities that are within the scope of this assessment. This cycle encompasses activities involving water that support hydraulic fracturing and consists of five stages:

1. **Water Acquisition:** the withdrawal of groundwater or surface water to make hydraulic fracturing fluids;
2. **Chemical Mixing:** the mixing of a base fluid (typically water), proppant, and additives at the well site to create hydraulic fracturing fluids;[1]
3. **Well Injection:** the injection and movement of hydraulic fracturing fluids through the oil and gas production well and in the targeted rock formation;
4. **Produced Water Handling:** the on-site collection and handling of water that returns to the surface after hydraulic fracturing and the transportation of that water for disposal or reuse; and [2]
5. **Wastewater Disposal and Reuse:** the disposal and reuse of hydraulic fracturing wastewater.[3]

The hydraulic fracturing water cycle, and thus the scope of this assessment, was developed with input from stakeholders (i.e., federal, state, and tribal partners; industry and non-governmental organizations; and the general public) and the EPA's Science Advisory Board (SAB) (U.S. EPA, 2011d). The hydraulic fracturing water cycle and our assessment scope reflect interest from stakeholders in understanding impacts from the act of hydraulic fracturing itself as well as the activities involving water that support it, without examining impacts from oil and gas production development broadly.

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[1] A base fluid is the fluid into which proppants and additives are mixed to make a hydraulic fracturing fluid; water is an example of a base fluid. Additives are chemicals or mixtures of chemicals that are added to the base fluid to change its properties.

[2] "Produced water" is defined in this report as water that flows from and through oil and gas wells to the surface as a by-product of oil and gas production.

[3] "Hydraulic fracturing wastewater" is defined in this report as produced water from hydraulically fractured oil and gas wells that is being managed using practices that include, but are not limited to, injection in Class II wells, reuse in other hydraulic fracturing operations, and various aboveground disposal practices. The term "wastewater" is being used as a general description of certain waters and is not intended to constitute a term of art for legal or regulatory purposes. Class II wells are used to inject wastewater associated with oil and gas production underground and are regulated under the Underground Injection Control Program of the Safe Drinking Water Act.

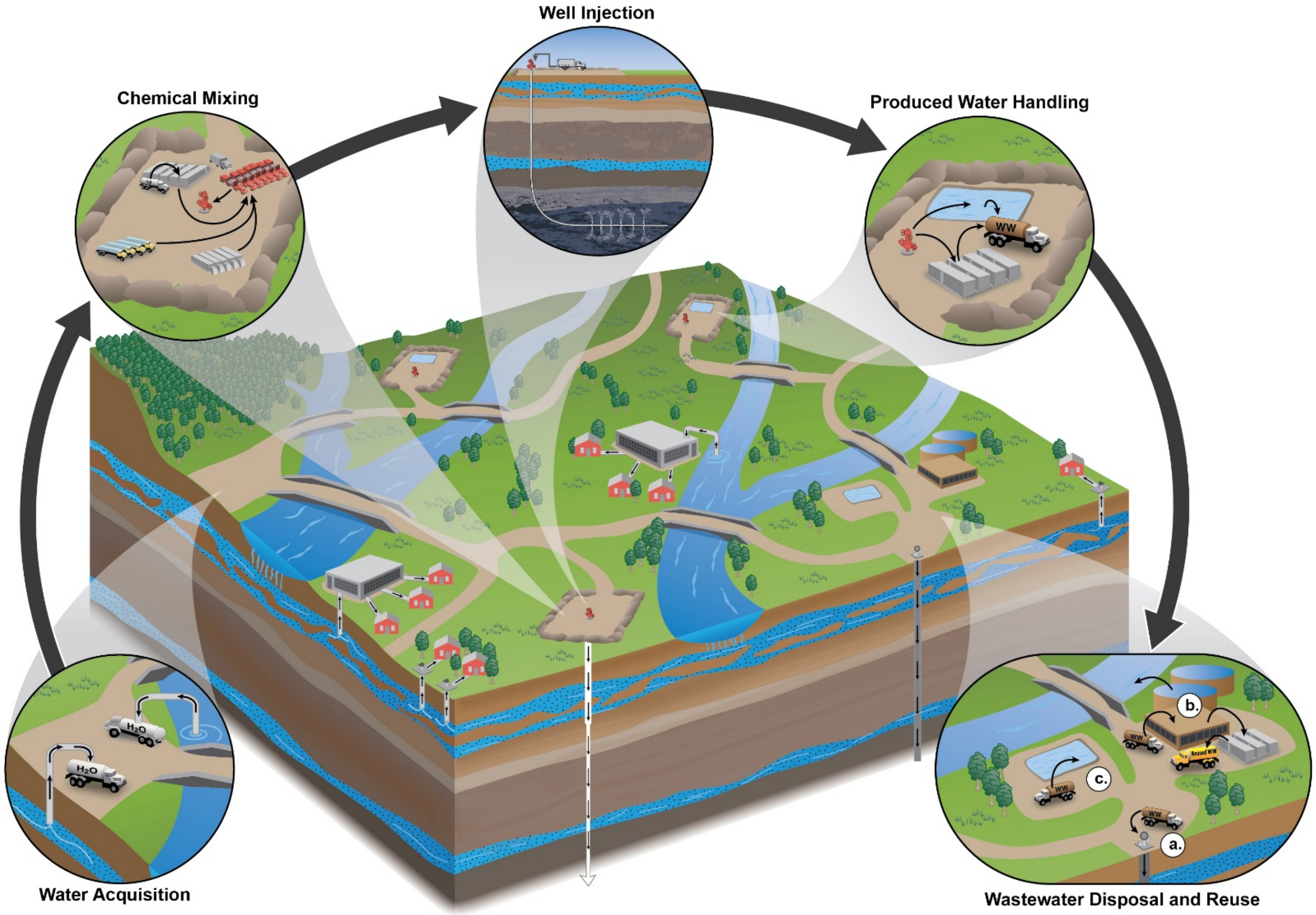

Figure 1-1. Conceptualized view of the stages of the hydraulic fracturing water cycle.

Shown here is a generalized landscape depicting simplified activities of the hydraulic fracturing water cycle, their relationship to each other, and their relationship to drinking water resources. Activities may take place in the same watershed or different watersheds and close to or far from drinking water resources. Drinking water resources are any groundwater or surface water that now serves, or in the future could serve, as a source of drinking water for public or private use. Arrows depict the movement of water and chemicals. Specific activities in the “Wastewater Disposal and Reuse” inset are (a) disposal via injection well, (b) wastewater treatment with reuse or discharge, and (c) evaporation or percolation pit disposal. Note: Figure not to scale.

This assessment focuses on hydraulic fracturing in onshore oil and gas wells in the contiguous United States; limited available information on hydraulic fracturing in Alaska is included. To the extent possible, this assessment addresses hydraulic fracturing in all types of oil- and gas-bearing formations in which it is conducted, including shale, so-called 'tight' formations (e.g., certain sandstones, siltstones, and carbonates), coalbeds, and conventional rock formations. The assessment tends to focus on hydraulic fracturing in shale, reflecting the abundance and availability of literature and data on hydraulic fracturing in this type of rock formation.

In this assessment, we consider how activities in the hydraulic fracturing water cycle interact with drinking water resources. Consistent with the Study Plan (U.S. EPA, 2011d), drinking water resources are defined within this assessment as any groundwater or surface water that now serves, or in the future could serve, as a source of drinking water for public or private use. This definition is broader than most regulatory definitions of "drinking water" to include both fresh and non-fresh bodies of water that are and could be used now or could be used in the future as sources of drinking water (Chapter 2). We note that drinking water resources provide not only water that individuals actually drink but also water used for many additional purposes such as cooking and bathing.

As part of the assessment, we evaluated immediate, near-term, and delayed effects on drinking water resources from normal operations and accidents. For example, we considered how surface spills of hydraulic fracturing fluids may have immediate or near-term impacts on neighboring surface water and shallow groundwater quality (Chapters 5 and 7). We also considered how the potential release of hydraulic fracturing fluids in the subsurface may take years to impact groundwater resources, because liquids and gas often move slowly in the subsurface (Chapter 6). Additionally, impacts may be transient or long-term, often depending on the characteristics of the affected drinking water resource. Finally, impacts may be detected near the hydraulic fracturing water cycle activity or some distance away. For instance, we considered that, depending on the constituents of treated hydraulic fracturing wastewater discharged to a stream and the flow in that stream, drinking water resource quality could be affected a significant distance downstream (Chapter 8).

This assessment focuses predominantly on activities supporting a single well or multiple wells at one site, accompanied by a more limited discussion of cumulative activities and the impacts that could result from having many wells on a landscape. Studies of cumulative effects are generally lacking, but we use the scientific literature to address this topic where possible.[1]

We examine *impacts* of hydraulic fracturing for oil and gas on drinking water resources and address *factors* that affect the *frequency* or *severity* of impacts. Specific definitions used in this assessment are provided below:

- An **impact** is any change in the quality or quantity of drinking water resources, regardless of severity, that results from an activity in the hydraulic fracturing water cycle.

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[1] Cumulative effects refer to combined changes in the environment that can take place as a result of multiple activities over time and/or space.

- A **factor** is a feature of hydraulic fracturing operations or an environmental condition that affects the frequency or severity of impacts.
- **Frequency** is the number of impacts per a given unit (e.g., per geographic area, per unit time, per number of hydraulically fractured wells, per number of water bodies). Reflecting the scientific literature, the most common representation of frequency in this assessment is number of impacts per hydraulically fractured well.
- **Severity** is the magnitude of change in the quality or quantity of a drinking water resource as measured by a given metric (e.g., duration, spatial extent, contaminant concentration).

We identify and discuss factors affecting the frequency or severity of impacts to avoid a simple inventory of all specific situations in which hydraulic fracturing might alter drinking water quality or quantity. This allows knowledge about the conditions under which impacts are likely or unlikely to occur to be applied to new circumstances (e.g., a new area of oil or gas development where hydraulic fracturing is expected to be used) and could inform the development of strategies to prevent impacts. Although no attempt has been made in this assessment to identify or evaluate comprehensive best practices for states, tribes, or the industry, we describe ways to avoid or reduce the frequency or severity of impacts from hydraulic fracturing activities as they have been reported in the scientific literature. Laws, regulations, and policies also exist to protect drinking water resources (Text Box 1-1), but a comprehensive summary and evaluation of current or proposed regulations and policies is beyond the scope of this assessment.

Text Box 1-1. Regulatory Protection for Drinking Water Resources.

The quality and quantity of drinking water resources are protected in the United States by a collection of federal, state, tribal, and local laws, regulations, and polices. They differ with respect to how water resources are defined (Chapter 2) and thus which resources qualify for protection. Some policies protect water resources from oil and gas industry activities as part of a larger set of regulated industries, or from oil and gas industry activities only, or from hydraulic fracturing-related activities, specifically. Multiple federal and state agencies, departments, or divisions are responsible for implementing these laws, regulations, and policies. An exhaustive summary of current and emerging laws, regulations, and policies, those responsible for implementing them, and enforcement or effectiveness is not in the scope of this assessment. The following information is designed to give the reader a general understanding of how the U.S. government and states protect drinking water resources from the potential impacts of activities in the hydraulic fracturing water cycle.

On the federal level, the U.S. government regulates some activities in the hydraulic fracturing water cycle to protect drinking water resources. For example, under the Clean Water Act, the National Pollution Discharge Elimination System (NPDES) program regulates surface discharge of wastewater from the oil and gas sector (in addition to many other industries). Issuance and enforcement of NPDES discharge permits is primarily the responsibility of the states that have received NPDES program authorization from the EPA. In addition, the Safe Drinking Water Act's (SDWA) Underground Injection Control program regulates the underground disposal of hydraulic fracturing wastewater (and wastewater generated in other industries) and, like the NPDES program, allows states to seek program authorization from the EPA. The federal government does not have the authority to regulate hydraulic fracturing as an injection activity under the SDWA except when it

(Text Box 1-1 is continued on the following page.)

Text Box 1-1 (continued). Regulatory Protection for Drinking Water Resources.

(1) involves diesel fuel, a result of legislation passed in 2005, or (2) causes an imminent and substantial endangerment to the health of persons. Additionally, produced water is exempted from regulation as a hazardous waste under the Resource Conservation and Recovery Act Subtitle C. In 2015, the U.S. Department of the Interior published a set of regulations for conducting hydraulic fracturing operations on federal public and tribal lands. It includes requirements to help protect groundwater by updating standards for well mechanical integrity, wastewater disposal, and public disclosure of chemicals. As of late 2016, a federal district court judge has set aside these regulations as outside the scope of the U.S. Department of the Interior's authority, and this decision is being appealed.

States generally have the primary responsibility for protecting drinking water resources from the impacts of hydraulic fracturing activities (Guralnick, 2016; Zirogannis et al., 2016). Some states have put in place broad restrictions or moratoria on hydraulic fracturing activities due in part to concerns about potential risks to drinking water resources. Many other states allow hydraulic fracturing activities, and several sources of information track and/or summarize their laws, regulations, and policies. An online database of statutes and regulations applicable to the oil and gas industry and related to water quality, water quantity, and air quality in 17 states is maintained by LawAtlas (www. lawatlas.org/oilandgas).

State approaches vary widely, from comprehensive laws addressing all aspects of hydraulic fracturing activities to regulations addressing specific activities (Guralnick, 2016). In 2009 and 2014, the Ground Water Protection Council (GWPC) summarized regulations that are designed to protect water resources and applicable to the oil and gas industry in 27 states; they did not investigate compliance (GWPC, 2014, 2009). The summaries revealed that regulations are carried out by either oil and gas agencies, environmental agencies, or both, depending on the state. They also identified general categories of existing regulations that could control impacts on drinking water resources from activities in the hydraulic fracturing water cycle, including permitting, well design and integrity, injection activities, and surface management of fluids. Categories were comprised of regulatory "elements." Certain elements had been adopted across 90% or more of states included in the summaries that allowed hydraulic fracturing as of July 2013: surface casing generally must be set below the deepest protected groundwater zone; protected groundwater depth is determined on a well-specific basis or by rule; and surface casing must be cemented from bottom to top. All other elements were adopted at lower and widely varying rates. For example, as of July 2013, a requirement for water well testing and monitoring adjacent to hydraulic fracturing operations existed in five states. Other states, including California, have added this requirement since then.

State laws, regulations, and policies are continually changing. Changes may be initiated by state legislatures or regulatory agencies (sometimes in response to legal decisions) and generally apply to new wells or future hydraulic fracturing operations and not existing wells or wells that have been hydraulically fractured in the past. Third-party groups, like the State Review of Oil and Natural Gas Environmental Regulations (STRONGER) organization, offer multi-stakeholder reviews of state oil and gas regulatory programs and recommendations to improve those programs according to guidelines developed by their workgroups. Interstate organizations of state agency representatives also have initiatives to develop oil and gas resources while protecting water and other environmental resources, initiatives like the GWPC and Interstate Oil and Gas Compact Commission's States First. In combination with changing policies, new technologies (such as those that make it possible to reuse hydraulic fracturing wastewater in subsequent hydraulic fracturing operations) have the potential to further reduce impacts on drinking water resources.

We identify and evaluate potential human health hazards of hydraulic fracturing-related chemicals (Chapter 9), but this assessment is not a human health risk assessment. It does not identify populations that are exposed to chemicals or other stressors in the environment, estimate the extent of exposure, or estimate the incidence of human health impacts. Relatedly, we did not conduct site-specific predictive modeling to quantitatively estimate contaminant concentrations in drinking water resources, although modeling studies conducted by others are described.

This assessment focuses on the potential for impacts from activities in the hydraulic fracturing water cycle on drinking water resources. It does not address all concerns that have been raised about hydraulic fracturing nor about oil and gas exploration and production more generally. Activities that are not considered in this assessment include acquisition and transport of constituents of hydraulic fracturing fluids besides water (e.g., sand mining and chemical production); site selection and development; other infrastructure development (e.g., roads, pipelines, compressor stations); site reclamation; and well closure. We consider these activities to be outside the scope of the hydraulic fracturing water cycle and, therefore, their impacts are not addressed in this assessment. Disposal of hydraulic fracturing wastewater in underground injection control wells is described and characterized, but consistent with the Study Plan, potential for impacts of this practice on drinking water resources is not included. Additionally, this report does not discuss the potential impacts of hydraulic fracturing on other water uses (e.g., agriculture or industry), other aspects of the environment (e.g., air quality, induced seismicity, or ecosystems), worker health and safety, or communities. Finally, this assessment focuses on the available science and does not review, consider, or recommend policy options.

1.4 Approach

This assessment relies on scientific literature and data that address topics within the scope of the hydraulic fracturing water cycle. Scientific journal articles and peer-reviewed EPA reports containing results from the EPA's hydraulic fracturing study comprise one set of applicable literature. Other literature evaluated includes articles published in science and engineering journals, federal and state government reports, non-governmental organization (NGO) reports, and oil and gas industry publications. Data sources examined include federal- and state-collected data sets, databases curated by federal and state government agencies, other publicly available data and information, and data submitted by industry to the EPA.[1] In total, we cite approximately 1,200 sources of scientific data and information in this assessment.

1.4.1 EPA Hydraulic Fracturing Study Publications

The research topic areas and projects described in the Study Plan were developed with substantial expert and public input and were designed to meet the data and information needs of this assessment. As such, peer-reviewed results of research that the EPA conducted under the Study Plan, published separately as EPA reports or as journal articles, are incorporated and cited

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[1] Confidential and non-confidential business information was provided to the EPA by nine hydraulic fracturing service companies in response to a September 2010 information request and by nine oil and gas well operators in response to an August 2011 information request.

frequently throughout this assessment. As is customary in assessments that synthesize a large body of literature and data, the results of EPA research are contextualized and interpreted in combination with the other literature and data described in Section 1.4.2. The journal articles and EPA reports that give complete and detailed project results can be found on the EPA's hydraulic fracturing study website (www.epa.gov/hfstudy). For ease of reference, a description of the individual projects, the type of research activity they represent (i.e., analysis of existing data, scenario evaluation, laboratory study, or case study), and the corresponding citations of published journal articles and EPA reports that are referenced in this assessment can be found in Appendix A.

1.4.2 Literature and Data Search Strategy

We used a broad search strategy to identify approximately 4,100 sources of scientific information applicable to this assessment. This strategy included requesting input from scientists, stakeholders, and the public about relevant data and information, and thorough searches of published information and applicable data.[1]

Over 1,600 articles, reports, data, and other sources of information were obtained through outreach to the public, stakeholders, and scientific experts. The EPA requested material through many venues, as follows. We received recommended literature from the SAB, the EPA's independent federal scientific advisory committee, from its review of the EPA's draft Study Plan; from its consultation on the EPA's Progress Report; during an SAB briefing on new and emerging information related to hydraulic fracturing in fall 2013; and from its peer review of the external review draft of this assessment. Subject matter experts and stakeholders also recommended literature through a series of technical workshops and roundtables organized by the EPA between 2011 and 2013. In addition, the public submitted literature recommendations to the SAB during the SAB review of the draft Study Plan, consultation on the Progress Report, briefing on emerging information, and review of the external review draft of this assessment, as well as in response to a formal request for data and information posted in the *Federal Register* (EPA-HQ-ORD-2010-0674) in November 2012. The submission deadline was extended from April to November 2013 to provide the public with additional opportunity to provide information to the EPA.

Approximately 2,500 additional sources were identified by conducting searches via online scientific databases and federal, state, and stakeholder websites. We searched these databases and websites in particular for (1) materials addressing topics not covered by the documents submitted by experts, stakeholders, and the public as noted above, and (2) newly emerging scientific studies. Multiple targeted and iterative searches on topics determined to be within the scope of the assessment were conducted until June 1, 2016. After that time, we included newer literature as it was recommended to us during our internal technical reviews or as it came to our attention and was determined to be important for filling a gap in information.

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[1] This study did not review information contained in state and federal enforcement actions concerning alleged contamination of drinking water resources.

1.4.3 Literature and Data Evaluation Strategy

We evaluated the literature and data identified in the search strategy using the five assessment factors outlined by the EPA Science Policy Council in *A Summary of General Assessment Factors for Evaluating the Quality of Scientific and Technical Information* (U.S. EPA, 2003c). The factors are (1) applicability and utility, (2) evaluation and review, (3) soundness, (4) clarity and completeness, and (5) uncertainty and variability. Table 1-1 lists these factors along with the specific criteria developed for this assessment. We first evaluated all materials for applicability. If we determined that the material was “applicable” under the criteria, the reference was evaluated on the basis of the other four factors.

Our objective was to consider and then cite literature in the assessment that fully conforms to all criteria defining each assessment factor. However, in some cases, literature on a topic did not fully conform to an aspect of the outlined criteria. For instance, the preponderance of literature in some technical areas is published as white papers and reports for which independent peer review is not standard practice or is not well documented. To address these areas in which peer-reviewed literature was limited, we cited literature that may not have been peer-reviewed. These references often provided useful background information or corroborated conclusions in the peer-reviewed literature.

Table 1-1. The five factors and accompanying criteria used to evaluate literature and data cited in this assessment.

Criteria are consistent with those outlined by the EPA’s Science Policy Council (U.S. EPA, 2003c). Criteria are incorporated into the Quality Assurance Project Plans for this assessment (U.S. EPA, 2014d, 2013d).

Factor	Criteria
Applicability	Document provides information useful for assessing the potential pathways for hydraulic fracturing activities to change the quality or quantity of drinking water resources, identifies factors that affect the frequency and severity of impacts, or suggests ways that potential impacts may be avoided or reduced.
Review	Document has been peer-reviewed.
Soundness	Document relies on sound scientific theory and approaches, and conclusions are consistent with data presented.
Clarity/completeness	Document provides underlying data, assumptions, procedures, and model parameters, as applicable, as well as information about sponsorship and author affiliations.
Uncertainty/variability	Document identifies uncertainties, variability, sources of error, and/or bias and properly reflects them in any conclusions drawn.

1.4.4 Quality Assurance and Peer Review

The use of quality assurance (QA) and peer review helps ensure that the EPA conducts high-quality science that can be used to inform policymakers, industry, and the public. Quality assurance activities performed by the EPA ensure that the agency’s environmental data are of sufficient quantity and quality to support the data’s intended use. The EPA prepared a programmatic Quality

Management Plan (U.S. EPA, 2014e) for all of the research conducted under the EPA's Study Plan, including the review and synthesis of the scientific literature in this assessment. The hydraulic fracturing Quality Management Plan describes the QA program's organizational structure; defines and assigns QA and quality control (QC) responsibilities; and describes the processes and procedures used to plan, implement, and assess the effectiveness of the quality system. The broad plan is then supported by more detailed QA Project Plans (QAPPs). The QAPPs developed for this assessment provide the technical approach and associated QA/QC procedures for our data and literature search and evaluation strategies introduced in Section 1.4.2 and 1.4.3 (U.S. EPA, 2014d, 2013d). A QA audit was conducted by the QA Manager during the preparation of this assessment to verify that the appropriate QA procedures, criteria, reviews, and data verification were adequately performed and documented. Identifying uncertainties is another aspect of QA; uncertainty, including data gaps and data limitations, is discussed throughout this assessment.

This report is classified as a Highly Influential Scientific Assessment (HISA), which is defined by the Office of Management and Budget (OMB) as a scientific assessment that (1) could have a potential impact of more than $500 million in any year or (2) is novel, controversial, or precedent-setting or has significant interagency interest (OMB, 2004). The OMB describes specific peer review requirements for HISAs. To meet these requirements, the EPA often engages the SAB as an independent federal advisory committee to conduct peer reviews of high-profile scientific matters relevant to the agency. Members of an ad hoc panel, the same panel that was convened under the auspices of the SAB to provide comment on the Progress Report, also provided comment on an external review draft of this assessment.[1] Panel members were nominated by the public and chosen to create a balanced review panel based on factors such as technical expertise, knowledge, experience, and absence of any real or perceived conflicts of interest. Both peer review comments provided by the SAB panel (SAB, 2016) and public comments submitted to the panel during their deliberations about the external review draft of this assessment were carefully considered in the development of this final document.

1.5 Organization

This assessment begins with an Executive Summary that summarizes our overall content and conclusions. The Executive Summary is written to be accessible to all members of the public.[2]

This introductory chapter establishes the goals, scope, and approach for the rest of the assessment. Following is a characterization of drinking water resources in the contiguous United States (Chapter 2). Next, we present a general description of hydraulic fracturing activities and the role of hydraulic fracturing in the oil and gas industry in the United States (Chapter 3). Chapter 1 is written

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[1] Information about this process is available online at http://yosemite.epa.gov/sab/sabproduct.nsf/02ad90b136fc21ef85256eba00436459/b436304ba804e3f885257a5b00521b3b!OpenDocument.

[2] The terminology used in the data and literature cited in this assessment can be very technical in nature and sometimes inconsistent. An attempt has been made throughout this document to provide definitions of technical terms and to use terminology in a consistent way that enhances understanding of the topics presented for the audiences targeted by each part of the assessment.

to be accessible to all members of the public. Chapters 2 and 3 are written to be accessible to an audience with general science knowledge.

Chapters 4 through 8 are organized around the stages of the hydraulic fracturing water cycle (Figure 1-1) and address the potential for activities conducted during those stages to change the quality or quantity of drinking water resources. Each stage is covered by a separate chapter. There is also a chapter devoted to an examination of the properties of the chemicals and constituents in hydraulic fracturing-related fluids (Chapter 9). These chapters are written to be accessible to an audience with a moderate amount of technical training and expertise in the respective topic areas.

The final chapter provides a synthesis of the information in the assessment (Chapter 10). This chapter is written to be accessible to an audience with general science knowledge.

The appendices supply information that support the chapters of the assessment. This includes an appendix with a table of all individual products published under the EPA's hydraulic fracturing study and cited in this assessment, as well as answers to the research questions posed in the Study Plan (Appendix A). These answers were informed by the products of the study and the data and literature reviewed in this assessment.

1.6 Intended Use

This state-of-the-science assessment will contribute to the understanding of the potential impacts of activities in the hydraulic fracturing water cycle on drinking water resources and the factors that influence those impacts. The data and findings can be used by federal, tribal, state, and local officials; industry; and the public to better understand and address vulnerabilities of drinking water resources to hydraulic fracturing activities.

We expect this report will be used to help facilitate and inform dialogue among interested stakeholders, including Congress, other federal agencies, states, tribal governments, the international community, industry, NGOs, academia, and the general public. Additionally, the identification of knowledge gaps will promote greater attention to these areas by researchers.

This report may support future assessment efforts. We anticipate that it could contribute context to site-specific exposure or risk assessments of hydraulic fracturing, to regional public health assessments, or to assessments of cumulative impacts of hydraulic fracturing on drinking water resources over time or over defined geographic areas of interest.

Finally, and most importantly, this assessment presents the science to inform decisions by federal, state, tribal, and local officials; industry; and the public on how best to protect drinking water resources now and in the future.

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Chapter 2. Drinking Water Resources in the United States

Abstract

In this assessment, drinking water resources are defined as any body of groundwater or surface water that now serves, or in the future could serve, as a source of drinking water for public or private use. An estimated 86% of the United States population derives its household drinking water from public water systems (PWSs), which mostly use surface water sources, while nearly all of the remaining 14% of people self-supply their drinking water from groundwater.

Future access to high-quality drinking water in the United States will likely be affected by changes in climate and water use. The existing distribution and abundance of the drinking water resources may not be sufficient in some locations to meet future demand. Since 2000, about 30% of the total area of the contiguous United States has experienced moderate drought conditions and about 20% has experienced severe drought conditions, which often correlates with diminishment of drinking water supplies. As a result, non-fresh water resources, such as wastewater from sewage treatment plants, brackish surface water and groundwater, and seawater are increasingly treated and used to meet the demand for drinking water.

Hydraulically fractured oil and gas production wells can be located near drinking water sources. Between 2000 and 2013, approximately 3,900 PWSs had between one and 144 wells hydraulically fractured within 1 mile of their water source; these PWSs served more than 8.6 million people year-round in 2013. An additional 740,000 people self-supply their drinking water in counties where at least 30% of the population relies on groundwater and where there were at least 400 hydraulically fractured wells. Belowground, hydraulic fracturing can occur in close vertical proximity to drinking water resources. Available data show that depths to hydraulically fractured rock formations containing oil and gas resources can range from less than 1,000 feet (300 meters) to more than 10,000 feet (3,000 meters), while drinking water resources may be found between a few tens of feet to as much as 8,000 feet (2,000 meters) below the surface. The EPA found that, along individual wellbores, where data were available, the distance between these two resources ranged from no separation to more than 10,000 feet (3,000 meters). There is considerable uncertainty in this range of values, however. In many cases, the lack of accessible information about the depth to the base of formations containing groundwater resources in need of current and future protection prevents calculation of a vertical separation distance.

The locations of drinking water resources relative to hydraulically fractured oil and gas production wells influence the potential for activities in the hydraulic fracturing water cycle to impact drinking water resources. With increased proximity, activities in the hydraulic fracturing water cycle have more potential to affect aboveground and belowground drinking water resources.

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2. Drinking Water Resources in the United States

2.1 Introduction

Drinking water resources provide the water humans consume, cook with, bathe in, and need for other purposes. In this assessment, drinking water resources are considered to be any groundwater or surface water that now serves, or in the future could serve, as a source of drinking water for public or private use. [1] This chapter provides information about drinking water resources in the United States, including current sources and indications of future trends for drinking water resources. Assessment of whether and where activities in the hydraulic fracturing water cycle may impact drinking water resources requires consideration, in part, of the locations of water and oil and gas resources and what physically separates them. More information about oil and gas resources and the areas of the United States where hydraulic fracturing occurs is described in Chapter 3, however this chapter focuses on the lateral (horizontal) and vertical distances between hydraulic fracturing operations and drinking water resources.

2.2 Ground and Surface Water Resources

All drinking water derives from the finite amount of water found on or below the earth's surface. Fresh water serves as the source for most drinking water.[2] To get an idea of the fresh water fraction of all water, this section presents an estimate of the earth's water abundance. Shiklomanov (1993) estimates the amounts of all water on earth, and here these amounts are expressed as the percent of the earth's total water volume:

- Oceans account for about 96.5%.
- Saline groundwater, saline lakes, and water in the form of ice or vapor account for 2.7%.
- Fresh groundwater, swamps, lakes, and rivers account for the remaining 0.8%, of which about 99% is groundwater.

Hydrologic Cycle. The process describing the movement of the earth's water through the atmosphere, land, and oceans is referred to as the hydrologic cycle. Text Box 2-1 describes the hydrologic cycle, including the manner in which the finite amount of water on the earth moves through different locations during the stages of the cycle. On land, surface water and groundwater interact, shown in the text box as surface water infiltrating into the ground, and separately as an example of groundwater flowing into the river. Water consumption (for example when used for agriculture, incorporated into a product, or for drinking purposes), temporarily removes water

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[1] In this chapter, a "drinking water *source*" means the body of water is now supplying, or is known to be capable of supplying drinking water.

[2] Published estimates of worldwide water supplies, such as by Shiklomanov, do not use a salinity threshold value to define "fresh" or "saline" water. "Fresh" water is characterized in these published estimates as serving as a source for domestic, agricultural, and industrial uses. As described further in Section 2.2.1.1, the term "fresh" in this chapter refers to water having total dissolved solids content up to 3,000 milligrams per liter.

from one local place in the hydrologic cycle, but it may be returned to a different point in the hydrologic cycle. See Chapter 4 for additional discussion of water consumption.

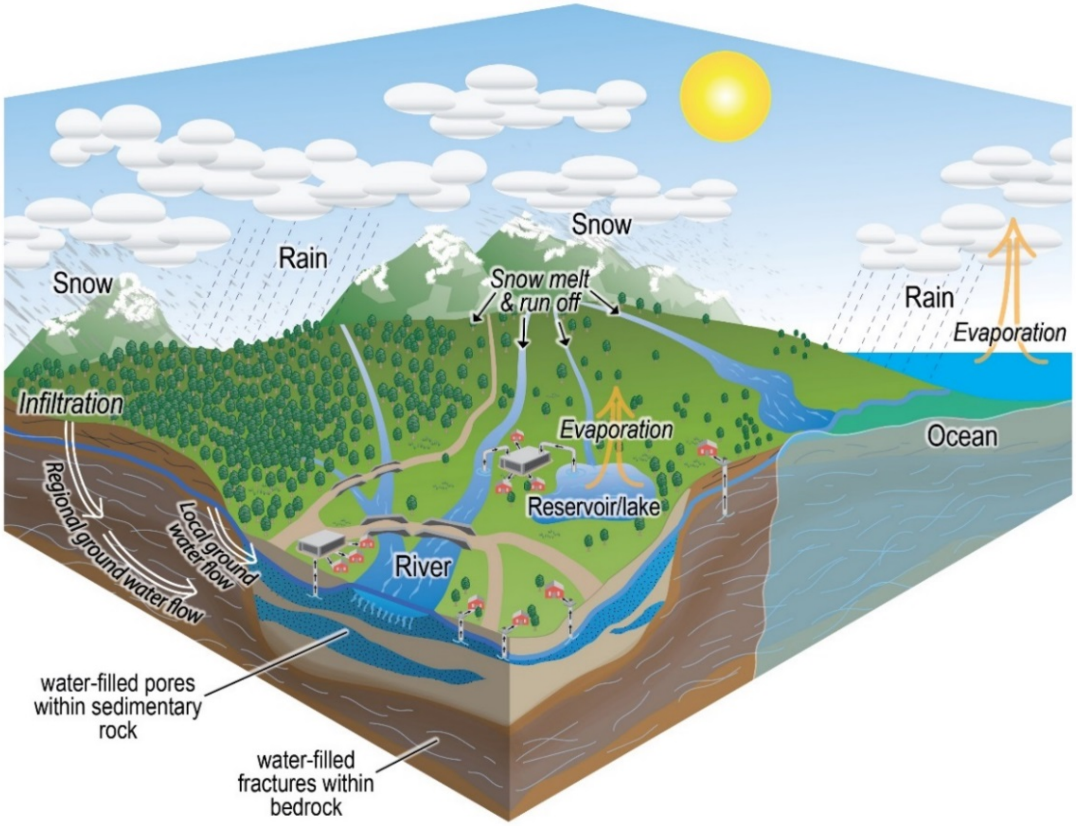
Text Box 2-1. The Hydrologic Cycle.

The finite amount of water and its movement on earth is often called the hydrologic cycle, depicted below. The three basic, and repeating, stages of this cycle include:

1. Rainfall transfers water from the atmosphere into oceans or onto land,

2. Water on land moves among surface water bodies and groundwater, and

3. Evaporation from land and the oceans returns water to the atmosphere.



Rainwater and melted snow collect into rivers, lakes or other water bodies to become surface water, or infiltrates into the ground to become groundwater. Humans drink fresh surface and groundwater, and in some locations, ocean water treated by desalination. Water resides on land or in the ground for varying amounts of time before moving into another of stage of the hydrologic cycle. Residence times for water found in different land locations can range from days to millions of years, depending on the path water takes. Residence time affects water quality on land or in the ground because water dissolves natural earth salts when in contact with those materials. When water on or under land reaches the ocean, its salt content ultimately stays in the ocean because evaporation leaves behind dissolved salt creating freshwater vapor. Evaporation from land and the ocean contribute fresh water to the atmosphere where it can precipitate once again, thus completing a hydrologic cycle. As drawn in this depiction, evaporation includes the release of water vapor from plant leaves that originally entered plant root systems in a process known as transpiration.

2.2.1 Groundwater Resources

Groundwater can be found in the subsurface nearly everywhere, but it varies in quality and quantity. Groundwater exists in that part of the hydrologic cycle where surface water infiltrates through soil into subsurface cracks and voids in rock, creating and sustaining aquifers, a natural process known as groundwater recharge.[1] The opposite natural process from recharge is discharge, where groundwater flows to the surface at springs or through the bottoms of lakes and rivers. Groundwater also includes water trapped in the pores of sedimentary rocks as they were deposited.

The scale of groundwater flow systems can be local, regional, or something in between. Local groundwater flows may be small enough to be measured in the tens of feet while regional groundwater flows may be large enough to be measured in hundreds of miles (Alley et al., 1999). Groundwater movement is related to the rate of groundwater recharge, gravity's effect on the groundwater, and the permeability of the rock through which groundwater flows. Localized groundwater flow tends to occur along shallower flow paths with shorter overall residence times, whereas regional groundwater flow tends to occur along deeper flow paths with longer residence times (Winter et al., 1998). Text Box 2-1 depicts differences between local and regional flow regimes.

The U.S. Geological Survey (USGS) has mapped and described more than 60 principal aquifers in the United States, although these aquifers are not the only occurrences of groundwater (USGS, 2009).[2] Although the depth to the water table can vary from ground surface to a few tens of feet below ground surface, the depth to the base of groundwater can be tens of thousands of feet below ground.[3] The depth to the base of individual principal aquifers can be a relatively uniform or may vary by thousands of feet across the aquifer's areal extent due to sloping geologic formations and/or changes in topography.

2.2.1.1 Groundwater Quality

The quality of groundwater often correlates with its age, which ranges from days to millions of years (Alley et al., 1999; Freeze and Cherry, 1979a; Chebotarev, 1955).[4] As explained in Text Box 2-1, groundwater salinity tends to increase with increasing residence time due to gradual dissolution of contacted earth materials. Some groundwater can become very saline. These waters can result from exposure to soluble sedimentary rocks and/or concentration of salt content due to evaporation of liquid water in the subsurface (Zolfaghari et al., 2016; Levorsen, 1965). It is also possible that sea water was trapped in sediments during deposition in ancient oceans, which were subsequently buried over geologic time. There are instances where groundwater is found at great

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[1] An aquifer is a water-bearing geologic formation, group of formations, or part of a formation. Groundwater is the water in an aquifer.

[2] Principal aquifers are defined as a regionally extensive aquifer or aquifer system that has the potential to be used to supply potable water. Principal aquifers in Puerto Rico and the U.S. Virgin Islands are included.

[3] The water table refers to the top, or uppermost surface, of groundwater. Below the water table, the ground is saturated with water.

[4] Groundwater age used here refers to how long the water has been in the ground.

depths but is relatively fresh. This can be caused by groundwater moving from the surface to deep locations relatively quickly with little time to pick up dissolved solids and become saline. This phenomenon is more pronounced in mountains where rainwater or melted snow in upland areas supply groundwater that moves downward through steeply dipping, permeable sedimentary rock layers to reach great depths. Chemicals occurring naturally in groundwater include both inorganic (e.g., salts, metals) and organic (carbon-based) types.

Salinity variation. Salinity is often the principal characteristic used to describe the overall quality of groundwater. The term “fresh” groundwater often means groundwater containing no more than 1,000 milligrams per liter of total dissolved solids (mg/L TDS) but it is sometimes used to refer to groundwater containing no more than 3,000 mg/L TDS (Maupin et al., 2014; U.S. EPA, 2012e; Freeze and Cherry, 1979a). When characterizing groundwater quality, scientists generally consider the relative abundance of sodium, calcium, potassium, magnesium, chloride, bicarbonate, and sulfate to account for the bulk of dissolved constituents (Freeze and Cherry, 1979a). Natural salinity ranges from less than 100 mg/L to over 300,000 mg/L TDS (Lauer et al., 2016; Clark and Veil, 2009). Higher salinity groundwater can contribute to palatability problems, and in the very high salinity ranges, causes water to be unhealthful for human consumption (Ellis, 1997). People have a range of reactions to drinking water salinity. Some people object to the taste of drinking water having comparatively lower salinity levels while other people reach this objection threshold at higher salinity levels (Burlingame and Waer, 2002). Desalinating water containing salinity values of 10,000 mg/L TDS to render it potable is technically and economically feasible (Esser et al., 2015).[1] As a result, groundwater with salinity values up to 10,000 mg/L TDS is often defined as a protected groundwater resource under several laws, including the regulations implementing the federal Safe Drinking Water Act (SDWA) and the U.S. Bureau of Land Management (BLM) Onshore Order #2. The complete basis and standards for defining a protected groundwater in all locations within the United States is beyond the scope of this report. Additional information about protections given to groundwater is described in Chapter 1 in Text Box 1-1.

Groundwater suitable for drinking is found within a large range of depths around the United States. The groundwater quality profile with depth varies around the United States. Feth (1965) described patterns in the relationship of depth to groundwater containing salinity ranging from 1,000 to 3,000 mg/L TDS.[2] The patterns include: (1) large portions of the Southeast and middle Midwest have at least 1,000 ft (300 m) of separation between the land surface and groundwater containing 1,000-3,000 mg/L TDS, and (2) significant portions of the Northeast, northern Midwest, and parts of the West have less than 500 ft (200 m) separating the land surface from groundwater containing 1,000-3,000 mg/L TDS. The report does not contain information about the base or thickness of groundwater having certain quality. As a result, these depths represent minimum distances between the land surface and bottom depth of groundwater having this salinity range.

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[1] For instance, desalination of sea water (approximately 35,000 mg/L TDS) now occurs in Florida, California, and Texas.

[2] Salinity and total dissolved solids are frequently interchangeable terms. The vast majority of dissolved constituents in natural water are inorganic salts, although a minor fraction of dissolved constituents can be organic matter. Feth (1965) maps groundwater found at ranges of depth with spans of salinity. Singular depth and salinity values are not present on the map.

Methane in groundwater. Methane can be found naturally at detectable levels in groundwater (Kappel and Nystrom, 2012; Eltschlager et al., 2001; Coleman et al., 1988). There are different origins of methane in groundwater. Biogenic methane is produced at comparatively low temperature and pressure from biologic decay of carbon-bearing matter, while thermogenic methane is formed over geologic time when carbon-bearing matter is exposed to elevated pressure and temperature conditions typically associated with deep burial (Baldassare et al., 2014). Given the buoyancy of natural gas, if a pathway exists or enough time is available, it can move upward and accumulate at shallower depths. Natural gas found in small, uneconomic quantities in shallow zones may have originated in place or may have migrated upward, and is often referred to as stray gas. For more discussion about the issue of stray gas, see Text Box 6-3 in Chapter 6. When consumed in drinking water, methane does not generally have human health effects,[1] however, it is an explosive gas if it comprises between 5% and 15% of a volume of air (Astle and Weast, 1984). If methane from well water enters the atmosphere within a confined space under conditions that allow it to concentrate, it can pose an explosive threat if it reaches this threshold.

2.2.1.2 Groundwater Quantity

Groundwater quantity can be characterized as the total subsurface water available, although a practical limiting property is the rate at which groundwater can be withdrawn from the subsurface, a property known as yield (Freeze and Cherry, 1979a). If rock formations in the subsurface contain water within exceedingly small or poorly connected pore spaces, then the low yield may preclude its practical use as a source of drinking water.

When recharge and discharge are in balance, the volume of groundwater existing in the subsurface remains the same. Recharge and discharge also occur in connection with human-caused activity. Groundwater recharge increases due to irrigation, underground injection wells, surface impoundments, and dammed reservoirs, while groundwater discharge increases through well withdrawals for irrigation, household use, etc. (Winter et al., 1998). These activities can locally affect the natural balance between groundwater recharge and discharge. Climatic variation that changes precipitation rates also affects groundwater recharge rates, which in turn leads to changes in subsurface groundwater volume (Winter et al., 1998).

When an aquifer consistently yields water at rates suitable for human use, and the water is of good enough quality to drink or be treated for drinking, it can serve as a source of drinking water.

2.2.2 Surface Water Resources

Surface water is that part of the hydrologic cycle that occurs on land surface and includes water in the ocean as well as rainwater or meltwater. Surface water collects into depressions or along channels in sufficient volume to create standing or running water all or much of the time. Non-ocean surface water has often had little time to become saline, because much of it is not in direct contact with anything other than more water in the surrounding surface water body. Non-ocean surface water can quickly move into the next phase of the hydrological cycle, either evaporating

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[1] There is no enforceable drinking water standard established for dissolved methane in drinking water.

into the atmosphere or infiltrating the subsurface. Because surface water is open to the atmosphere and is generally located at the lowest points on a landscape, it is susceptible to contamination. Contamination sources include atmospheric deposition, and run-off from urban land areas or lands used for agricultural or industrial activities (Winter et al., 1998). Many non-ocean surface water bodies in the United States have a set of water quality standards based on their designated use, which can include recreation, drinking water, supportive of aquatic life, fishery, industrial supply, and other uses. In turn, National Discharge Pollution Elimination (NPDES) permits governing point source discharge into the surface water bodies are issued under the Clean Water Act and contain limits on pollutants designed to achieve these water quality standards.[1] When taken together, these permits are meant to ensure that the surface water achieves a water quality consistent with the designated use.

2.2.2.1 Surface Water Quality

Studies conducted in connection with the National Water Quality Assessment Program show the presence of human-made chemicals at low concentrations in the streams surveyed (Kingsbury et al., 2008).[2] Based on dissolved solids alone, sampled streams range from less than 100 mg/L TDS to more than 500 mg/L TDS (Anning and Flynn, 2014). Large lakes can range in salinity from less than 500 mg/L TDS to more than 200,000 mg/L. By comparison, ocean water has a salinity of about 35,000 mg/L TDS. Considering the vast array of possible chemical, biological, and radiological content in surface water, it is beyond the scope of this report to describe in detail the surface water qualities that exist in the United States.

2.2.2.2 Surface Water Quantity

About 7% of the surface area of the United States is covered by surface water, but it is not uniformly distributed. The portion of the United States located east of the Mississippi River comprises about 25% of the total area, yet it contains about 42% of the total land area covered by surface water (USGS, 2016; U.S. Census Bureau, 2012). The Great Lakes alone, located in the eastern half of the United States, contain about one-fifth of the world’s surface fresh water (Government of Canada and U.S. EPA, 1995).[3] In contrast, the western part of the United States has a lower proportion of land covered by surface water with streams that tend to be more intermittent in nature.[4] For instance, 81 percent of the streams in Arizona, New Mexico, Nevada, Utah, Colorado, and California are not permanent streams (Levick et al., 2008). Certain parts of the western U.S. are presently experiencing less surface water availability as indicated by declining water reservoir levels with some reservoirs in the southwest currently below 50% of their capacity.[5] For example, according to

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[1] Title 40, United States Code of Federal Regulations, Part 131, as of May 25, 2016.

[2] See USGS (2012) for more information about this program.

[3] Including the portion of the Great Lakes lying within Canada.

[4] Not all western states follow this trend. Hawaii and Alaska, for instance, have a significantly higher percentage of land mass covered by surface water (41% and 14%, respectively) than the national average.

[5] See for instance U.S. DOI (2016b), California Department of Water Resources (2016), and SRP (2016).

the U.S. Department of the Interior (DOI), the largest capacity reservoir in the United States, Lake Mead, holds about 37% of its volume capacity as of the fall of 2016 (U.S. DOI, 2016a).

2.3 Current Drinking Water Sources

Drinking water is supplied to households and businesses by either public water systems (PWSs) or non-public systems (non-PWSs).[1] In 2010, approximately 270 million people (86% of the population) in the United States relied on PWSs to supply their homes with drinking water (Maupin et al., 2014; U.S. EPA, 2013b). These PWSs provided households with nearly 24 billion gal (91 billion L) of water per day (Maupin et al., 2014).[2] In areas without service by PWSs, approximately 45 million people (14% of the population) obtain drinking water from non-PWSs, using mostly water wells. Non-PWSs account for about 3.6 billion gal (14 billion L) of daily water withdrawals (Maupin et al., 2014).[3]

Both groundwater and surface water serve as drinking water sources in the United States. Surface water accounts for about 58% of all drinking water withdrawals and groundwater supplies the remaining 42%. Table 2-1 portrays the relative abundance of surface water and groundwater as sources for both publicly and non-publicly supplied drinking water.

Of the population receiving water supplied by PWSs, the relative importance of surface and groundwater sources for supplying drinking water varies geographically (Figure 2-1). Most larger PWSs rely on surface water and are located in urban areas (U.S. EPA, 2011c), whereas most smaller PWSs rely on groundwater and are located in rural areas (U.S. EPA, 2014h, 2013b). More than 95% of households in rural areas obtain their drinking water from groundwater (U.S. EPA, 2011c).

PWSs are subject to routine monitoring and testing requirements required under the National Primary Drinking Water Standards regulations, whereas no such monitoring or testing is required for non-PWSs.[4] The required monitoring and testing at PWSs ensures that the public has information regarding the extent to which delivered water meets drinking water standards, whereas users of non-PWSs (e.g., private water wells) make individual, voluntary decisions about how often they monitor and test their water. Lack of monitoring may make non-PWS users more vulnerable to contamination, if present, than PWS users.

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[1] PWSs provide water for human consumption from surface water or groundwater through pipes or other infrastructure to at least 15 service connections or serve an average of at least 25 people for at least 60 days a year (U.S. EPA, 2012g). The EPA categorizes PWSs as either community water systems, which supply water to the same population year-round, or non-community water systems, which supply water to at least 25 of the same people at least six months per year, but not year-round. Non-public water systems (non-PWSs) have fewer than 15 service connections and serve fewer than 25 individuals (U.S. EPA, 1991). Non-PWSs are often private water wells supplying drinking water to a singular residence.

[2] The USGS compiles data in cooperation with local, state, and federal environmental agencies to produce water-use information aggregated at the county, state, and national levels. Every five years, data at the county level are compiled into a national water use census and state-level data are published. The most recent USGS water use report was released in 2014, and contains water use estimates from 2010. Water withdrawals are distinguished from and are greater than water deliveries due to water loss during the process of delivering finished water (Maupin et al., 2014; USGS, 2014b).

[3] A withdrawal means the volume of water taken from its source regardless of how much of that volume is either returned to the local hydrologic cycle or is consumed without being returned to the local hydrologic cycle.

[4] See Title 40 of the Code of Federal Regulations, Part 141, promulgated pursuant to the SDWA.

Table 2-1. Summary of drinking water sources in the United States in 2010.

The volume and percentages of daily domestic water withdrawals in the United States are shown by public and non-public water systems, total withdrawal, and whether the source is surface water or groundwater. Volume is in billions of gallons per day (Bgal/day) and percentages are of either water supply type or total volume withdrawn, as indicated in italics. Some figures shown are rounded values. Source of data: Maupin et al. (2014).

Drinking water source	Public water supply	Non-public water supply	Total volume withdrawn
Surface Water			
Daily volume withdrawn (billion gallons)	26.3	0.1	26.4
Percent of water supply type	63	2	58
Groundwater			
Daily volume withdrawn (billion gallons)	15.7	3.5	19.2
Percent of water supply type	37	98	42
Total			
Daily volume withdrawn (billion gallons)	42.0	3.6	45.6
Percent of water supply type	92	8	100

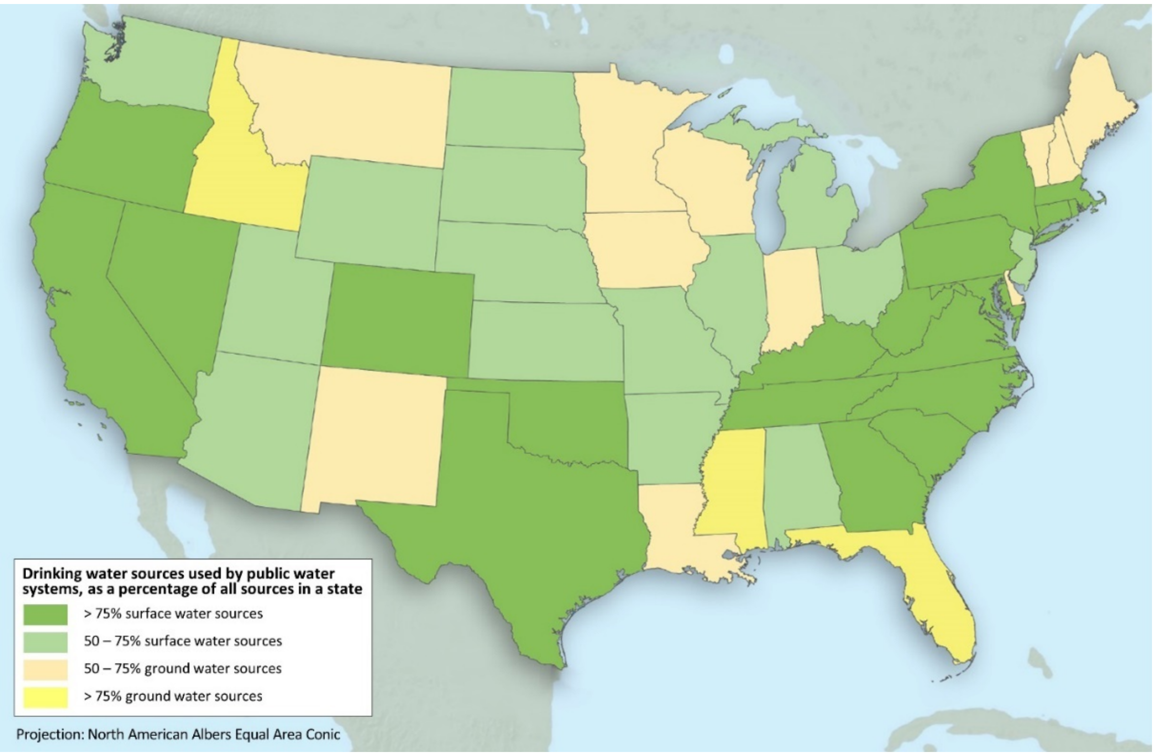

Figure 2-1. Geographic variability in drinking water sources for public water systems.

The relative importance of surface and groundwater as sources for public water systems varies by state. The public water system sources used in this analysis include infiltration galleries, intakes, reservoirs, springs, and wells. Sources: ESRI (2010), U.S. Census Bureau (2013), and U.S. EPA (2013b).

2.3.1 Factors Affecting How Water Becomes a Drinking Water Source

The most common source of drinking water in the world, including in the United States, is fresh water (see Section 2.2.1.1). There can be exceptions to the use of fresh water as a drinking water source. For instance, projects in California, Florida, Arizona and Texas desalinate sea water or brackish groundwater to produce drinking water.[1] The principle of supply and demand that affects availability of commercial products in the marketplace is also applicable to drinking water resources. Water not considered a practical drinking water source under one demand condition may become desirable as a drinking water source under different demand conditions. Text Box 2-2 presents El Paso, Texas as such an example.

Text Box 2-2. El Paso's Use of Higher Salinity Water for Drinking Water.

The El Paso Water Utility (EPWU) provides drinking water to over 600,000 people in the City of El Paso, Texas and surrounding communities. Historically, the EPWU has withdrawn surface water from the Rio Grande River and groundwater to meet water needs. Salinity from the freshwater aquifers typically ranges between 300 and 1,000 mg/L TDS. With increases in population and periodic drought conditions stressing the water supply, the EPWU instituted a number of different measures to diversify its water supply portfolio. Components of the EPWU water supply portfolio include water conservation, surface water, groundwater and, more recently, desalinating saline groundwater. Continued long-term pumping of fresh groundwater allowed higher salinity groundwater to enter into one of EPWU's well fields from more saline parts of the aquifer. This well field is now used as the source for the Kay Bailey Desalination Plant, which began operation in 2007 and desalinates groundwater with salinity ranging from 1,000 and 5,000 mg/L TDS (El Paso Water Utilities, 2016). The plant uses reverse osmosis technology to remove the high salt content thereby creating additional fresh water supplies. Use of this higher salinity water supply has added approximately 25% more water availability, decreasing the stress on the original fresh water supplies available to the EPWU and highlights the potential value of groundwater that had not formerly been considered a drinking water source.

2.3.1.1 General Considerations Applicable to All Water as Source of Drinking Water

Factors to consider when assessing a possible source of drinking water include availability, contaminants in the water, and the cost to obtain and treat water. Surface water in streams, lakes, or reservoirs is almost always considered to be a source for drinking water, because they contain fresh, readily accessible water. Groundwater is a critically important drinking water source in many parts of the United States, especially where surface water is less abundant. Challenges for use as drinking water exist for both surface and groundwater. Surface water may not suffice as a drinking water source when it exists only temporarily or cannot supply the volume demand. Both surface water and groundwater may have contaminant levels that require expensive treatment technology. For instance, in an extensive report, the USGS describes how human activities cause unnaturally fast and deep groundwater movement, which degrades water quality over long periods in the

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[1] Brackish water is often a general term used for water having a salinity content intermediate between fresh water and sea water, although it may also have a more specific definition, such as the 1,000 – 10,000 mg/L TDS value used in some USGS publications.

nation's principal aquifers (DeSimone et al., 2014). Despite these challenges, changes in the demand for water affect the consideration of sources of water for drinking purposes.

2.3.1.2 Considerations Applicable to Groundwater as a Drinking Water Source

Determining what groundwater is eligible for use as a drinking water source can include additional challenges. Groundwater may be located at significant depth or within low-yield aquifers, requiring additional engineering solutions to make them practical and/or cost effective as a drinking water source. Aquifers, or parts of aquifers, not in use today for drinking water purposes may nonetheless eventually be considered a drinking water source. The future viability of currently unused aquifers depends on the definition of what constitutes a drinking water resource and knowledge of the physical and chemical characteristics of the aquifers. The extent of knowledge about what exists in the subsurface depends on extrapolation from limited subsurface data (e.g., water samples collected from wells in, or passing through, aquifers). Although salinity is a common criterion for designating an aquifer as a drinking water resource (see Section 2.2.1.4), there is not a uniform threshold value for making that determination. The Groundwater Protection Council (GWPC) notes:

> There is a great deal of variation between states with respect to defining protected groundwater. The reasons for these variations relate to factors such as the quality of water, the depth of Underground Sources of Drinking Water, the availability of groundwater, and the actual use of groundwater (GWPC, 2009).[1]

In addition to variation in applicable water quality criteria, the availability of information regarding groundwater that meets an applicable criterion (if one exists) is also variable. For instance, the bottom depth of aquifers or parts of aquifers that may be defined as a drinking water resource are not always readily publicly available. In some locations, such as the State of Texas, estimates of the bottom depth of groundwater meeting certain regulatory threshold criteria are made public on a website.[2] In other parts of the United States the depth of identified protected subsurface drinking water resources may not be publicly available. No centralized compilation of groundwater depth and quality exists for all locations in the United States, nor does such a reference exist for depths to protected groundwater resources. The depths to protected groundwater resources can vary. In one example, the EPA described the reported bottom depths of protected groundwater resources as ranging from just below ground surface to 8,000 ft (2,000 m) (U.S. EPA, 2015n).[3]

Even in regions where the bottom depth of protected groundwater resources are generally known, there can remain uncertainty regarding precise depths at specific locations. Examples include the states of Indiana and Michigan according to the EPA Region 5 Underground Injection Control (UIC)

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[1] An underground source of drinking water (USDW) is defined in the federal regulations that implement the UIC program. A USDW is generally considered to be any aquifer, or its portion, that currently serves as a source for a public water system; or which contains enough groundwater to supply a public drinking water system, and either now supplies water for human consumption, or contains fewer than 10,000 mg/L TDS. See Title 40 of the Code of Federal Regulation, Section 144.3.

[2] See http://www.beg.utexas.edu/sce/index.html.

[3] This reference provided 1,000-foot (305 meters) depth resolution for the reported base of protected groundwater.

program, the State of Utah according to the Utah Geological Survey, and the State of California according to the California State Water Resources Board (Esser et al., 2015; Anderson et al., 2012; U.S. EPA, 2012e). In these examples, the depth to groundwater meeting the salinity threshold necessary for decision-making is stated not to be known with precision, and collection of additional groundwater quality information is advised.[1]

2.4 Future Drinking Water Sources

The future availability of fresh drinking water sources in the United States (Section 2.2.1.1) will likely be affected by changes in climate and water use (Georgakakos et al., 2014). Since 2000, about 30% of the total area of the contiguous United States has experienced moderate drought conditions and about 20% has experienced severe drought conditions (National Drought Mitigation Center, 2015; U.S. EPA, 2015p). Declines in surface water resources have already led to increased withdrawals and cumulative net depletions of groundwater in some areas (Castle et al., 2014; Georgakakos et al., 2014; Konikow, 2013; Famiglietti et al., 2011). Loss of approximately 240 mi^3 (1,000 km^3) of groundwater between 1900 and 2008 has been documented by the USGS. USGS reports that about 20% of that loss occurred in the final eight years of that timeframe and that depletion is greater in the arid and semi-arid western states than in the more humid eastern states (Konikow, 2013). Other sources of water that might not be considered fresh, such as wastewater from sewage treatment plants, brackish and saline surface and groundwater, as well as sea water, are also increasingly being used to meet water demand. Through treatment or desalination, these water sources can reduce the use of high-quality, potable fresh water for industrial processes, irrigation, recreation, and toilet flushing (i.e., non-potable uses). In addition, in 2010, approximately 355 million gal per day (1.3 billion L per day) of treated wastewater was reclaimed through potable reuse projects (NRC, 2012). Such projects use reclaimed wastewater to augment surface drinking water sources or to recharge aquifers that supply drinking water to PWSs (NRC, 2012; Sheng, 2005). In 2007, among approximately 13,000 desalination plants worldwide, there existed the capacity to produce about 14.7 billion gal (55.6 billion L) of fresh water each day. In 2005, the United States had approximately 11 % of that volume capacity (Gleick, 2008; Cooley et al., 2006).

An increasing number of states are developing new water supplies to augment existing drinking water sources through reuse of reclaimed water, recycling of storm water, and desalination (U.S. GAO, 2014). Most desalination programs currently use brackish water as a source, although plans are underway to expand the use of sea water. States with the highest installed capacity for desalination include Florida, California, Arizona, and Texas (Cooley et al., 2006). It is likely that various water treatment technologies will continue to expand drinking water sources beyond those that are currently being considered. In addition to treatment technologies, there are efforts by public water systems to alleviate demand on drinking water supplies such as encouraging more modest consumer water usage and repairing leaks in water infrastructure.

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[1] Decisions dependent on knowledge of threshold salinity values in groundwater can include permitting injection wells and oil and gas production well construction design approvals.

2.5 Proximity of Drinking Water Resources to Hydraulic Fracturing Operations

Hydraulic fracturing in oil and gas production wells necessarily takes place where oil and gas resources are located. The relative locations of drinking water resources influences the degree to which they may be affected by activities in the hydraulic fracturing water cycle. With increased proximity, hydraulic fracturing activities have a greater potential to affect surface and subsurface sources of current and future drinking water (Vengosh et al., 2014; Entrekin et al., 2011). To estimate potentially vulnerability populations that use drinking water resources, the EPA performed an analysis of the number of hydraulically fractured production wells that are located within 1 mi (1.6 km) of a PWS source. The EPA also presents subsurface separation distances between the depths of drinking water resources and hydraulic fracturing in production wells.

2.5.1 Lateral Distance between Public Water System Sources and Hydraulic Fracturing

The EPA analyzed the locations of the approximately 275,000 oil and gas wells that were assumed to be hydraulically fractured in 25 states between 2000 and 2013 (Chapter 3) to determine the number of fractured wells within a 1-mile radius of facilities that withdraw water for a PWS.[1,2,3] Based on 2000–2013 DrillingInfo data, the lateral distance from the nearest facility that withdraws water for PWS to a hydraulically fractured well ranged from 0.01 to 41 mi (0.02 to 66 km), with an average distance of 6.2 mi (10.0 km) and a median distance of 4.8 mi (7.7 km) (DrillingInfo, 2014a; U.S. EPA, 2014h). Of the approximately 275,000 wells that were estimated to have been hydraulically fractured in 25 states between 2000 and 2013, an estimated 21,900 (8%) were within 1 mile of at least one PWS groundwater well or surface water intake. Most of these approximately 6,800 individual facilities that withdraw water for a PWS were located in Colorado, Louisiana, Michigan, North Dakota, Ohio, Oklahoma, Pennsylvania, Texas, and Wyoming (Figure 2-2). These facilities that withdraw water for a PWS had an average of seven hydraulically fractured production wells and a maximum of 144 such production wells within a 1-mile radius. These water sources supplied water to 3,924 PWSs—1,609 of which are community water systems—that served more than 8.6 million people year-round in 2013 (U.S. EPA, 2014h; U.S. Census Bureau, 2013; U.S. EPA, 2013b).[4]

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[1] The EPA estimated the number of oil and gas production wells hydraulically fractured between 2000 and 2013. To do this, EPA assumed that all horizontal wells were hydraulically fractured in the year they started producing and assumed that all wells within a shale, coalbed, or low-permeability formation, regardless of well orientation, were hydraulically fractured in the year they started producing. More details are provided in U.S. EPA (2013c). Not all coalbed methane wells are hydraulically fractured, but coalbed methane wells represent production wells that sometimes uses hydraulic fracturing. Given that there were 15% of coalbed methane wells relative to all hydraulically fractured wells and the lack of data that distinguishes whether or not coalbed wells are hydraulically fractured, EPA included coalbed wells into all counts of wells that are hydraulically fractured.

[2] The selected 1-mile distance used in this analysis provides a consistent approach. Local topographic conditions could support the use of a different analysis at any specific site.

[3] A facility that withdraws water for a PWS includes water intakes, water wells, springs, infiltration galleries, and reservoirs. It is common for a PWS to operate multiple individual facilities to withdraw the cumulative water supplied by the PWS.

[4] All PWS types were included in the locational analyses performed. However, only community water systems were used to calculate the number of customers obtaining water from a PWS with at least one source within 1 mile of a hydraulically

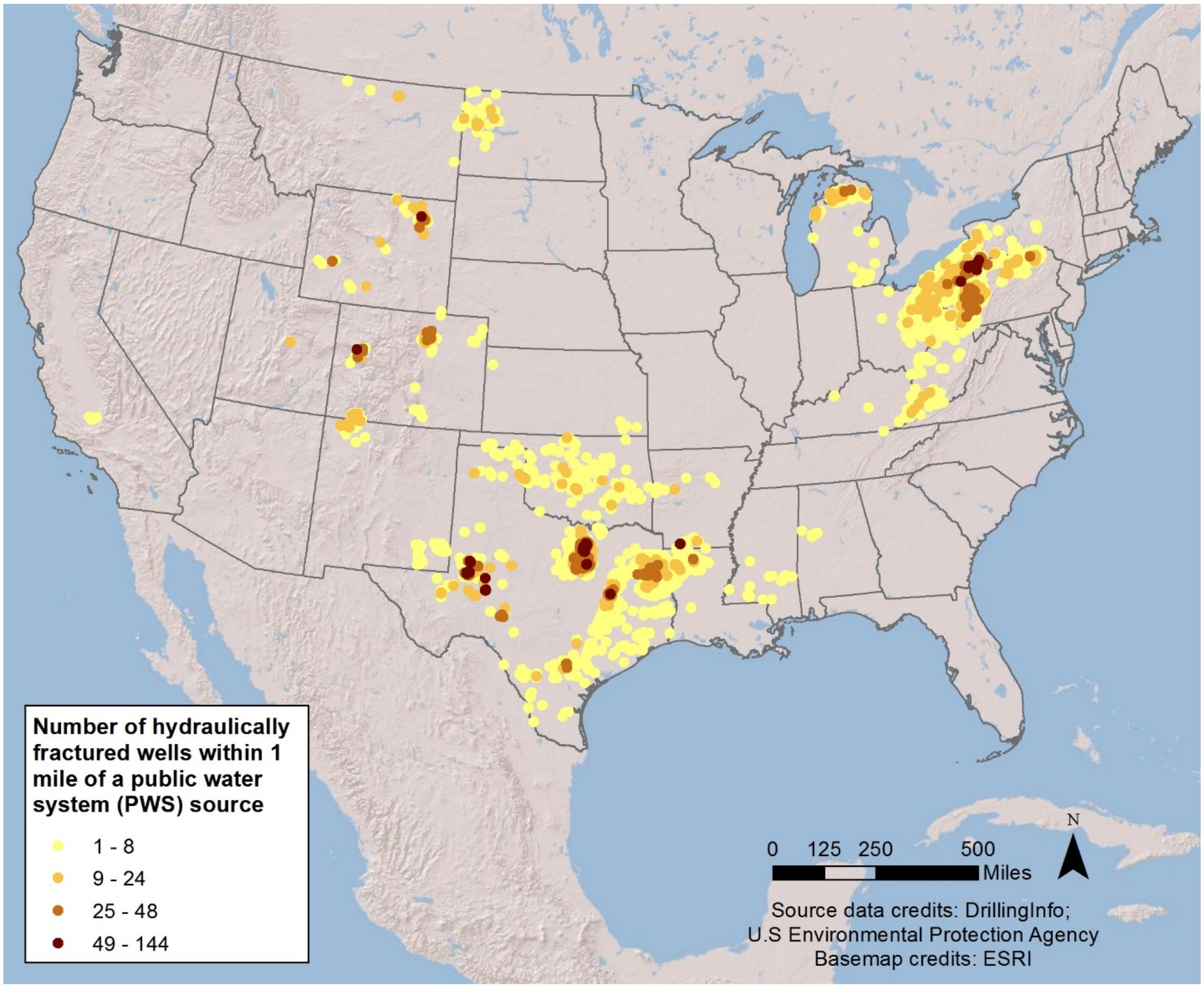

Figure 2-2. The location of public water system sources having hydraulically fractured wells within 1 mile.

Points indicate the location of public water system (PWS) sources; point color indicates the number of hydraulically fractured wells within 1 mile of each PWS source. The estimates of wells hydraulically fractured from 2000 to 2013 developed from the DrillingInfo data were based on assumptions described in Chapter 3. Sources: DrillingInfo (2014), U.S. EPA (2013b), and ESRI (2010).

The EPA also analyzed the location of hydraulically fractured wells relative to populations where a high proportion (≥30%, or at least twice the national average) obtain drinking water from non-PWSs (mostly private groundwater wells).[1] Based on DrillingInfo well location data and USGS drinking water data, between 2000 and 2013, approximately 3.6 million people live in counties

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fractured well. If non-community water systems are included, the estimated number of customers increases by 533,000 people (U.S. EPA, 2012g). A community water system is a PWS which serves at least 15 service connections used by year-round residents or regularly serves at least 25 year-round residents.

[1] There is no national data set of non-PWSs. In Maupin et al. (2014), the USGS estimates the proportion of the population reliant on non-PWSs, referred to as the "self-supplied population," by county, based on estimates of the population without connections to a public water system. The USGS estimates were used for this analysis.

with at least one hydraulically fractured well and where at least 30% of the population relies on non-PWSs for drinking water (DrillingInfo, 2014a; USGS, 2014b). The population changes to approximately 740,000 people living in counties with more than 400 hydraulically fractured wells and at least 30% of the population relies on non-PWSs for drinking water (DrillingInfo, 2014a; USGS, 2014b).[1] The counties having more than 400 hydraulically fractured wells and at least 30% of the population relying on non-PWSs for drinking water were located in Colorado, Kentucky, Michigan, Montana, New Mexico, New York, Oklahoma, Pennsylvania, Texas, and Wyoming.

As described in Chapter 1, this assessment defines five stages in the hydraulic fracturing water cycle. The lateral distance analysis presented here relates to the wellhead locations of hydraulically fractured production wells, and therefore addresses three stages that take place near production wellheads, evaluated in Chapters 5, 6, and 7, respectively (chemical mixing, well injection, and produced water handling).[2] A lateral distance analysis was not possible for the other two stages (water acquisition, wastewater disposal and reuse) because there is a lack information about where water is acquired for hydraulic fracturing and where the wastewater from any given hydraulically fractured well is disposed or treated.

2.5.2 Vertical Distance between Drinking Water Resources and Hydraulic Fracturing

The depth at which hydraulic fracturing takes place varies depending on the depth to the targeted production zone. For instance, in a study of wells representing approximately 23,000 production wells hydraulically fractured by nine service companies during 2009 and 2010, the EPA found that, when measured vertically from the surface to total depth, well depths ranged from less than 2,000 ft (600 m) to more than 11,000 ft (3,000 m) (U.S. EPA, 2015n). Similarly, based on more than 38,000 hydraulic fracturing disclosures to the FracFocus registry website, the middle 90% of these well disclosures had vertical depths between 2,900 and 13,000 ft (880 and 4,000 m) with a median value of about 8,100 ft (2,500 m) (U.S. EPA, 2015a). Hydraulic fracturing can occur at or near the bottom of a production well or it may take place at different intermediate depths depending on the location of economically producible oil and gas, and thus the total vertical depth of a production well does not necessarily correlate to the depth at which hydraulic fracturing occurs (Chapter 6). Hydraulic fracturing has been conducted at depths ranging from less than 1,000 ft (300 m) to greater than 10,000 ft (3,000 m) depth (U.S. EPA, 2015n; NETL, 2013). The distance from the base of the drinking water resource to the shallowest hydraulic fracturing initiation point in a production well serves as a separation distance.[3] The EPA reports separation distances in depth measured along the well ranging from no separation distance (where hydraulic fracturing took

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[1] Approximately 14% of the U.S. population is self-supplied by non-PWSs (Maupin et al., 2014). This analysis considers only counties in which more than double the national average—that is, at least 30% of the county's population—was supplied by non-PWSs.

[2] Chapter 7 (Produced Water Handling) examines potential effects on drinking water resources at hydraulically fractured wellhead locations, as well as away from wellhead locations.

[3] If measured vertically from the shallowest hydraulic fracturing initiation point to the bottom of the drinking water resource, this is referred to as a vertical separation distance. If measured along a borehole from the shallowest hydraulic fracturing initiation point to the bottom of the drinking water resource, this is referred to as a separation distance in measured depth.

place at depths shallower than the reported base of the drinking water resource) to more than 10,000 ft (3,000 m) (U.S. EPA, 2015n).

In a given setting, it is the geologic and hydrologic history that determines the depths to potential oil and gas and/or subsurface drinking water resources. In some settings, rock formations bearing economic quantities of oil or gas also contain groundwater that, based on salinity value alone, qualifies it as a drinking water resource. Large distances vertically separate these two resources in other settings. Figure 2-3 depicts two different types of these settings.

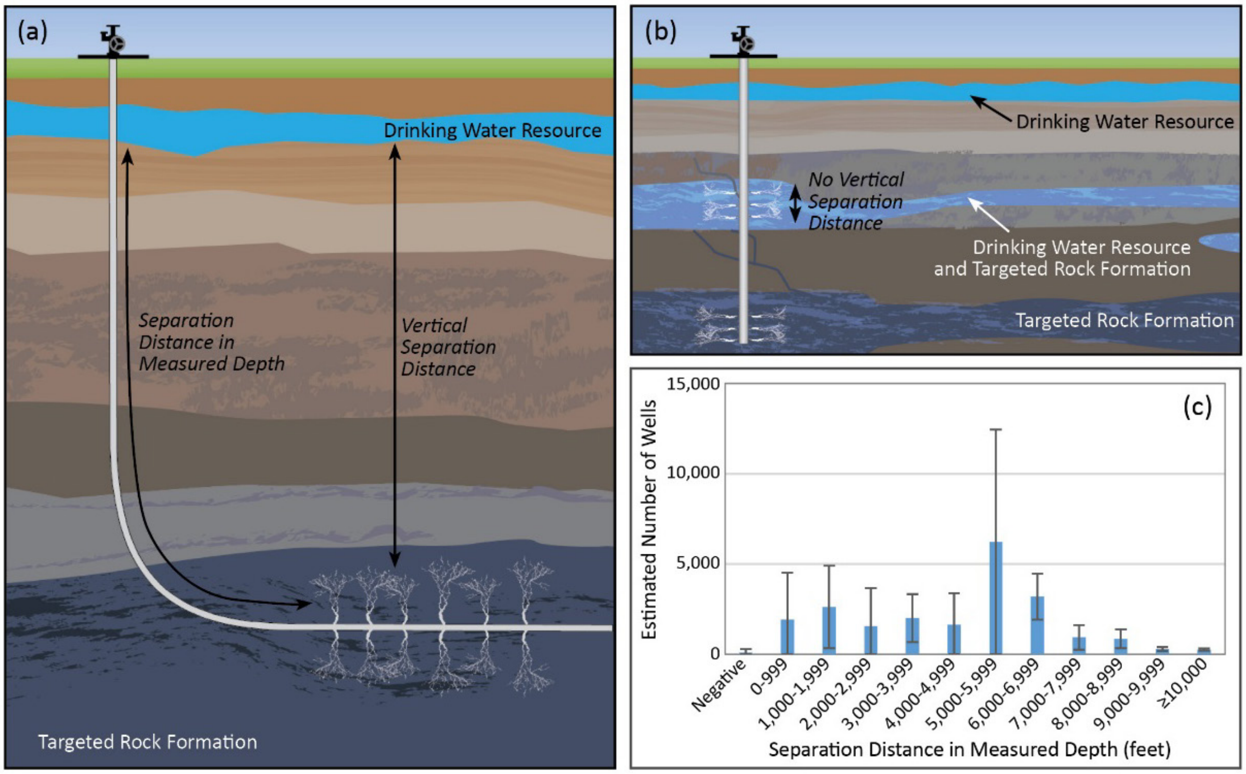


Figure 2-3. Separation distance between drinking water resources and hydraulically fractured intervals in wells

Schematic examples showing a relatively large separation distance (panel a) and the absence of any separation distance (panel b) between the shallowest fracture initiation depth in a well to the base of the protected drinking water resource. Distances may be presented as vertical or as a measured distance along a non-vertical well. Panel c shows result from wells studied representing approximately 23,000 production wells hydraulically fractured between 2009 and 2010 (U.S. EPA, 2015n). Error bars in panel c display 95% confidence intervals.

In Figure 2-3, panel (a), the hydraulically fractured oil- and gas-bearing zone is much deeper than drinking water resources, therefore separation distance is large. In panel (b), the hydraulically fractured oil- and gas-bearing zone is at the same depth as drinking water resources and there is no separation. The lack of separation distance can be due to the oil- and gas-bearing zone being shallow and/or the drinking water resource being deep. Panel (c) illustrates the distribution of separation distances in measured depth for study wells representing approximately 23,000 oil and gas production wells hydraulically fractured by nine service companies between 2009 and 2010, as reported in U.S. EPA (2015n). The calculation of 95% confidence intervals shown in panel (c) is described in the EPA report and was affected by the number of companies in the study and the well file selection methods.

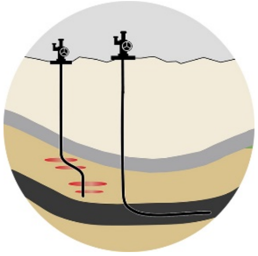
2.6 Conclusions

Drinking water resources provide the water humans consume, cook with, bathe in, and need for other purposes. An estimated 86% of the United States population derives its household drinking water from PWSs that serve at least 25 people. The remaining 14% self-supply their homes with drinking water from non-PWSs, which are largely private water wells. Publicly supplied drinking water is subject to monitoring and testing to determine compliance with drinking water standards while no such monitoring and testing is required at non-PWSs. Surface water is the source for an estimated 58% of the volume needed to supply drinking water and groundwater is the source for the remaining 42%.

The existing distribution and abundance of the drinking water resources in the United States may not be sufficient in some locations to meet future demand. The future availability of sources of drinking water that are considered fresh will likely be affected by changes in climate and water use. Since at least 2000, many areas of the United States have experienced significant drought, which often correlate with diminishment of ground and surface water supplies in these areas. Locally, measures are now being implemented to prolong use of current drinking water sources such as encouraging more modest drinking water use and using treated wastewater or other non-potable water sources to help meet demand.

Between 2000 and 2013, the EPA estimates there were approximately 275,000 oil and gas production wells hydraulically fractured in 25 states. To produce a consistent measure of proximity between these hydraulically fractured oil and gas production wells and drinking water resources during this time frame, the EPA counted the number hydraulically fractured oil and gas production wells located within 1 mile of public drinking water sources, and performed a count of the counties with a relatively high reliance on self-supplied drinking water that also contain one or more of these hydraulically fractured production wells. Between 2000 and 2013, approximately 3,900 public water systems had between one and 144 wells hydraulically fractured within 1 mile of their water source; these public water systems served more than 8.6 million people year-round in 2013. An additional 740,000 people between 2000 and 2013 self-supplied their drinking water in counties where at least 30% of the population relies on groundwater and having at least 400 hydraulically fractured wells.

Depending on the nature of the geologic setting, hydraulically fractured oil and gas production wells can be located near where people get their drinking water. Depths to hydraulically fractured oil and gas resources can range from less than 1,000 ft (300 f) to more than 10,000 ft (3,000 m) while drinking water resources may be found between a few tens of feet to as much as 8,000 ft (2,000 m) below the surface. There is limited publicly available information to determine the vertical distance separating the shallowest hydraulic fracturing initiation point in a production well from the deepest drinking water resource. The EPA found, among 323 wells studied statistically representing more than 23,000 production wells hydraulically fractured by nine service companies between 2009 and 2010, the distance along the wells between these two resources ranged from none to more than 10,000 ft (3,000 m).



Chapter 3. Hydraulic Fracturing for Oil and Gas in the United States

Abstract

This chapter provides a general description of the practice of hydraulic fracturing, where it is conducted, how prevalent it is, and how hydraulic fracturing-based oil and gas production fits into the context of energy production in the United States. Some of the information in this chapter also serves as an introduction to the more in-depth technical chapters in the assessment.

Hydraulic fracturing is a technique used to increase oil and gas production from underground oil- and/or gas-bearing rock formations (reservoirs). The technique involves the injection of hydraulic fracturing fluids through the production well and into the reservoir under pressures great enough to fracture the reservoir rock. Hydraulic fracturing fluids typically consist mainly of water, a "proppant" (typically sand) that props open the created fractures, and additives (usually chemicals) that modify the properties of the fluid for fracturing. Fractures created during hydraulic fracturing enable better flow of oil and gas from the reservoir into the production well. Water that naturally occurs in the oil and gas reservoirs also typically flows into and through the production well to the surface as a byproduct of the oil and gas production process.

Since the mid-2000s, the combination of modern hydraulic fracturing and directional drilling has become widespread and significantly contributed to a surge in oil and gas production in the United States. Slightly more than 50% of oil production and nearly 70% of gas production in 2015 is estimated to have occurred using hydraulic fracturing. Hydraulic fracturing is widely used in unconventional (low permeability) oil and gas reservoirs that include shales, so-called tight oil and tight gas formations, and coalbeds, but it is also used in conventional reservoirs.

There is no comprehensive national database of wells that are hydraulically fractured in the United States. Using data from several commercial and public sources, the EPA estimates that 25,000 to 30,000 new wells were drilled and hydraulically fractured in the United States annually between 2011 and 2014. These hydraulic fracturing wells are geographically concentrated; in 2011 and 2012 almost half of hydraulic fracturing wells were located in Texas, and a little more than a quarter were located in the four states of Colorado, Pennsylvania, North Dakota, and Oklahoma.

New drilling activity for hydraulic fracturing wells is generally linked with oil and gas prices, and those peaked in the United States between 2005 and 2008 for gas and between 2011 and 2014 for oil. Following price declines, the number of new hydraulically fractured wells in 2015 decreased to about 20,000. Despite recent declines in prices and new drilling, U.S. gas and oil production continues at levels above those in recent decades, and production for both is predicted to continue growing in the long term, led by hydraulic fracture-based production from unconventional reservoirs.

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3. Hydraulic Fracturing for Oil and Gas in the United States

3.1 Introduction

This chapter provides general background information on hydraulic fracturing and will help the reader understand the in-depth technical chapters that follow. We describe the purpose and process of hydraulic fracturing and the situations and settings in which it is used (Section 3.1). Then we provide a general description of activities at a hydraulic fracturing well site including assessing and preparing the well site, well drilling and construction, the hydraulic fracturing event, the oil and gas production phase, and eventual site closure (Section 3.3). A characterization of the prevalence of hydraulic fracturing in the United States is then presented (Section 3.4), followed by a review of its current and future importance in the oil and gas industry and its role in the U.S. energy sector (Section 3.5), and a brief conclusion (Section 3.6).

3.2 What is Hydraulic Fracturing?

Hydraulic fracturing is a technique used to increase oil and gas production from underground oil- or gas-bearing rock formations (reservoirs).[1] The technique involves the injection of hydraulic fracturing fluids through the production well and into the reservoir under pressures great enough to fracture the reservoir rock. The injected hydraulic fracturing fluid carries "proppant" (typically sand) into the fractures so that they remain propped open after the pressurized injection is stopped. In addition to water, which typically makes up most of the injected fracturing fluid, the fluid also contains chemical additives (additives) that serve a variety of purposes. These additives, for example, can increase the fluid viscosity (how "thick" the fluid is) so that it carries the proppant into the fractures more effectively, can help control well corrosion, can help minimize microbial growth in the well, and so on (King and Durham, 2015; Gupta and Valkó, 2007). The resulting fractures enable better flow of oil and gas from the reservoir into the production well. Water that naturally occurs in the reservoirs also typically flows into and through the production well to the surface as a byproduct of the production process.

Although hydraulic fracturing is not new, how and where it is employed has changed (Text Box 3-1). For about a half-century after its introduction in the late 1940s, it was used to increase production from vertical wells in conventional oil and gas reservoirs. Conventional reservoirs develop over geologic time (many millions of years) when naturally buoyant oil and gas very slowly migrate upward from the shale rock formations in which they formed until they are trapped by geologic formations or structures and accumulate under a confining layer (Figure 3-1). As the oil and gas accumulate, the pressure may increase. If the reservoir is under enough pressure and has

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[1] A version of hydraulic fracturing, sometimes called hydrofracturing or hydrofracking, can be used to increase water yields from water wells and is typically done by injecting only water under pressure. This application of hydraulic fracturing is out of the scope of this assessment.

Text Box 3-1. Hydraulic Fracturing: Not New, but Different and Still Changing.

From the mid-1800s to the 1940s, operators of oil and gas wells occasionally tried to increase production by pumping fluids or sometimes dropping explosives into wells. In the late 1940s, a fracturing technique to increase production was patented by the Stanolind Oil and Gas Company and licensed to the Halliburton Oil Well Cementing Company (Montgomery and Smith, 2010). Close to 1 million wells were hydraulically fractured from the late 1940s to about 2000 (IOGCC, 2002). The typical well design and hydraulic fracturing operations during most of that time, though, were very different from today's modern hydraulic fracturing operations.

The groundwork for the transformation to modern hydraulic fracturing was laid in the 1970s and early 1980s. Public-private research and development (R&D) partnerships that included industry, the Department of Energy, and the Gas Research Institute were established because large amounts of natural gas were known to occur in some shale rock formations yet traditional production well technology was not able to recover much of the gas (Avila, 1976). These R&D programs played a key role in advancing technologies such as deep horizontal drilling and fracturing with higher water volumes that ultimately enabled production from shales and other unconventional sources of gas and oil (DOE, 2015; NRC: Committee on Benefits of DOE R&D on Energy Efficiency and Fossil Energy, 2001). During this period, the U.S. Congress began offering tax incentives for producers to use the developing technologies in the field (Wang and Krupnick, 2013; EIA, 2011a; Yergin, 2011). Advances in directional drilling technologies led to the first horizontal wells being drilled in the mid-1980s in the Austin Chalk oil-bearing rock formation in Texas (Pearson, 2011; Haymond, 1991). Directional drilling and other technologies matured in the late 1990s. In 2001, the Mitchell Energy company developed a cost-effective technique to fracture the Barnett Shale in Texas. The company was bought by Devon Energy, a company with advanced experience in directional and horizontal drilling, that, in 2002, drilled seven wells and developed in the Barnett Shale using the combination of horizontal drilling and hydraulic fracturing; fifty-five more wells were completed in 2003 (Yergin, 2011). The techniques were rapidly adopted and further developed by others (DOE, 2011b; Montgomery and Smith, 2010). By 2005, the techniques were being used in unconventional (low-permeability) oil and gas reservoirs outside of Texas. Modern hydraulic fracturing quickly became the industry standard, driving a surge in U.S. production of oil and natural gas.

Hydraulic fracturing techniques and technologies continue to evolve. Wells are being drilled with longer horizontal sections and are more closely spaced. Multiple, horizontal sections extending from a single vertical well enable production from larger subsurface areas from a single well pad on the land's surface. These historic and continuing technological developments enable production from previously unused oil and gas-bearing geologic formations, altering and expanding the geographic range of oil and gas production activities.

Left: Early hydraulic fracturing site, late 1940s (source: Halliburton, used with permission). Right: Contemporary hydraulic fracturing operation, late 2000s (source: NYSDEC (2015), used with permission).

adequate natural permeability, the economic extraction of oil and/or gas may only require using a drilled well to bring the oil or gas to the surface.[1]

If the natural pressure is not high enough for the oil and gas to readily flow to the surface, various pumping and "lift" techniques can be used to help the oil and gas move up the well to the surface (Hyne, 2012). In other situations, operators may pump water or a mix of water and carbon dioxide (or other similar mixtures) into the reservoir through injection wells to help move and enhance the extraction of oil and gas through nearby production wells. These techniques address pressure and fluid characteristics in the reservoir, are not designed to fracture the reservoir rock, and therefore are production-increasing techniques that are distinct from hydraulic fracturing. The discussions in the remainder of this chapter focus on hydraulic fracturing in unconventional reservoirs.

Hydraulic fracturing is now combined with directional drilling technologies to access oil and gas in unconventional reservoirs (although hydraulic fracturing is still used in conventional reservoirs, too).[2] Unconventional reservoirs have a very low natural permeability, which prevents oil and gas from flowing through the rock into wells in economic amounts. Production from unconventional reservoirs becomes economically feasible when wells, typically horizontal or deviated, are drilled and hydraulically fractured through long portions of the production zone (the targeted oil- and gas-bearing zones within a reservoir). See Figure 3-1 for a diagram of horizontal and other well types and the reservoir types from which they can produce. Text Box 3-2 provides a brief discussion on the use of the terms conventional and unconventional.

More details about the geologic formations that can be unconventional reservoirs are presented below:

- ***Shales.*** Some organic-rich black shales serve as the source of oil and gas found in conventional resources when, over geologic time, the lighter and more buoyant oil and gas migrate upward from these shales and become trapped under impermeable confining layers (Figure 3-1). Shales have very low permeability and the oil and gas are contained in poorly connected pore space in the shale rock. With hydraulic fracturing and directional drilling now enabling oil and gas production from very low permeability formations, some of these shale source rocks are now unconventional reservoirs in addition to being sources. Some shales produce predominantly gas and others predominantly oil; often there will be some co-production of gas from oil wells and co-production of liquid oil from gas wells (USGS, 2013a; EIA, 2011a).
- ***Tight formations.*** Some oil- and gas-bearing sandstone, siltstone, and carbonate formations can be referred to as "tight" formations (for example, "tight sands") because of their relatively low permeability and the fact that oil and gas are contained in small, poorly connected pore spaces. Given a range of permeabilities, some tight formations require

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[1] Permeability in rocks is the ability of fluids, including oil and gas, to flow through well-connected pores or small openings in the rock.

[2] Directional drilling is the practice of controlling the direction and deviation (angle) of a borehole during drilling to extend the borehole in a predetermined orientation and to a targeted area in the subsurface. Directional drilling is required for drilling a deviated or horizontal well and is common in unconventional reservoirs. The terms deviated wells and directional wells are often used interchangeably.

hydraulic fracturing for economic production and some do not. In the literature, "tight gas" generally refers to gas in tight sands and is distinguished from "shale gas." Oil resources from shale and other tight formations, in contrast, are frequently referred together under the label "shale oil" or "tight oil" (Schlumberger, 2014; USGS, 2014a).

- ***Coalbeds.*** Organic-rich coal, found in coalbeds, can be a source of methane (natural gas). The gas primarily adheres to the coal surface rather than being contained in pore space or structurally trapped in the formation. A range of techniques can be used to extract methane from coalbeds and these techniques sometimes, but not always, employ hydraulic fracturing. A key component of all coalbed methane production is the need to "dewater" the coalbeds (pumping out naturally occurring or injected water) to reduce the pressure in the coal allowing the methane to be released and flow from the coal into the production well (Palmer, 2010; Al-Jubori et al., 2009; USGS, 2000).

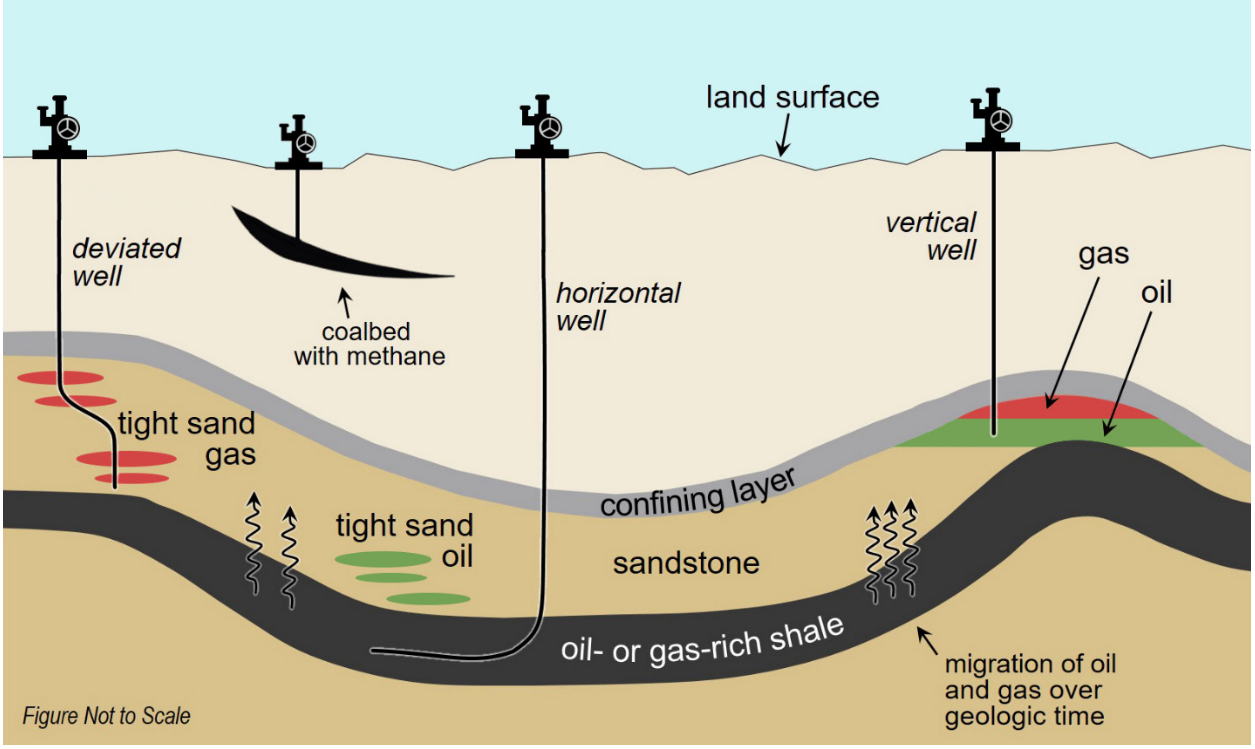

Figure 3-1. Conceptual illustration of the types of oil and gas reservoirs and production wells used in hydraulic fracturing.

A vertical well is producing from a conventional oil and gas reservoir (right). The impermeable gray confining layer (sometimes called a cap rock) traps the lighter and more buoyant gas (red) and oil (green) as it migrates up from the deeper oil- or gas-rich shale source rock. Also shown are wells producing from unconventional reservoirs: a horizontal well producing from a deep shale (center); a vertical well producing methane (gas) from coalbeds (second from left); and a deviated well producing from a tight sand reservoir (left). Multiple deviated or horizontal wells can be constructed and operated from a single well site. Note that the oil- or gas-rich shale serves as both a source and a reservoir. Modified from Schenk and Pollastro (2002) and Newell (2011).

Text Box 3-2. "Conventional" Versus "Unconventional."

The terms "conventional" and "unconventional" are widely used in articles and reports to distinguish types of oil and gas reservoirs, wells, production techniques, and more. In this report, the terms are mainly used to distinguish different types of oil and gas reservoirs: "conventional" reservoirs are those that can support the economically feasible production of oil and gas using long-established technologies, and "unconventional" reservoirs are those in which production has become economical only with the advances that have occurred in hydraulic fracturing (often combined with directional drilling) in recent years.

Note that as hydraulic fracturing has increasingly become a standard industry technique, the word "unconventional" is less apt than it once was to describe these oil and gas reservoirs. In a sense, "the unconventional has become the new conventional" (NETL, 2013).

The following three maps show the locations of major shale gas and oil resources, tight gas resources, and coalbed methane resources, respectively, in the contiguous United States (Figure 3-2, Figure 3-3, and Figure 3-4). To explain the terminology used in the maps: a group of known or possible oil and gas accumulations in the same region and with similar geologic characteristics can be referred to as a *play* (Schlumberger, 2014). Plays can sometimes be geologically layered atop one another (or "stacked") and are located in broad depressions filled with sedimentary rock formations in the earth's continental crust known as *basins*. A group of similar coalbed methane (gas) reservoirs can be referred to as coalbed methane *fields* (rather than plays) and are also found in basins. The plays and fields in the maps below represent unconventional reservoirs that are being exploited now or could be exploited in the future using hydraulic fracturing.

There is a wide range of depths at which hydraulic fracturing occurs across the country. For example, approximate average depths for some of the largest gas-producing reservoirs are as deep as 6,000 ft (2,000 m) in the Marcellus Shale in Pennsylvania and West Virginia, 7,500 ft (2,300 m) in the Barnett Shale in Texas, and 12,000 ft (3,700 m) for the Haynesville-Bossier Shale in Louisiana and Texas (NETL, 2013).[1] A few other, smaller plays are shallower, with depths less than 2,000 ft (600 m) in parts of the Antrim (Michigan), Fayetteville (Arkansas), and New Albany (Indiana and Kentucky) shale plays (NETL, 2013; GWPC and ALL Consulting, 2009). Coal seams that can be drilled to produce gas (coalbed methane) range in depth from less than 600 ft (200 m) to more than 6,000 ft (2,000 m) with production often occurring at depths between 1,000 and 3,000 ft (300 and 900 m) (U.S. EPA, 2006; ALL Consulting, 2004). Coalbed methane production occurs in the San Juan Basin in New Mexico, the Powder River Basin in Wyoming and Montana, and the Black Warrior Basin in Alabama and Mississippi. See Chapter 6 for more information on the general locations and depths of formations being hydraulically fractured.

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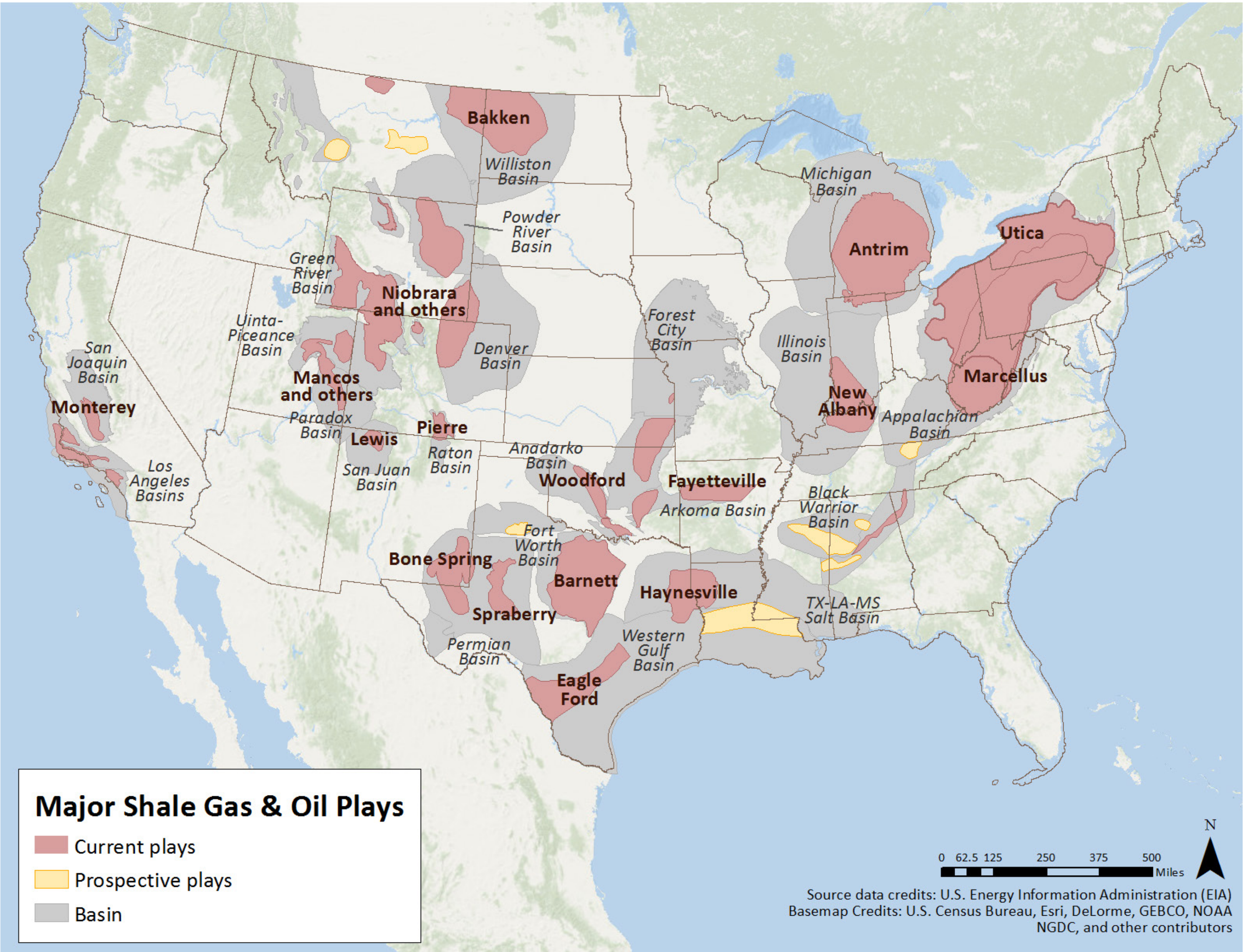
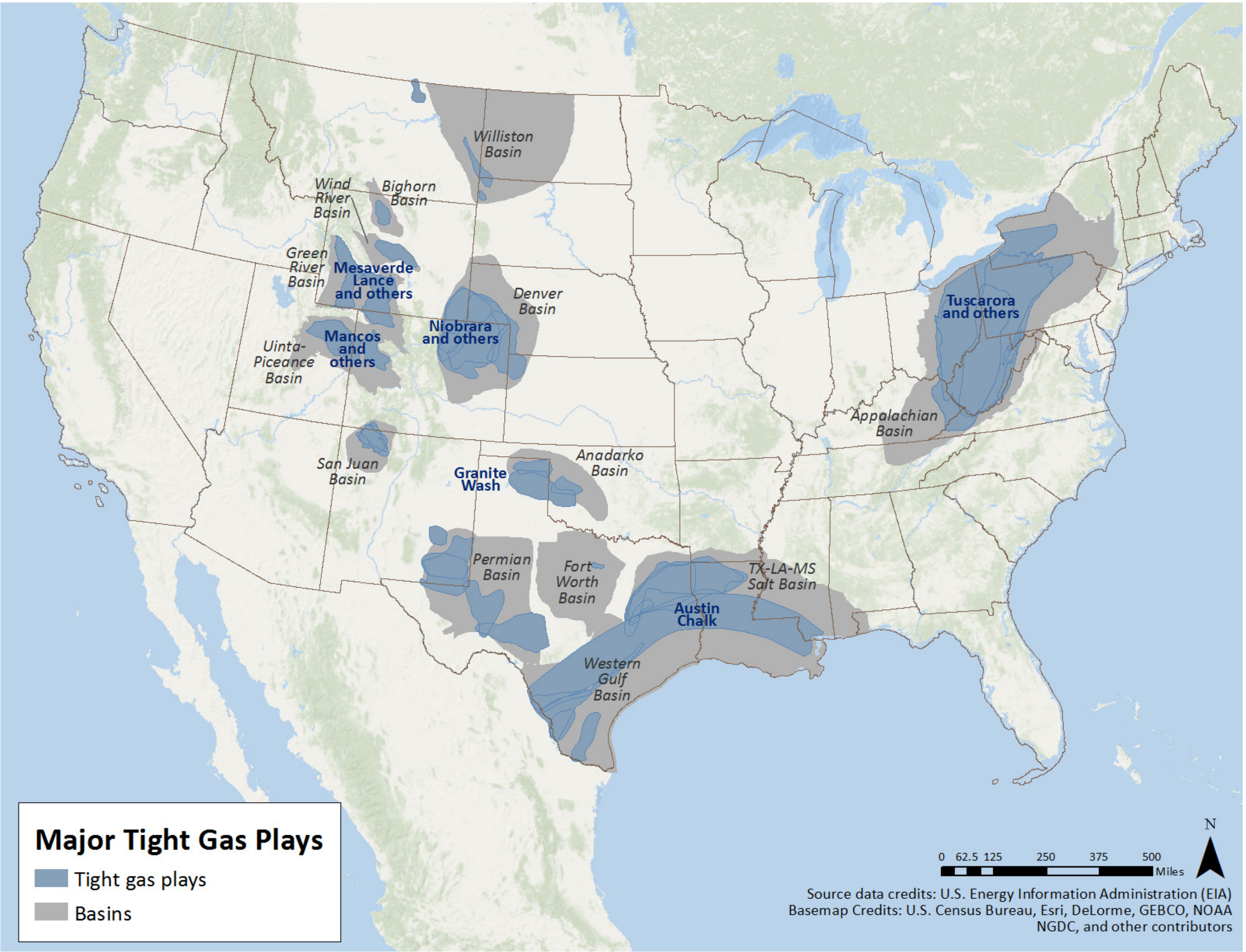
[1] These are approximate average depths; hydraulic fracturing occurs in shallower and deeper zones in all these plays.



Source data credits: U.S. Energy Information Administration (EIA)
Basemap Credits: U.S. Census Bureau, Esri, DeLorme, GEBCO, NOAA NGDC, and other contributors

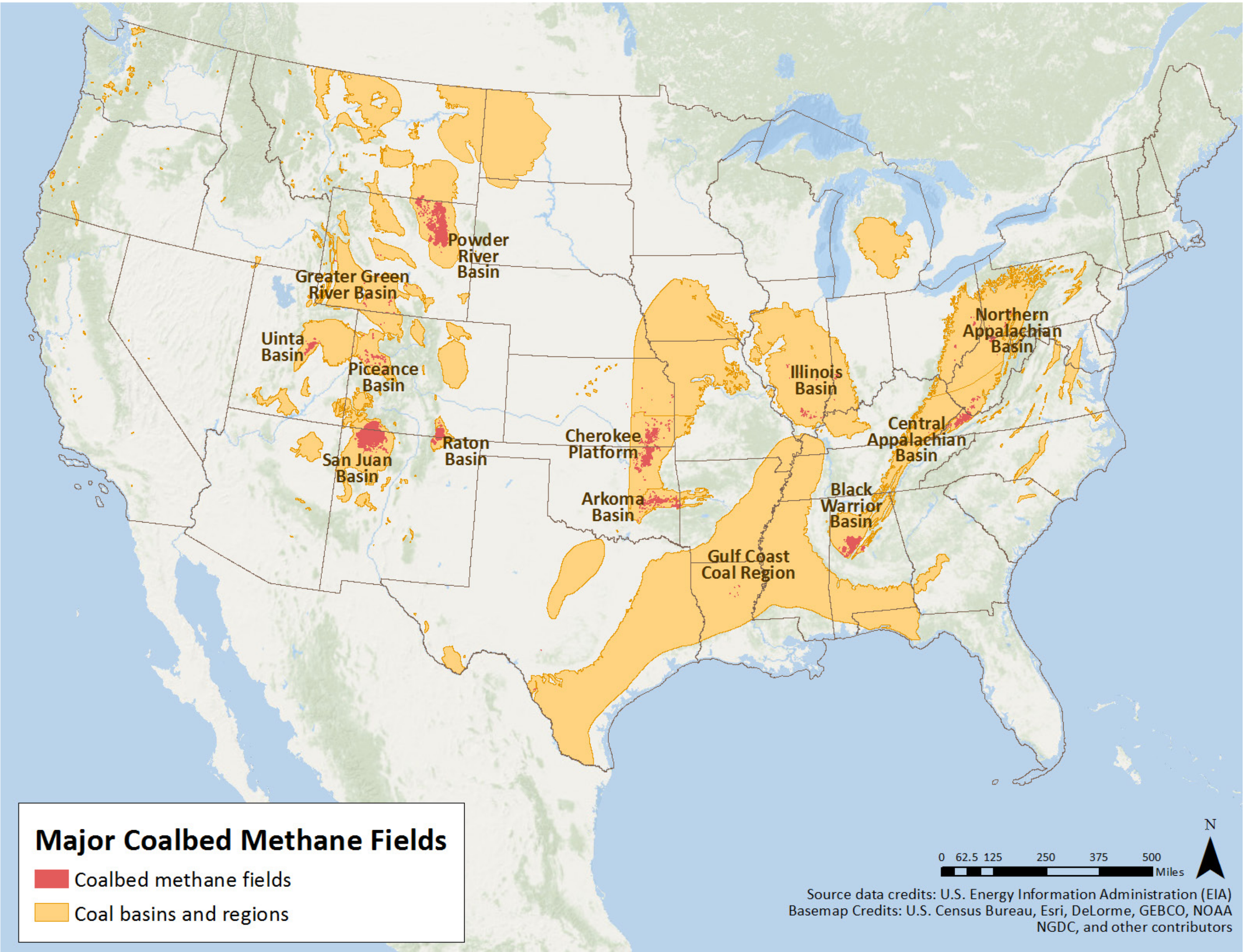
Figure 3-2. Major shale gas and oil plays in the contiguous United States.

The plays represent geologically similar accumulations of oil and gas that are or could be developed. Adapted from EIA (2015).



Source data credits: U.S. Energy Information Administration (EIA)
Basemap Credits: U.S. Census Bureau, Esri, DeLorme, GEBCO, NOAA NGDC, and other contributors

Figure 3-3. Major tight gas plays in the contiguous United States.
The plays represent geologically similar accumulations of gas that are or could be developed. Adapted from EIA (2011b).



Source data credits: U.S. Energy Information Administration (EIA)
Basemap Credits: U.S. Census Bureau, Esri, DeLorme, GEBCO, NOAA NGDC, and other contributors

Figure 3-4. Coalbed methane fields and coal basins in the contiguous United States.
The fields represent gas-bearing coal deposits that are or could be developed. Adapted from EIA (2011b).

How a hydraulic fracturing operation is conducted depends on the characteristics of the oil- or gas-bearing formation (such as the geology, depth, and other factors). Hydraulic fracturing operations in shales, such as the Marcellus and Haynesville, require that relatively large volumes of water and proppant to be pumped at high pressures through deep wells with long horizontal sections in the production zone. In some tight formations, such as in the Permian Basin, hydraulic fracturing can be conducted with smaller water volumes and using less pressure in shorter vertical or deviated wells (Gallegos and Varela, 2015). Hydraulic fracturing technologies can be applied to coalbed methane production in various ways, for example, with much smaller water volumes and no proppant, or with water-based gels or foams and proppant. Coalbed methane production sometimes involves no hydraulic fracturing, with only pumping of the naturally occurring formation water out of the coalbeds to enable the release and production of the trapped methane.[1]

3.3 Hydraulic Fracturing and the Life of a Well

A variety of activities take place at a well site over the course of the operational life of a hydraulically fractured oil and gas production well. Not all of these activities are within the scope of this assessment (that includes water acquisition, chemical mixing, well injection, produced water handling, and wastewater disposal and reuse). However, in this chapter we include some information on a wider range of activities related to the well site to provide context for the reader.

The overview of well operations presented in this section is broad, illustrates common activities, and describes some specific operational details. The details of well preparation, hydraulic fracturing and production operations, and closure can vary between companies, reservoirs, and states, and even from well to well. The activities involved in well development and operations may be conducted by the well owner and/or operator, their representatives, and/or service companies working for the well owner.

Figure 3-5 shows the general sequence and duration of activities at a hydraulic fracturing well site, including the activities that comprise the five stages of the hydraulic fracturing water cycle (noted above and defined in Chapter 1). The hydraulic fracturing event itself is the period of the most operational activity during the life of a well and is short in duration compared to the other well site activities. The hydraulic fracturing activity typically lasts from about a day to several weeks (U.S. EPA, 2016c; Halliburton, 2013; NYSDEC, 2011). The subsequent phase of oil and gas production, during which produced water also flows from the well, is the longest phase during the life of the well and can last decades (King and Durham, 2015).[2]

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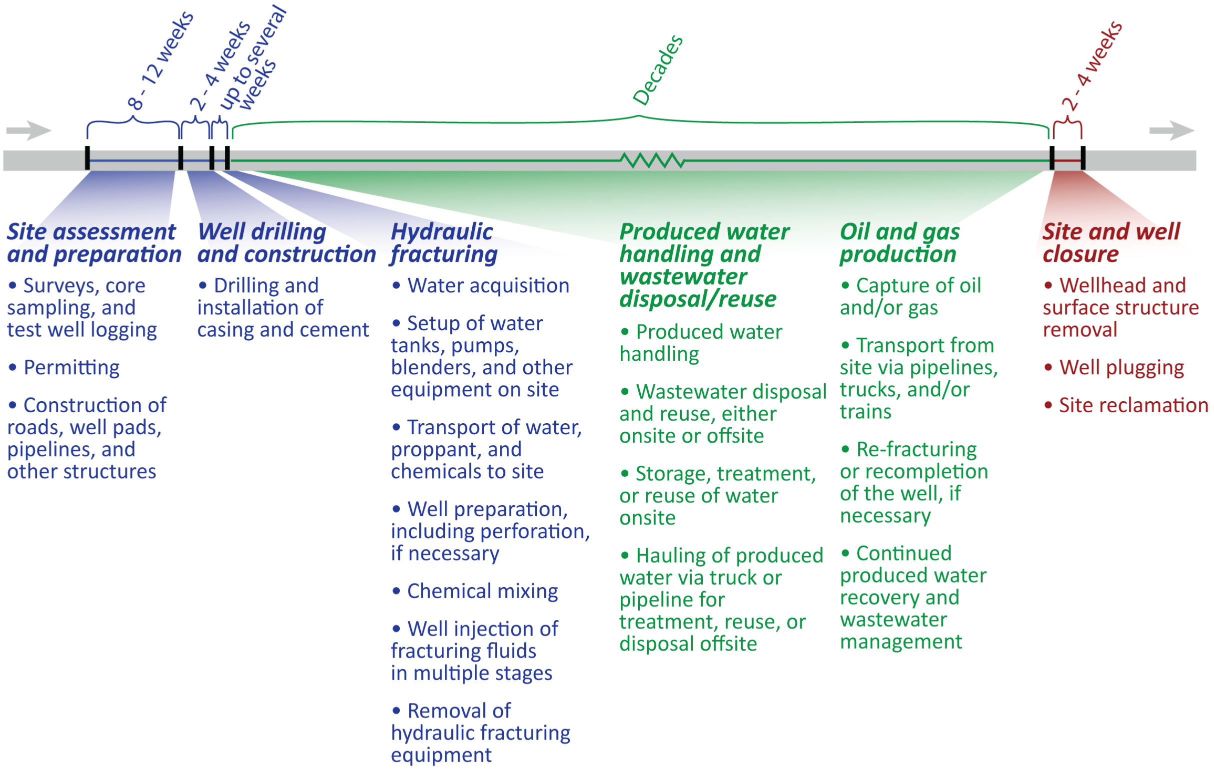
[1] Some subsurface geologic formations, including coalbeds and oil and gas reservoirs, can contain naturally occurring water that is commonly referred to as “formation water,” “native water,” or (if salty) “native brines.”

[2] In general, produced water is water that flows from the subsurface through oil and gas wells to the surface as a by-product of oil and gas production. See Section 3.3.3 and Chapter 7 for more details.



Site assessment and preparation
- Surveys, core sampling, and test well logging
- Permitting
- Construction of roads, well pads, pipelines, and other structures

Well drilling and construction
- Drilling and installation of casing and cement

Hydraulic fracturing
- Water acquisition
- Setup of water tanks, pumps, blenders, and other equipment on site
- Transport of water, proppant, and chemicals to site
- Well preparation, including perforation, if necessary
- Chemical mixing
- Well injection of fracturing fluids in multiple stages
- Removal of hydraulic fracturing equipment

Produced water handling and wastewater disposal/reuse
- Produced water handling
- Wastewater disposal and reuse, either onsite or offsite
- Storage, treatment, or reuse of water onsite
- Hauling of produced water via truck or pipeline for treatment, reuse, or disposal offsite

Oil and gas production
- Capture of oil and/or gas
- Transport from site via pipelines, trucks, and/or trains
- Re-fracturing or recompletion of the well, if necessary
- Continued produced water recovery and wastewater management

Site and well closure
- Wellhead and surface structure removal
- Well plugging
- Site reclamation

Figure 3-5. General timeline and summary of activities that take place during the preparation and through the operations of an oil or gas well site at which hydraulic fracturing is used.

3.3.1 Site Preparation and Well Construction

Before hydraulic fracturing and production can occur, preliminary steps include assessing and preparing the site, and drilling and constructing the production well.

3.3.1.1 Site Assessment and Preparation

Selecting a suitable well site requires an assessment of geologic (subsurface) and geographic (surface) factors. Geophysical surveys of the subsurface can be conducted using data gathering techniques from the land surface or subsurface, and rock samples may be gathered from outcrops or from exploratory or test wells. Other information is obtained by well logging in which geophysical instruments that collect data on subsurface conditions are lowered into or installed in a well (Kundert and Mullen, 2009).[1] Analyzing all of this information together enables operators to develop an understanding of the potential reservoir characteristics (such as permeability and the presence of natural fractures and water), the position of such formations in relation to other

---

[1] Well logging is used to obtain information on mechanical integrity, well performance, and reservoir properties that can affect oil and gas production. Well logging data from other wells in the nearby area also provides information on the reservoir. More information on well logging is found in Chapter 6 and Appendix D.

formations, including water-bearing zones, and details about the quantity and quality of the oil and gas resource.

Geographic factors involved in well site assessment include topography and land cover; proximity to roads, pipelines, water sources, other oil and gas wells, and abandoned oil or gas wells; possible well setback requirements; potential for site erosion; location relative to environmentally sensitive areas; and location relative to populated areas (Drohan and Brittingham, 2012; Arthur et al., 2009a).[1] Land ownership also plays an important role in well site selection. During site assessment and before site development and well drilling, the well owner/operator obtains a mineral rights lease, negotiates with landowners, and applies for necessary permits from the appropriate federal, state, and local authorities (Hyne, 2012). This initial site assessment phase of the process may take several months (King and Durham, 2015; King, 2012).

The site is typically surveyed to plan and finalize well site location and access. Sometimes an access road may need to be built to accommodate trucks delivering equipment and supplies to be used at the site (Hyne, 2012). The operator levels and grades the well site to manage drainage, complete access routes, and prepare the well pad. The well pad is a smaller area within the broader well site where the production well will be drilled and the hydraulic fracturing activities will be concentrated. Well pads can range in size from less than an acre to several acres depending on the scope of the operations (King, 2012; NYSDEC, 2011). Multiple wells can be located on a single well pad at a well site (King, 2012; NYSDEC, 2011)

To manage the various fluids that are used for or generated during operations, storage pits (sometimes referred to as impoundments) are excavated, graded and constructed on the well site, and/or steel tanks are installed. These are used to hold water and materials (such as drilling mud) related to the well-drilling activities, water used in the hydraulic fracturing process, or the produced water that is generated post-fracturing (Hyne, 2012). Pit construction is generally governed by local regulations. In some areas, regulations may prohibit the use of pits or require pits to be lined to prevent fluid seepage into the shallow subsurface. One alternative to constructing a pit for drilling fluids is the use of a closed loop drilling system that stores, partly treats, and recycles the drilling fluid (Astrella and Wiemers, 1996). Often piping is installed along the surface or in the shallow subsurface of the well site to deliver water for hydraulic fracturing, remove produced water, or transport the oil and gas once production begins (Arthur et al., 2009a).

Water may be acquired from local surface water or groundwater resources, or reused from other well sites. Water is required for the drilling phase as well as for hydraulic fracturing (Chapter 4). Figure 3-6 depicts the pumping of water for well site operation from a local surface water source.

After site and well pad preparation, drill rigs and associated equipment (including the drill rig platform, generators, well blowout preventer, fuel storage tanks, cement pumps, drill pipe, and casing) are brought onto the site.

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[1] Regarding well setbacks, some states and sometimes local city or county governments can have requirements that define how close an oil and gas well can be located to drinking water supplies or other water bodies.

Figure 3-6. Surface water being pumped for oil and gas development.
Photo credit: Arkansas Water Science Center (USGS).

3.3.1.2 Well Drilling and Construction

Wells are generally drilled and constructed by repeating several basic steps. The operator begins by using the drill rig (temporarily located on the well pad) to hoist a section of long drill pipe up and attaching a drill bit to the bottom of the drill pipe. The drill rig is then used to rotate and advance the drill pipe/drill bit combination (also known as the drill string) downward through the soil and rock. As the drill string continues moves downward, new sections of pipe are added at the surface, enabling the drilling to proceed deeper (Hyne, 2012). During drilling, a drilling fluid is pumped down through the center of the drill string to the drill bit to lubricate and cool it, and to help remove the drill cuttings from the well (King, 2012).[1]

Drilling is temporarily halted at certain pre-determined intervals, the drill string is removed from the wellbore (also called the borehole), and long sections of another type of steel pipe called casing are lowered into the wellbore and set in place.[2] Cement is then pumped into the space between the outside of the casing and the wellbore. This process is repeated, with the next interval of drilling

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[1] Drilling fluids, sometimes called drilling mud, consist primarily of water, foam, oil or air, with the most common drilling mud consisting mainly of water and clay (Williamson, 2013). Drill cuttings are the small pieces of broken and ground-up rock generated during the drilling process.

[2] The wellbore is the drilled hole and can refer to both the open hole or an uncased portion of the well.

using a smaller diameter drill bit that fits inside the existing casing. The result can be multiple layers of casing and cement with surface casing and cement typically set below the groundwater resource to be protected. Figure 3-7 illustrates different types of casing as defined by their locations within the well, shows multiple casing and cement layers, and shows examples of two wells with differences in the extent of cement.[1]

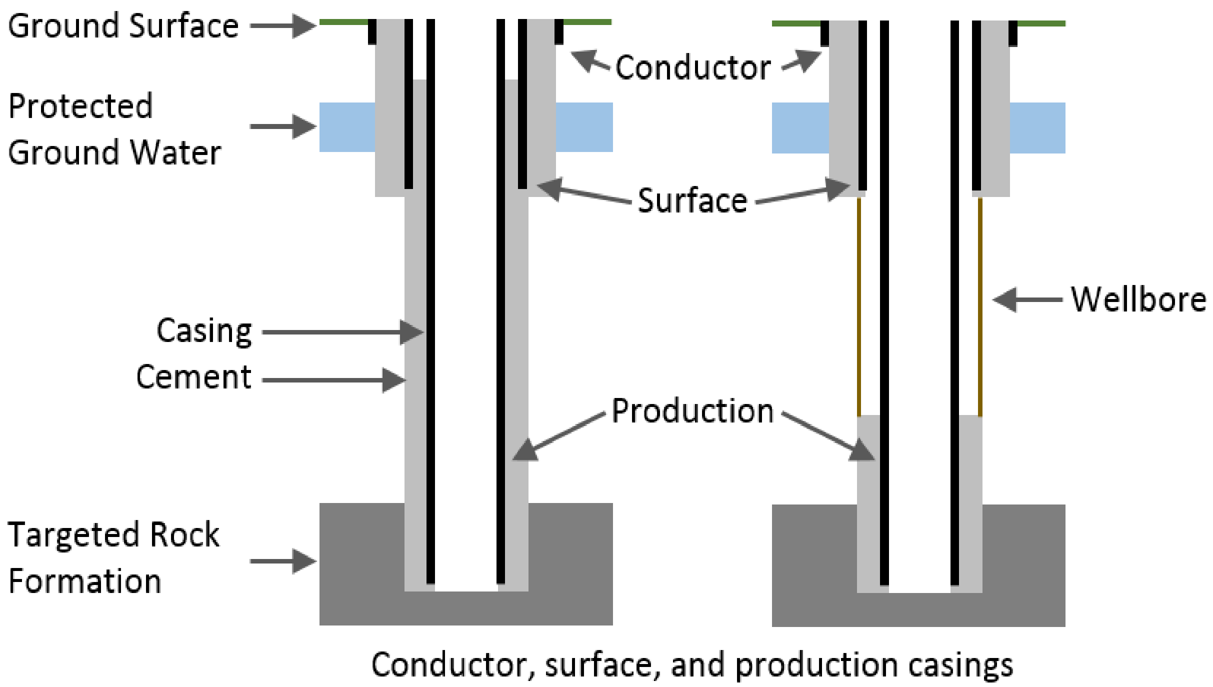

Figure 3-7. Illustration of well construction showing different types of casing and cement.

The well on the left is cemented continuously from the surface to the production zone and the well on the right has cement in sections, including sections cemented across protected groundwater.

The cement protects the casing from corrosion by formation water, helps physically support the casing in the borehole, and stabilizes the borehole against collapse or deformation (Renpu, 2011).[2] The casing and cement help to isolate geologic zones of high pressure, isolate water-bearing zones, and maintain the integrity of the production well for transporting oil and gas to the surface. Casing and cement provide important barriers that keep fluids within the well (oil, gas, hydraulic fracturing fluids) isolated and separated from fluids outside the well (formation water) (Hyne, 2012). Figure 3-8 shows sections of casing ready for installation.

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[1] In different portions of the well, multiple concentric sections of casing of different diameters can be used as shown by the surface and production casings in Figure 3-7. The largest casing diameter can range between 30 in. (76 cm) to 42 in. (107 cm) with casing diameters typically larger in the shallower portions of a well and smaller in the deeper portions (Hyne, 2012). See Appendix D for details on well construction and casing diameters.

[2] Some naturally occurring formation water can be very saline (salty or briny), which can be corrosive to metal.

Figure 3-8. Sections of well casing ready for installation at a well site in Colorado.
Photo credit: Gregory Oberley (U.S. EPA).

Some wells are cemented continuously from the surface down to the production zone. Other wells are partially cemented with, for example, cement from the surface to some distance below the deepest protected groundwater zone and perhaps cement across high pressure or water- or oil-bearing zones. Sometimes there can be multiple casing and cement layers (Figure 3-7). There are advantages, in some situations, to not fully cementing the casing as long as high pressure or water- and oil-bearing zones are cemented. For example, some sections may not be cemented to allow monitoring of the pressure in the space between the casing and the borehole or to prevent damage to weak rock formations due to the weight of the cement[1] (King and Durham, 2015; API, 2009).

Although wells are initially drilled vertically (more or less straight down), the sections of the wells that are hydraulically fractured in the production zone of the reservoir can be vertical, deviated, or horizontal (Figure 3-1). The operator determines the well orientation that will provide the best access to the targeted zone(s) within a reservoir and that will align the production section of the well with natural fractures and other geologic structures in a way that helps improve production. Deviated wells may be "S" shaped or continuously slanted. So-called "horizontal wells" have one or more extensions or branches oriented approximately 90 degrees from the vertical portion of the well; these horizontal sections are often referred to as "laterals." The lengths of laterals can range from 2,000 to 10,000 ft (600 to 3,000 m) or more (Hyne, 2012; Miskimins, 2008; Bosworth et al., 1998). Multiple laterals can extend in different directions from a single well (and multiple wells can be located on a single well site). This allows access to more of the production zone with a higher well density in the subsurface, which can be required for unconventional reservoirs, while having fewer well sites on the land surface.

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[1] The use of lighter cement or special cementing techniques can also prevent damage of weaker rock formations. See Chapter 6 and Appendix D for more details on well construction and cementing.

Once well construction is completed, the operator can move the drilling rig and related drilling equipment, install the wellhead (the top portion of the well), and prepare the well for hydraulic fracturing and subsequent production of oil and gas. Chapter 6 and Appendix D contain more details on well construction, casing, and cement.

Figure 3-9 (from northeastern Pennsylvania) and Figure 3-10 (from northwestern North Dakota) show, in the context of the local landscape, well sites during well drilling and construction prior to hydraulic fracturing activities.

Figure 3-9. Aerial photograph of two hydraulic fracturing well sites and a service road in Springville Township, Pennsylvania.

Photo credit: Image@J Henry Fair / Flights provided by LightHawk.

Figure 3-10. Aerial photograph of hydraulic fracturing well sites near Williston, North Dakota.
Photo credit: Image@J Henry Fair / Flights provided by LightHawk.

3.3.2 Hydraulic Fracturing

The hydraulic fracturing phase is an intense phase of work in the life of the well that involves complex operational activities at the well site. This phase of work is short in duration, compared to other work phases in the life of a well, and typically lasts less than two weeks per well. It consists of multiple activities, is typically a process done in repetitive stages, and requires a variety of equipment and materials. During this phase of work, the well is prepared for hydraulic fracturing, specialized equipment is hauled to the well site, the hydraulic fracturing fluid components –the water, proppant, and additives– are moved to the well site, and the hydraulic fracturing fluid is mixed and injected under pressure through the well and into the targeted production zone in the subsurface (Figure 3-11).

Figure 3-11. Well site with equipment (and pits in the background) in preparation for hydraulic fracturing in Troy, Pennsylvania.

Image from NYSDEC (2015). Reprinted with permission.

3.3.2.1 Injection Process

The section of well located in the production zone can be prepared for the injection and fracturing process in several different ways. One approach is used when the production casing and cement extend all the way into the production zone; this requires the use of focused explosive charges to perforate (blast holes in) the casing and cement in a segment of the well within the production zone. In another approach, known as a formation packer completion, only the casing, equipped with holes that can be opened and closed, is extended into the production zone. The resulting perforations or holes allow the injected hydraulic fracturing fluids to flow out of the well to fracture the reservoir rock and allow the oil and gas to flow into the well. Another technique is an open hole completion in which the casing is set and cemented just to the edge of the production zone, so the borehole extends open (with no casing or cement) into the production zone. In open hole completions, oil and gas flow directly into the borehole and eventually into the cased section of the well leading to the surface (Hyne, 2012; Cramer, 2008; Economides and Martin, 2007).

After the subsurface portion of the well is prepared for injection, a wellhead assembly is temporarily installed on the wellhead to which high pressure fluid lines are connected for injection of the fluids into the well. Figure 3-12 shows three wellheads with injection piping attached in preparation for hydraulic fracturing injection. Pressures required for fracturing can vary widely depending on depth, formation pressure, and rock type and can range from 2,000 psi to 12,000 psi (U.S. EPA, 2016c; Salehi and Ciezobka, 2013; Abou-Sayed et al., 2011; Thompson, 2010).

Figure 3-12. Three wellheads on a multi-well pad connected to the piping used for hydraulic fracturing injection.
Photo credit: DOE/NETL

The portion of the well to be fractured can sometimes be done all at once or done in multiple interval (U.S. EPA, 2016c; GWPC and ALL Consulting, 2009). When done in multiple intervals, shorter lengths or segments of the well are closed-off (using equipment inserted down into the well) and fractured independently in “stages” (Lee et al., 2011). Fluids are first injected to clean the well (removing any cement or debris). Then, for each stage fractured, a series of hydraulic fracturing fluid mixtures is injected to initiate fractures and carry the proppant into the fractures (Hyne, 2012; GWPC and ALL Consulting, 2009). The fracturing process can require moving millions of gallons of fluids around the well site through various hoses and lines, blending and mixing the fluids with proppant, and injecting the mixture at high pressures down the well. For more details on hydraulic fracturing chemical mixtures and stages, see Chapter 5.

The hydraulic fracturing produces propped-open fractures that extend into the production zone and create more flow paths that contact a greater volume of the oil- and gas-bearing rock within the production zone of the reservoir. This increase in flow paths and in the volume of the production zone accessed by the production well is how hydraulic fracturing increases production. In this regarding, hydraulic fracturing can be considered a production or well "stimulation" technique.

The process and the fracturing pressures during injection are closely monitored throughout the fracturing event. Microseismic monitoring (a geophysical survey technique) can be used to estimate the horizontal and vertical extent of the fractures created and, used with other monitoring and operational data, provides important information for designing subsequent fracture jobs (Cipolla et al., 2011). Engineers can design fracture systems using modeling software to help optimize the process. More details of injection, fracturing, and related monitoring are provided in Chapter 6 and Appendix D.

3.3.2.2 Fracturing Fluids

To conduct the chemical mixing and preparation of the hydraulic fracturing fluids, water- and chemical-filled tanks and other storage containers are transported and installed on site. The components that make up the hydraulic fracturing fluid for injection are commonly mixed on a truck-mounted blender on the well pad. Hoses and pipes are used to transfer the water, proppant, and chemicals from storage units to the mixing equipment and to the well into which the mixed hydraulic fracturing fluid will be injected. The injection process happens in stages with specific chemicals added at different times during each stage. The composition of the hydraulic fracturing fluid, therefore, can change over time during the process (Knappe and Fireline, 2012; Fink, 2003). See Chapter 5 for more details on mixing and staged injection.

Hydraulic fracturing fluids (sometimes referred to as "fluid systems") are generally either water-based or gel-based. Other fluid systems include foams or emulsions made with nitrogen, carbon dioxide, or hydrocarbons; acid-based fluids; and others (Montgomery, 2013; Saba et al., 2012; Gupta and Hlidek, 2009; Gupta and Valkó, 2007; Halliburton, 1988). Water-based systems are used more often with the most common type being "slickwater" formulations, which include polymers as friction reducers and are typically used in very low permeability reservoirs such as shales (Barati and Liang, 2014). Because slickwater fluids are thinner (have lower viscosity) they do not as easily carry sand proppant into fractures, so larger volumes of water and greater pumping pressures are required to effectively transport proppants into fractures. In contrast, gelled fluids (used in "gel fracs") are more viscous, and more proppant can be transported with less water as compared to slickwater fractures (Brannon et al., 2009). Gel fracs are generally used in reservoirs with higher permeability (Barati and Liang, 2014).

The composition of a typical water-based hydraulic fracturing fluid by volume is 90% to 97% water, 2% to 10% proppant, and 2% or less additives (U.S. EPA, 2015a; OSHA, 2014a, b; Carter et al., 2013; Knappe and Fireline, 2012; Spellman, 2012; Sjolander et al., 2011; SWN, 2011). In a detailed study, the EPA analysis of FracFocus 1.0 data for nearly 39,000 wells nationally in 2011 and 2012 indicates that the fracturing fluid injected into a well consists of nearly 90% water, 10% proppant, and less than 1% additives (on a mass basis) (U.S. EPA, 2015a). The proportions of water, proppant, and additives in the fracturing fluid, and the specific additives used, can vary depending on a number of factors, including the rock type and the chemistry of the reservoir, whether oil or gas is being produced, operator preference, and to some degree on local or regional availability of chemicals (Arthur et al., 2014; Spellman, 2012; GWPC and ALL Consulting, 2009; Gupta and Valkó, 2007). Hydraulic fracturing fluid composition and chemical use changes as processes are tested and refined by companies and operators. These changes are driven by economics, scientific and technological developments, and concerns about environmental and health impacts. Further detail on hydraulic fracturing fluid systems is presented in Chapter 5.

Sources of water for hydraulic fracturing fluid include groundwater, surface water, and reused wastewater (URS Corporation, 2011; Blauch, 2010; Kargbo et al., 2010). The water may be brought to the production well from an offsite regional source via trucks or piping, or it may be more locally sourced (for example, pumped from a nearby river or a groundwater well). Selection of water source depends upon availability, cost, water quality needs, and the logistics of delivering it to the site. Figure 3-13 shows a row of water tankers storing water on a well site. Chapter 4 provides additional details on water acquisition and the amounts of water used for hydraulic fracturing.

Figure 3-13. Water tanks (blue, foreground) lined up for hydraulic fracturing at a well site in central Arkansas.
Photo credit: Martha Roberts (U.S. EPA).

Proppants are most commonly silicate minerals, primarily quartz sand (GWPC and ALL Consulting, 2009). Sand proppants can be coated with resins that make them more durable. Ceramic materials are also sometimes used as proppants due to their high strength and resistance to crushing and deformation (Beckwith, 2011).

Additives generally constitute less than 2.0% of hydraulic fracturing fluids (Carter et al., 2013; Knappe and Fireline, 2012; GWPC and ALL Consulting, 2009). The EPA analyzed additive data in the EPA FracFocus 1.0 project database and estimated that chemicals used as additives were about 0.43% (the median value by mass) of the total amount of fluid injected for hydraulic fracturing (U.S. EPA, 2015a). Given the total volume of hydraulic fracturing fluid, these small percentages of chemicals in the fluid mean that a typical hydraulic fracturing job can handle, mix, and inject tens of thousands of gallons of chemicals. Chapter 5 includes details on the number, types, and estimated quantities of chemicals typically used in hydraulic fracturing.

3.3.3 Fluid Recovery, Handling, and Disposal or Reuse

At the end of the hydraulic fracturing process, the pressurized injection is stopped and the direction of fluid flow reverses. Initially, the fluid flowing back into the well and to the surface is mostly the injected fracturing fluid (sometimes referred to as flowback). The composition of the fluid changes over time, though, and after the first few weeks or months the proportion of hydraulic fracturing fluid flowing back into the well decreases and the proportion of formation water flowing into the well and to the surface increases (NYSDEC, 2011). In this assessment, the water that flows from the subsurface through oil and gas wells to the surface as a by-product of oil and gas production is referred to as produced water. The amount of produced oil or gas flowing into the well gradually increases until it is the primary constituent of the fluid emerging from the well at the surface. Produced water continues to flow from the production well along with the oil or gas throughout the operating life of the production well (Barbot et al., 2013). See Chapter 7 for details, descriptions, and discussions of the chemical composition and quantities of produced water recovered.

Produced water is sometimes referred to as hydraulic fracturing wastewater. Along with other liquid waste collected from the well pad (such as rainwater runoff), it is typically stored temporarily on-site in pits (Figure 3-14) or tanks. This wastewater can be moved offsite via truck or pipelines for treatment and reuse or for disposal. Most hydraulic fracturing wastewater in the United States is disposed of by injection into deep, porous geologic rock formations, often located away from the production well site. This disposal-by-injection occurs not through oil and gas production wells, but through wastewater injection wells regulated by EPA Underground Injection Control (UIC) programs under the Safe Drinking Water Act.[1] See Chapter 8 for a brief discussion of wastewater injection.

Figure 3-14. A pit on the site of a hydraulic fracturing operation in central Arkansas.
Photo credit: Caroline E. Ridley (U.S. EPA).

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[1] States may be given federal EPA approval to run a UIC program under the Safe Drinking Water Act. Most oil- and gas-related UIC programs are implemented by the states although some are implemented by the EPA.

Other wastewater handling options include discharge to surface water bodies either with or without treatment, evaporation or percolation pits, or reuse for subsequent fracturing operations either with or without treatment (U.S. EPA, 2012h; U.S. GAO, 2012). Decisions regarding wastewater handling are driven by factors such as cost (including costs of temporary storage and transportation), availability of facilities for treatment, reuse, or disposal, and regulations (Rassenfoss, 2011). Chapter 8 contains details of the treatment, reuse, and disposal of wastewater.

3.3.4 Oil and Gas Production

After the hydraulic fracturing activity is completed, the fracturing-related equipment is removed and operators drain, fill in with soil, and regrade pits that are no longer needed unless multiple wells are drilled and fractured on the same pad. The well pad size is reduced as the operation moves toward the production phase (NYSDEC, 2011). Prior to and during production, the operator runs production tests to determine the maximum flow rate that the well can sustain and to determine optimum equipment settings (Hyne, 2012; Schlumberger, 2006). During production, monitoring of mechanical integrity and performance (with pressure tests, corrosion monitoring, etc.) can be conducted to ensure that the well is performing as intended. Such well tests and monitoring may be required by state regulations.

Produced gas typically flows from the well through a pipe to a "separator" that separates the gas from water and any liquid oil and gas (NYSDEC, 2011). The finished gas is typically piped to a compressor station where it is pressurized and then piped to a main pipeline for sale (Hyne, 2012). Production at oil wells proceeds similarly, although oil/water or oil/water/gas separation typically occurs on the well pad, no compressor is needed, and the oil can be hauled by truck or train, or piped from the well pad to offsite storage and sale facilities.[1]

During the life of the well it may be necessary to repair components of the well and replace old equipment. Sometimes the well is re-fractured to boost production.[2] Routine maintenance activities, often referred to as "workovers," may be done with the well still in production (Vesterkjaer, 2002) or sometimes require stopping production and removing the wellhead to clean out debris or repair components of the well (Hyne, 2012). More extensive re-workings of a well, sometimes referred to as "re-completions," can include making additional perforations in the well in new sections to produce oil and/or gas from another production zone, lengthening the borehole, or drilling new horizontal extensions (laterals) from an existing borehole.

3.3.4.1 Production Rates and Duration

The production life of a well depends on a number of factors, such as the amount of oil or gas in the reservoir, the reservoir pressure, the rate of production, and the economics of well operations, including the price of oil and gas. In hydraulically fractured wells in unconventional reservoirs,

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[1] In some oil production operations, the oil reservoir being tapped may include some natural gas that is extracted along with oil through the production wells. In cases where no facilities or pipelines are in place to handle the natural gas or move it to a market, the gas can be "flared" (ignited and burned at the well site) or vented into the atmosphere.

[2] Sometimes boosting or reinvigorating production in a well is referred to as "well stimulation." In some cases, well stimulation can refer to either the initial well hydraulic fracturing event or the re-fracturing of a well.

initial high production is typically followed by a rapid drop and then a slower decline in production (Patzek et al., 2013). The production phase may be 40 to 60 years in tight gas reservoirs (Ross and King, 2007) or range from 5 to 70 years in a gas- or liquids-rich shale (King and Durham, 2015). However, because the current hydraulic fracturing-led production surge is less than a decade old with limited well production history, there is an incomplete picture of production declines and it is not known how much and for how long these wells will ultimately produce (Patzek et al., 2013).

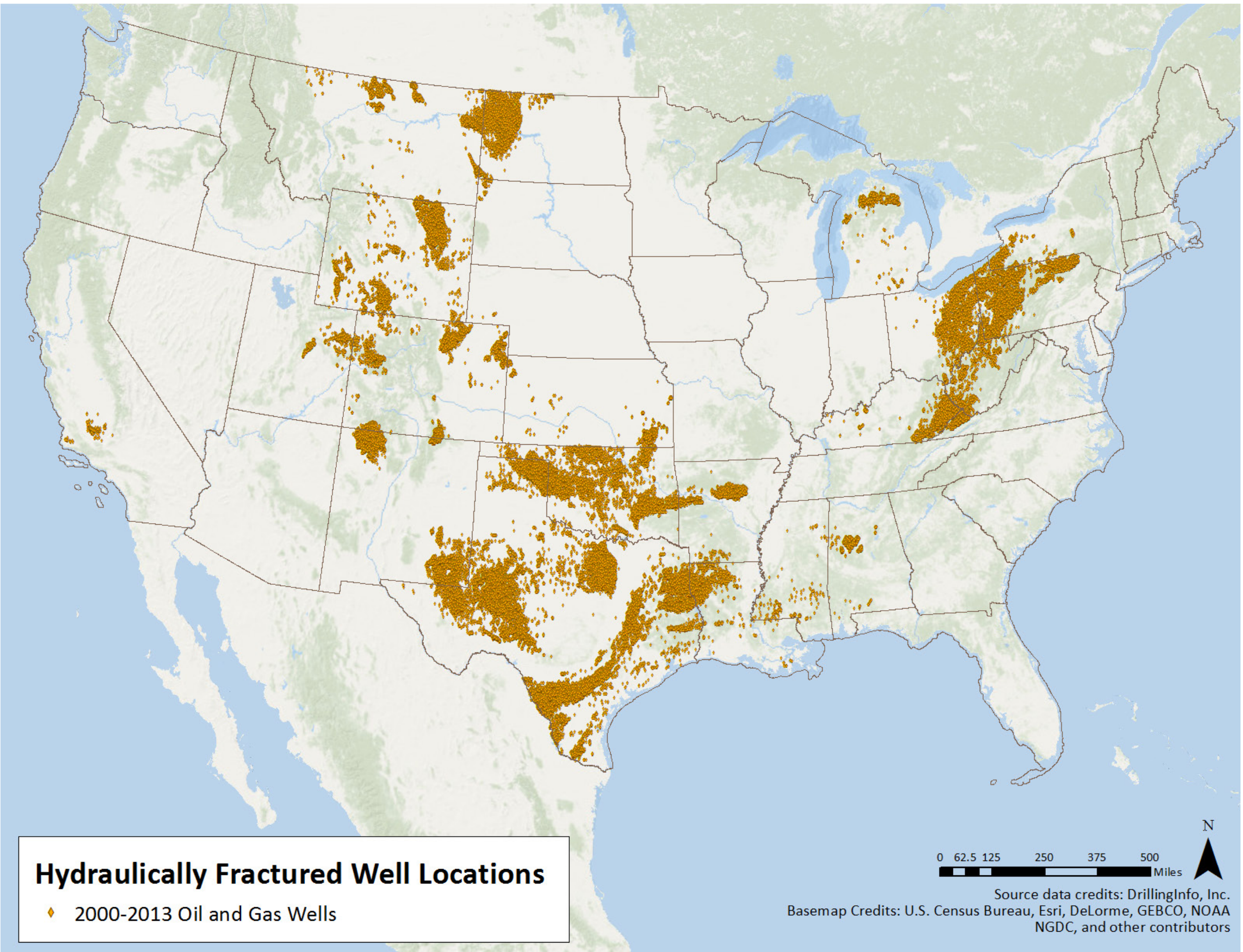
3.3.5 Site and Well Closure

Once a well reaches the end of its useful life, it is removed from production and disconnected from any pipelines that transferred produced oil or gas offsite. The well is then sealed to prevent any movement of fluids inside or along the borehole. This is done by removing the wellhead, cutting the casing off below ground surface, and then sealing portions of the well with one or more cement or mechanical plugs placed permanently in sections of the well. Spaces between plugs may be filled with a thick clay (bentonite) or drilling mud (NPC, 2011b). State regulations identify plugging locations within the borehole and the materials for plugging (Calvert and Smith, 1994). After plugging and cementing, a steel plate is welded on top of the well casing to provide a complete seal (API, 2010). Permanently closing a well like this is called “plugging” a well. Some states require formal notification of the location of these plugged wells. Proper plugging prevents fluids at the surface from seeping down the borehole and migration of fluids through the borehole (NPC, 2011b). See Chapter 6 for more details regarding fluid movement in wells and through the borehole.

To complete site closure, any remaining production-related equipment is removed and the site land cover and topography are restored to pre-well pad conditions to the extent possible. Some surface structures from the former operations may be left in place for subsequent reuse.

3.4 How Widespread is Hydraulic Fracturing?

There is no national database or complete national registry of wells that have been hydraulically fractured. However, hydraulic fracturing activity for oil and gas production in the United States is substantial based on various reports and data sources. According to the Interstate Oil and Gas Compact Commission (IOGCC), close to 1 million wells had been hydraulically fractured in the United States by the early 2000s (IOGCC, 2002). A recent U.S. Geological Survey report estimated approximately 1 million wells with 1.8 million hydraulic fracturing treatment records from 1947 to 2010 (more than one fracturing event, or treatment, can be conducted on a single well) (Gallegos and Varela, 2015). Roughly a third of these 1 million wells were drilled and hydraulically fractured between 2000 and 2013/2014 based on estimates from FracFocus (2016); Baker Hughes (2015); Gallegos et al. (2015); DrillingInfo (2014a); IHS Inc. (2014). This timeframe marks the beginning of modern hydraulic fracturing (refer to Text Box 3-1). Figure 3-15 shows the location of the approximately 275,000 oil and gas wells that were drilled and hydraulically fractured between 2000 and 2013 across the United States based on well and locational data from DrillingInfo (DrillingInfo, 2014a).



Source data credits: DrillingInfo, Inc.
Basemap Credits: U.S. Census Bureau, Esri, DeLorme, GEBCO, NOAA NGDC, and other contributors

Figure 3-15. Locations of the approximately 275,000 wells drilled and hydraulically fractured between 2000 and 2013.
Based on data from the DrillingInfo Database.

The following two satellite photographs show hydraulic fracturing well sites in a regional context. These Landsat images show the locations, number, and density of hydraulic fracturing well sites across landscapes in northwest Louisiana (Figure 3-16) and western Wyoming (Figure 3-17). The orange circles around some of the well sites identify them as operations for which well information was reported to the FracFocus 1.0 registry and included in the EPA FracFocus 1.0 project database (U.S. EPA, 2015c). Note that some of the well sites in the Landsat images, taken in 2014, are for wells that were constructed after the development of the EPA FracFocus 1.0 project database.

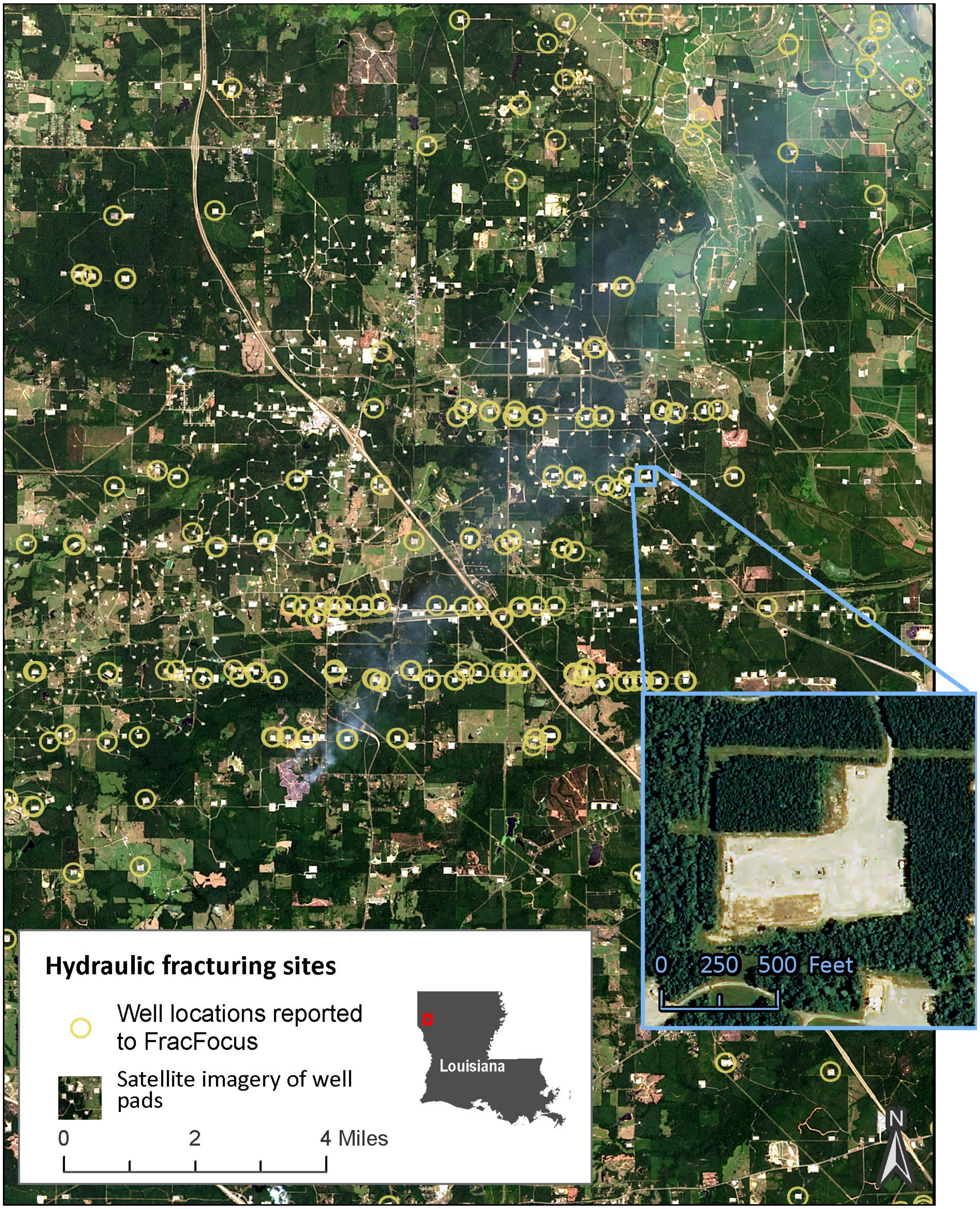


Figure 3-16. Landsat photo showing hydraulic fracturing well sites near Frierson, Louisiana.
Imagery from USGS Earth Resources Observation and Science, Landsat 8 Operational Land Imager (scene LC80250382014232LGN00) captured 8/20/2014, accessed 5/1/2015 from USGS's EarthExplorer (http://earthexplorer.usgs.gov/). Inset imagery from United States Department of Agriculture National Agriculture Imagery Program (entity M 3209351_NE 15_1_20130703_20131107) captured 7/3/2013, accessed 5/1/2015 from USGS's EarthExplorer (http://earthexplorer.usgs.gov/). FracFocus well locations are from the EPA FracFocus 1.0 project database (U.S. EPA, 2015c).

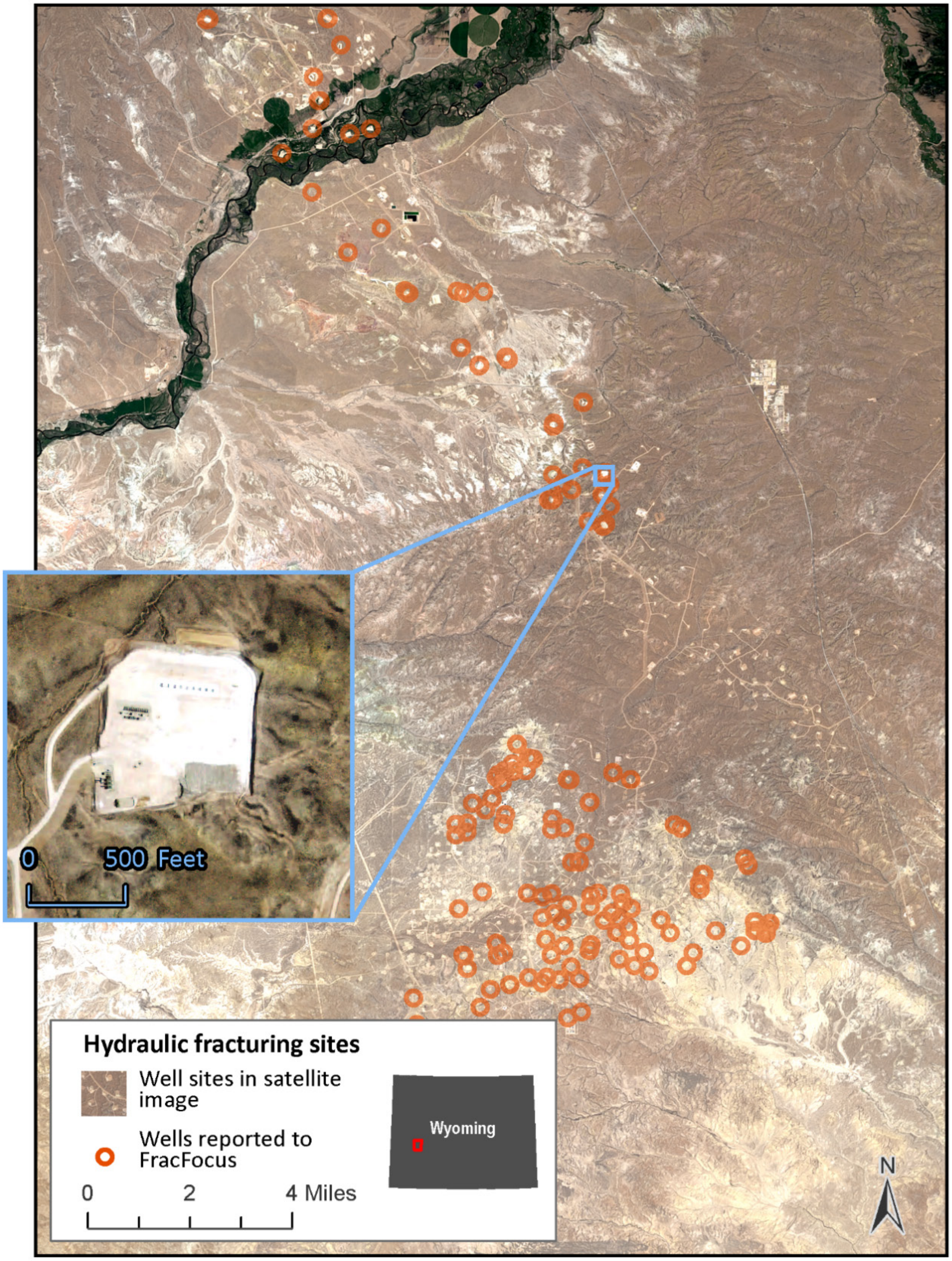


Figure 3-17. Landsat photo showing hydraulic fracturing well sites near Pinedale, Wyoming.
Imagery from USGS Earth Resources Observation and Science, Landsat 8 Operational Land Imager (scene LC80370302014188LGN00) captured 7/7/2014, accessed 5/1/2015 from USGS's EarthExplorer (http://earthexplorer.usgs.gov/). Inset imagery from United States Department of Agriculture National Agriculture Imagery Program (entity M 4210927_NW 12_1_20120623_20121004) captured 6/23/2012, accessed 5/1/2015 from USGS's EarthExplorer (http://earthexplorer.usgs.gov/). FracFocus well locations are from the EPA FracFocus 1.0 project database (U.S. EPA, 2015c).

3.4.1 Number of Wells Fractured per Year

Approximately 25,000 to 30,000 new oil and gas wells were hydraulically fractured each year in the United States between 2011 and 2014 based on data from several commercial data sets and publicly available data from organizations that track drilling and hydraulic fracturing activities (Table 3-1). These estimates do not include fracturing activity in older, existing wells (wells more than one-year old that may or may not have been hydraulically fractured in the past). Likely following the decline in oil prices (starting in about 2014) and gas prices (in about 2008), the estimated number of new hydraulically fractured wells declined to about 20,000 in 2015 according to well information submitted to FracFocus (FracFocus, 2016). Future drilling activity and the annual number of new wells will be influenced by future oil and gas prices.

Table 3-1. Estimated number of new wells hydraulically fractured nationally by year from various sources.

Data from FracFocus (2016); Baker Hughes (2015); DrillingInfo (2014a); IHS Inc. (2014) as provided in Gallegos et al. (2015).

Data Source	2011	2012	2013	2014
IHS	29,650	31,073	29,114	11,980 [a]
DrillingInfo	23,144	22,865	15,903 [b]	NA
Baker Hughes	NA	24,948	25,368	26,548
FracFocus [c]	14,025	22,471	26,400	28,285

[a] The IHS well count for 2014 is incomplete as it represents data only for 8 months (January through August).

[b] The DrillingInfo well count for 2013 is incomplete because some months are missing from some state data sets.

[c] The FracFocus 2011 and 2012 counts are underestimates because reporting well information to FracFocus was voluntary when it began in 2011. The number of states requiring reporting to FracFocus has increased over time. See FracFocus discussion below. The FracFocus well counts for 2011 and 2012 are from the EPA FracFocus 1.0 project database (U.S. EPA, 2015c) developed from the FracFocus national registry, and the FracFocus counts for 2013 and 2014 are from (FracFocus, 2016).

The Information Handling Services (IHS) annual well count estimates presented in Table 3-1 are from IHS data made available in a U.S. Geological Survey publication that evaluated well data from 2000 to 2014 (Gallegos et al., 2015). The IHS data are compiled from a variety of public and private sources and are commercially available from IHS Energy. A well is identified as a hydraulic fracturing well apparently based on well operational information. Gallegos et al. (2015) estimated, based on the IHS data, that approximately 371,000 wells were hydraulically fractured between January 2000 and August 2014.

DrillingInfo, another commercial database, is developed using data obtained from individual state oil and gas agencies (DrillingInfo, 2014a). Because DrillingInfo data does not identify whether a well has been hydraulically fractured, EPA relied on information about well orientation and the oil- or gas-producing rock formation type to infer which wells were likely hydraulically fractured. This is a similar approach to that used by the EPA for estimating oil and gas well counts for its greenhouse gas inventory work (U.S. EPA, 2013c).[1] Using this approach, we estimate from the DrillingInfo data the annual numbers presented in Table 3-1 above and also estimate that a total of approximately 275,000 oil and gas wells were drilled and hydraulically fractured between 2000 and 2013.[2]

Well counts tracked by Baker Hughes provide another estimate of new wells fractured annually. This field service company compiles new-well information based on its extensive field work in oil and gas producing areas and through state agencies. Baker Hughes started compiling this publicly available well count data in 2012, but stopped in 2014. The well count data are categorized into 14 basins containing reservoirs that are mostly unconventional (and, therefore, likely hydraulically fractured wells) and one "other" category (Baker Hughes, 2015). The well count estimates in the table above are for the 14 basins and, therefore, are considered estimates of new wells hydraulically fractured in each year.

FracFocus is a national registry for operators of hydraulically fractured oil and gas wells to report information about well location and depth, date of operations, and water and chemical use. The registry, publicly accessible online (www.fracfocus.org), was developed by the Groundwater Protection Council and the Interstate Oil and Gas Compact Commission. Submission of information to FracFocus was initially voluntary (starting in January 2011), but many states now require reporting of hydraulic fracturing well activities to FracFocus. As of May 2015, 23 states required reporting to FracFocus (Konschnik and Dayalu, 2016). The annual well counts in the table above are from the EPA FracFocus 1.0 project database for 2011 and 2012 (U.S. EPA, 2015c) and from the FracFocus 2016 Quarterly Report for 2013 and 2014 (FracFocus, 2016). The well counts in the earliest years are underestimates because not all states required oil and gas well operators to submit hydraulic fracturing data to FracFocus.[3] The FracFocus registry has undergone several updates since its launch in 2011. For more details on FracFocus, see FracFocus (2016), Konschnik and Dayalu (2016), U.S. EPA (2015a), U.S. EPA (2015c), and DOE (2014a).[4]

In addition to these new well counts, some portion of existing wells are also re-fractured. Several studies indicate that re-fracturing occurs in less than 2% of wells. Shires and Lev-On (2012)

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[1] Using the DrillingInfo data, EPA assumed that all horizontal wells were hydraulically fractured in the year they started producing and assumed that all wells within a shale, coalbed, or low-permeability formation, regardless of well orientation, were hydraulically fractured in the year they started producing. More details are provided in (U.S. EPA, 2013c). Not all coalbed methane wells are hydraulically fractured, but coalbed methane wells represent gas production that sometimes uses hydraulic fracturing. Given the small percent of coalbed methane wells relative to all hydraulically fractured wells and the lack of data that distinguishes whether or not coalbed wells are hydraulically fractured, EPA included coalbed production wells into all counts of wells that are hydraulically fractured.

[2] The different well count totals from IHS and DrillingInfo are likely due to different sources of data, different approaches for defining hydraulically fractured wells in those sources, and somewhat different timeframes. The higher IHS count likely includes hydraulically fractured vertical and deviated wells in conventional reservoirs (the DrillingInfo estimate does not) and covers a time period that is a year or more longer.

[3] We compared state records of hydraulic fracturing wells in North Dakota, Pennsylvania, and West Virginia in 2011 and 2012 to those reported to FracFocus during those same years and found the FracFocus wells counts underestimated the number of fracturing jobs in those states by approximately 30% on average. See Chapter 4, Text Box 4-1.

[4] Analyses of the FracFocus data based on the EPA FracFocus 1.0 project database (U.S. EPA, 2015c) are presented in Chapter 4 regarding water volumes and in Chapter 5 regarding chemical use.

suggested that the rate of re-fracturing in natural gas wells is about 1.6% whereas analysis for the EPA's 2012 Oil and Gas Sector New Source Performance Standards indicated a re-fracture rate of 1% for gas wells (U.S. EPA, 2012f). The percentage of hydraulically fractured producing gas wells that were re-fractured in a given year ranged from 0.3% to 1% across the 1990-2013 period according to the EPA's Inventory of U.S. Greenhouse Gas Emissions and Sinks (U.S. EPA, 2015h).

The above rates are calculated by comparing the number of re-fractured wells in a single year to all hydraulically fractured wells cumulatively over a multi-year time period. However, when calculating the rates of wells that conduct re-fracturing in a given year compared to the total number of wells in that same year, the re-fracturing rate is higher. Data provided to the EPA's Greenhouse Gas Reporting Program (GHGRP) for 2011 to 2013 suggest that 9-14% of the gas wells hydraulically fractured *in each year* were pre-existing wells undergoing re-fracturing (U.S. EPA, 2014b).[1] Another rate presenting a somewhat different measure (estimated by an EPA review of well records from 2009 to 2010) found that 16% of the surveyed wells had been re-fractured at least once (U.S. EPA, 2016c).[2]

In summary, a complete count of the number of hydraulically fractured wells in the United States is hampered by a lack of a definitive and readily accessible source of information, and the fact that existing well and drilling databases and registries track information differently and therefore are not entirely comparable. There is also uncertainty about whether existing information sources are representative of the nation (or parts of the nation), whether they include data for all production well types, and to what degree they include activities in both conventional and unconventional reservoirs. Taking these limitations into account, however, it is reasonable to conclude that between approximately 25,000 and 30,000 new wells (and, likely, additional pre-existing wells) were hydraulically fractured each year in the United States from about 2011 to 2014, and approximately 20,000 wells were hydraulically fractured in 2015.

3.4.2 Hydraulic Fracturing Rates

Estimates of hydraulic fracturing rates, or the proportion of all oil and gas production wells that are hydraulically fractured, also indicate widespread use of the practice. Data from IHS Inc. (2014) indicate that approximately 62% of all new oil and gas wells in 2013 were hydraulically fractured. Data from DrillingInfo (2014a), indicate a similar rate of 64% of all new production wells in 2012. Estimates of hydraulic fracturing rates reported by states in response to an IOGCC survey tended to be considerably higher. Of eleven oil and gas producing states that responded to the survey, ten (Arkansas, Colorado, New Mexico, North Dakota, Ohio, Oklahoma, Pennsylvania, Texas, Utah, and West Virginia) estimated that 78% to 99% of new wells in their states were hydraulically fractured in 2012. Louisiana was the one exception, reporting a fracturing rate of 3.9% (IOGCC, 2015).

Hydraulic fracturing may be more prevalent in gas wells than in oil wells. A 2010 to 2011 survey of 20 natural gas production companies reported that 94% of the gas wells that they operated were

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[1] The GHGRP reporting category that covers re-fracturing is "workovers with hydraulic fracturing." This re-fracturing data is for gas wells only (and does not include oil wells).

[2] This EPA report is based on a statistical survey so there is some uncertainty and a margin of error regarding the 16% re-fracturing rate. This rate includes both oil and gas wells. For more details, see Chapter 6 and U.S. EPA (2016).

fractured (Shires and Lev-On, 2012), a rate that is higher than many of the reported statistics for oil and gas together (presented in the previous paragraph). Recent EIA data on the portion of oil and gas production attributable to hydraulically fractured wells also suggest possibly higher rates of hydraulic fracturing for gas. In 2015, production from hydraulically fractured wells accounted for an estimated 67% of natural gas production (EIA, 2016d) and 51% of oil production (EIA, 2016c).

3.5 Trends and Outlook for the Future

Future oil and gas drilling and production activities, including hydraulic fracturing, will be primarily affected by the cost of well operation (partly driven by technology) and the price of oil and gas. Scenarios of increasing, stable, and decreasing hydraulic fracturing activity all appear to be possible (Weijermars, 2014). The section below provides some discussion on trends and future prospects for production quantities and locations.

Fossil fuels–oil, gas, and coal–have been dominant energy sources in the United States over the last half century (Figure 3-18). The relative importance of oil, gas, and coal has changed several times, with a significant recent shift starting in the mid-2000s as hydraulic fracturing transformed oil and gas production. Coal, the leading fossil fuel from the mid-1980s to the mid-2000s, has experienced a large decrease in production, dropping from approximately 33% of U.S. energy production in 2007 to approximately 20% (about 18 quadrillion Btus) by the end of 2015 (EIA, 2016a).[1] In contrast, natural gas production has risen to unprecedented levels, and oil production has resurged to levels not seen since the 1980s. Oil accounted for 15% of U.S. energy production in 2007 and increased to approximately 23% (about 20 quadrillion Btus) by the end of 2015, and natural gas as a portion of domestic energy production went from 31% to 37% (about 33 quadrillion Btus) (EIA, 2016a).

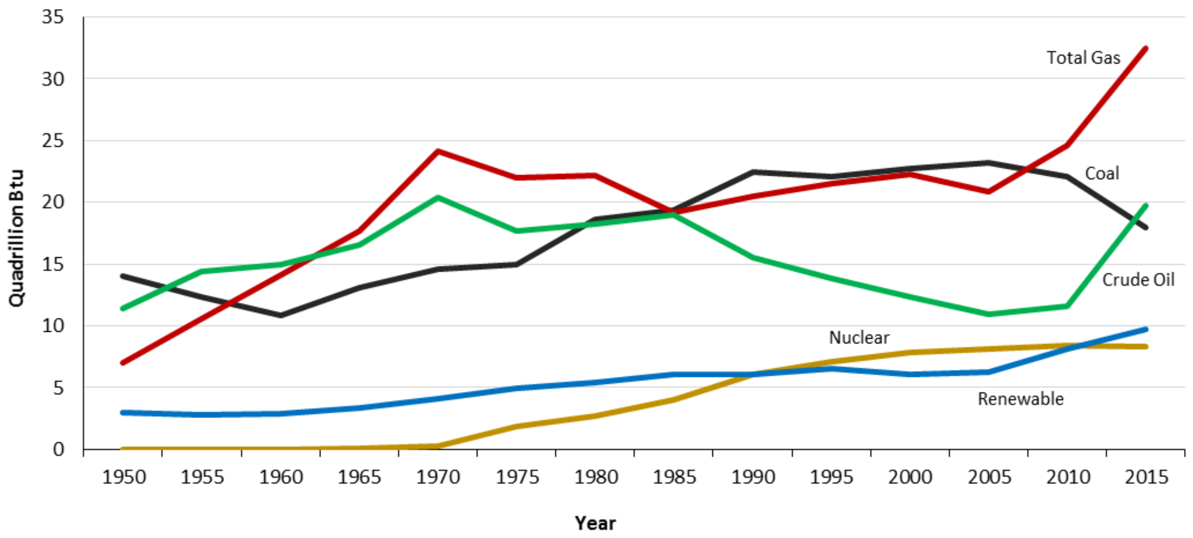

Figure 3-18. Primary U.S. energy production by source, 1950 to 2015.
Source: EIA (2016a).

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[1] A Btu, or British thermal unit, is a measure of the heat (or energy) content of fuels. At the scale of national U.S. production, the graph in Figure 3-18 presents Btus in quadrillions, or a thousand million million (which is 10^{15}, or a 1 with 15 zeros).

The surge in both oil and gas production started in the mid- to late-2000s and was driven by market forces (supply and demand) and the related developments in and expanded use of hydraulic fracturing. Figure 3-19 focuses on the years 2000 to 2015 and presents data showing the steady increase in the portion of oil and gas production coming from hydraulically fractured wells. Oil and gas production associated with hydraulic fracturing was insignificant in 2000, but by 2015 it accounted for an estimated 51% of US oil production and 67% of US gas production (Figure 3-19).

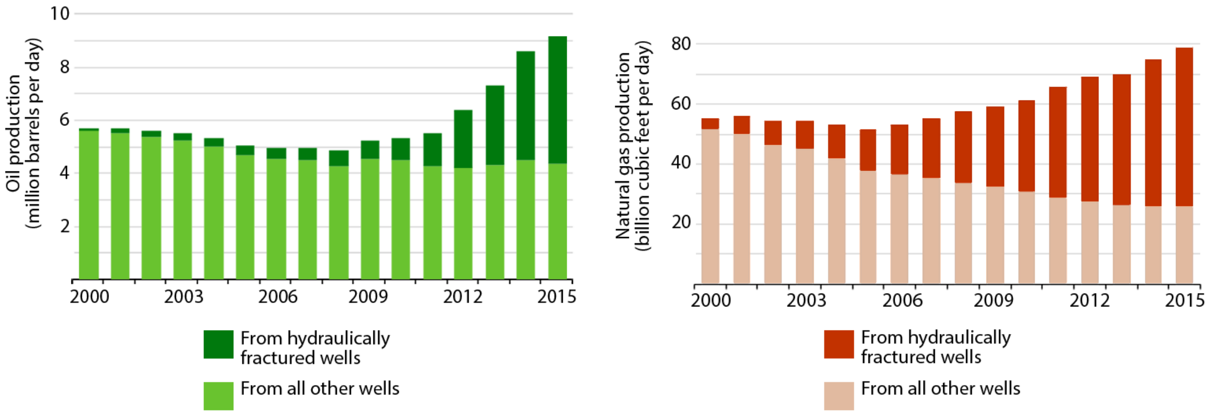

Figure 3-19. U.S. production of oil (left) and gas (right) from hydraulically fractured wells from 2000 to 2015.

Source: EIA (2016c) (oil) and EIA (2016d) (gas), based on IHS Global Insight and DrillingInfo, Inc.

Hydraulic fracturing activities are concentrated geographically in the United States. In 2011 and 2012 about half of hydraulic fracturing wells were located in Texas with another quarter located in the four states of Colorado, Pennsylvania, North Dakota, and Oklahoma (U.S. EPA, 2015c). The maps in Figure 3-20 show changes starting in 2000 in the national geography of oil and gas production through the increased use of horizontal drilling, which frequently is associated with hydraulic fracturing. Some traditional oil- and gas-producing parts of the country, such as Texas, have seen an expansion of historical production activity as a result of modern hydraulic fracturing. Pennsylvania, a leading oil- and gas-producing state a century ago, has seen a resurgence in oil and gas activity. Other states that experienced a steep increase in production, such as North Dakota, Arkansas, and Montana, have historically produced less oil and gas.

3.5.1 Natural Gas

Drilling of new natural gas wells declined markedly as natural gas prices fell in 2008 (Figure 3-21). Nevertheless, over the coming decades natural gas production is expected to increase and that increase will be associated significantly with wells that are hydraulically fractured. Projections by EIA indicate that gas production from shale (and tight oil reservoirs) will almost double from 2015 to 2040 when it will constitute nearly 70% of total natural gas production (EIA, 2016d). Slight increases are projected for production from tight gas reservoirs and coalbed methane production is expected to continue fairly steady at relatively low levels (EIA, 2016a) (Figure 3-22). These projections are dependent on estimated future prices of natural gas and other assumptions, and

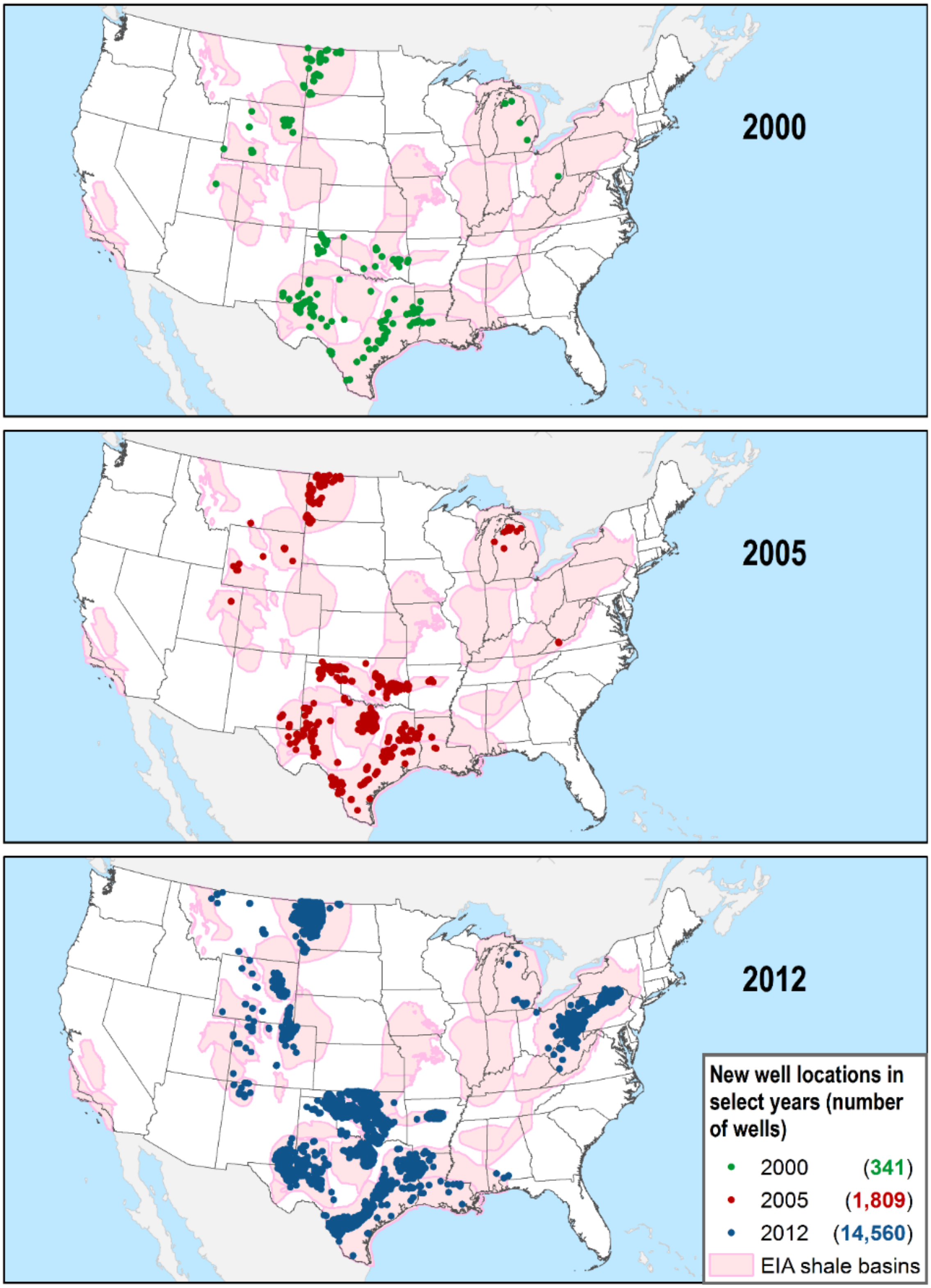

Figure 3-20. Location of horizontal wells that began producing oil or natural gas in 2000, 2005, and 2012.

Based on data from DrillingInfo (2014a).

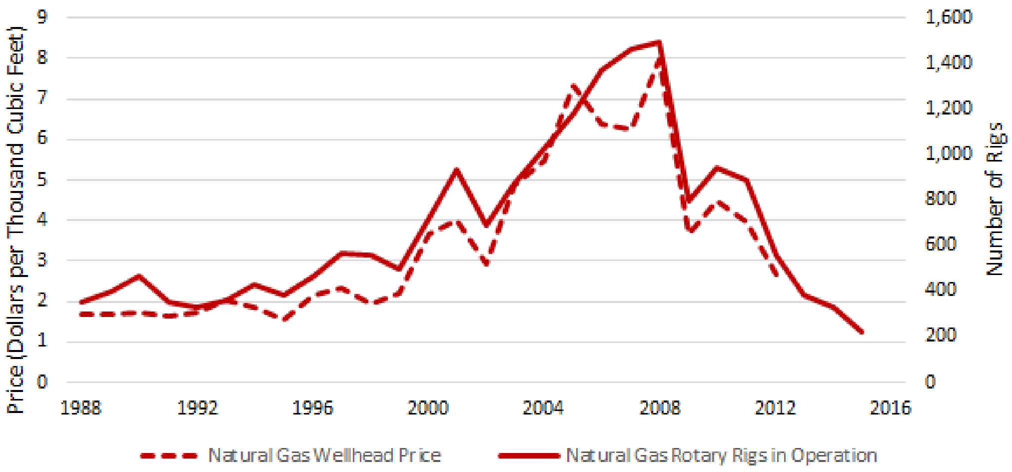

Figure 3-21. Natural gas prices and drilling activity, United States, 1988 to 2015.
Sources: EIA (2016b) and EIA (2016f).

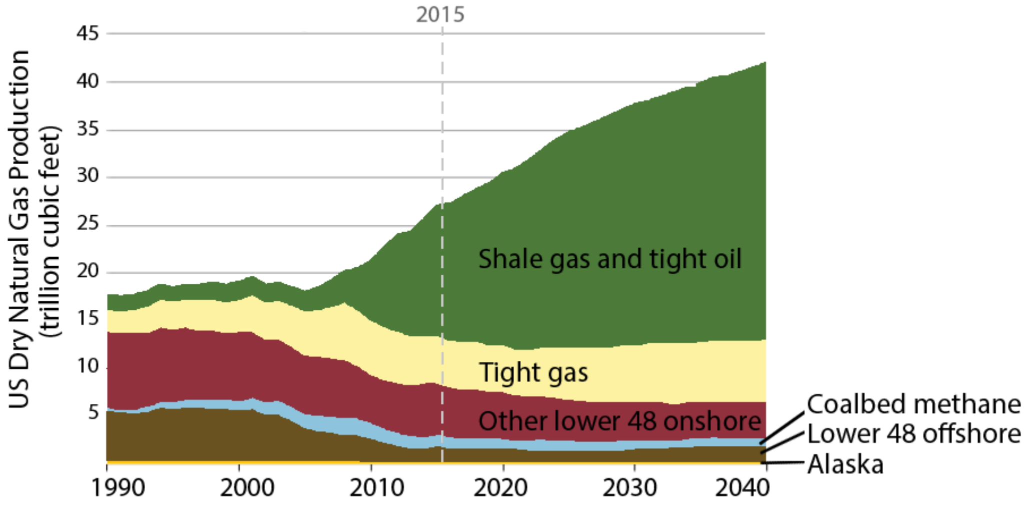

Figure 3-22. Historic and projected natural gas production by source (trillion cubic feet).
Source: EIA (2016a).

the details are subject to change. Nonetheless, a continuing increase in production is generally suggested and the locations of historical production identified in Figure 3-23 indicate areas of continued and future hydraulic fracturing activities for natural gas production.

The geographic concentration and trends in shale gas production by play (and identified by state) are shown in Figure 3-23. The Barnett Shale, where the modern hydraulic fracturing boom started, was the largest producer of shale gas until about 2010, producing 1.5 trillion cubic feet (tcf) (42.5 billion cubic meters [bcm]) that year and remains a significant producer. In 2009, the Marcellus and Haynesville plays produced 0.12 and 0.43 tcf (3.4 and 12.2 bcm), respectively, but by 2011, production from the Haynesville play surpassed that in the Barnett play, and by 2013 the Marcellus Shale surpassed both the Barnett and the Haynesville to become the play with the most production.

By 2014, the Marcellus play was producing 4.8 tcf (135.9 bcm) of gas annually, with the Eagle Ford, Haynesville, and Barnett each producing roughly 1.5 tcf (42.5 bcm). Estimates of technically recoverable resources, a general indicator of potential future production, are noted for the Marcellus (about 150 tcf [4.25 trillion cubic meters]), Haynesville (73 tcf [2.07 trillion cubic meters]), Eagle Ford in Texas (55 tcf [1.56 trillion cubic meters]), and Utica in Ohio, Pennsylvania, and West Virginia (55 tcf [1.56 trillion cubic meters]). This suggests that these four plays will be active contributors of shale gas production for the foreseeable future (EIA, 2013).[1] Other gas plays with significant resources include the Fayetteville in Arkansas, the Woodford in Oklahoma, and the Mancos in Colorado.

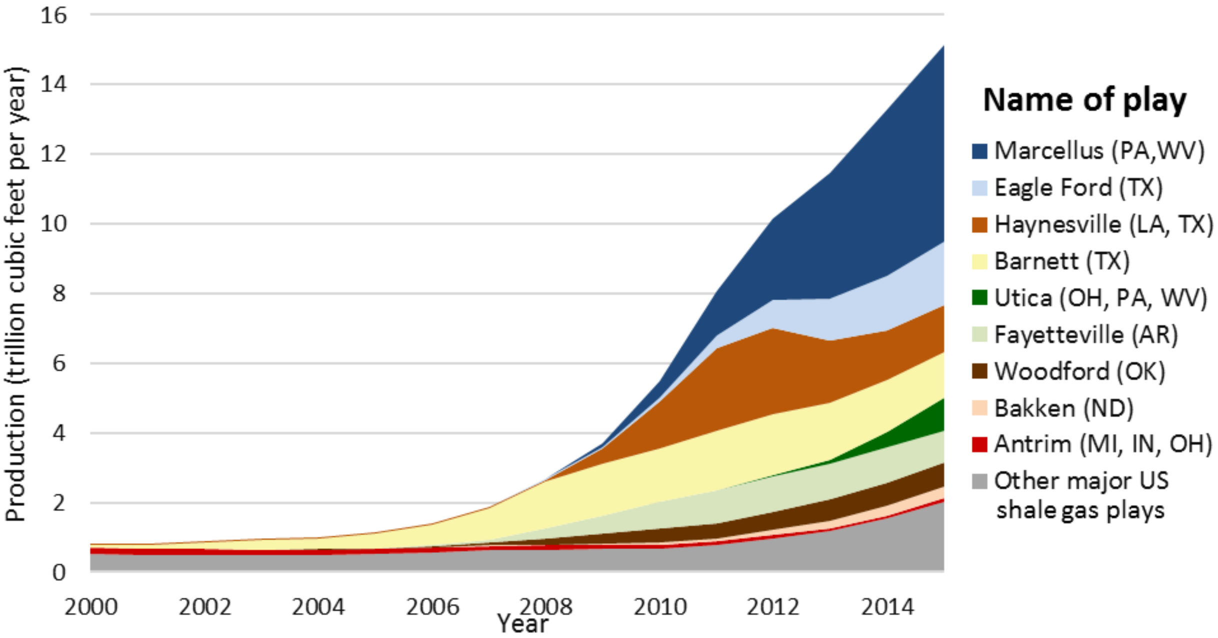

Figure 3-23. Production from U.S. shale gas plays, 2000-2014.

Source: EIA (2016g). The graph shows shale plays in the same vertical order as the legend.

3.5.2 Oil

While prices and drilling activity for natural gas were peaking between 2005 and 2008 and then falling (Figure 3-21), prices and drilling for oil were rising. These peaked between 2011 and 2014, and then rapidly declined as well (Figure 3-24). EIA projections to 2040 indicate a continued growth in total U.S. oil production, although the projected growth is not as fast or as large as that projected for natural gas. Tight oil production, presumably from hydraulically fractured wells, is expected to account for much of the projected growth (Figure 3-25); by 2040, tight oil is expected to account for nearly 65% of all U.S. crude oil production (EIA, 2016d). These production projections are dependent on estimated future prices of oil and other assumptions and, therefore, will likely be revised over time as energy markets and prices change. Currently, these projections

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[1] Technically recoverable resources are the volumes of oil or natural gas that could be produced with current technology, regardless of oil and natural gas prices and production costs (EIA, 2013).

indicate a continuing, but lower rate of growth (as compared to the period from about 2005 to 2015). The locations of historical production identified in Figure 3-26 indicate areas of continued and future hydraulic fracturing activities for oil.

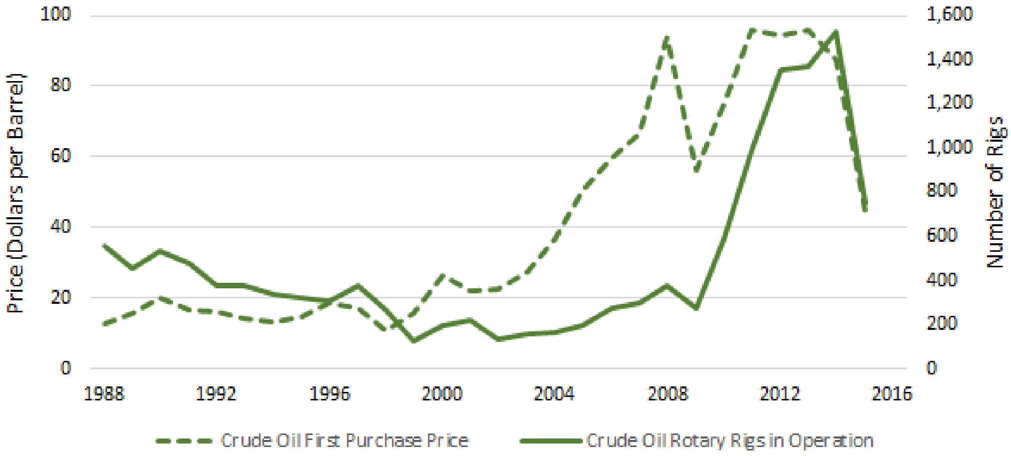

Figure 3-24. Crude oil prices and drilling activity, United States, 1988 to 2015.
Sources: EIA (2016b) and EIA (2016e).

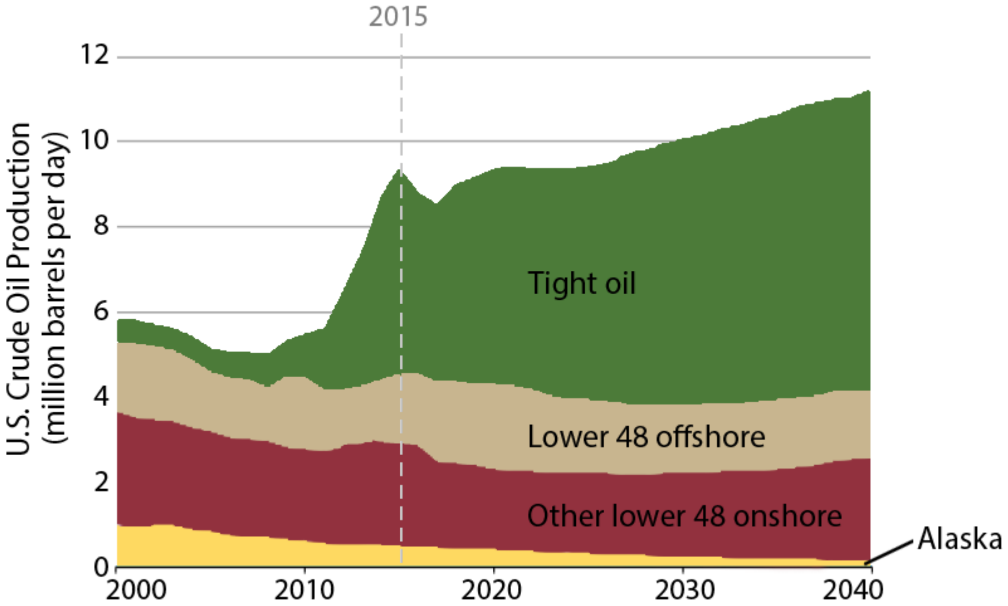

Figure 3-25. Historic and projected oil production by source (million barrels per day).
Source: EIA (2016a).

The geographic concentration and trends in tight oil production by play (and identified by state) are shown in Figure 3-26. Early tight oil production in the United States was centered in the Permian Basin in west Texas and New Mexico, at plays that included the Spraberry and the Bonespring. After 2009, the Bakken play (centered in western North Dakota) and the Eagle Ford play (in Texas) emerged as the largest-producing tight oil plays. Oil production in the Bakken increased from 99 million bbls (16,000 million L) in 2009 to 394 million bbls (63,600 million L) in 2014 (EIA, 2016g). Production from Eagle Ford increased from 12 million bbls (2,000 million L) in 2009 to 498 million bbls (79,100 million L) in 2014 (EIA, 2016g).

General estimates of potential resources suggest that future tight oil production in the United States will continue to be led by Texas and North Dakota. Technical recoverable resources are estimated at about 23 billion bbls (3,600 billion L) for the Bakken, about 21 billion bbls (3,300 billion L) for the Permian Basin, and about 10 billion bbls (1,600 billion L) for Eagle Ford (EIA, 2015). Other plays with significant estimated resources include the Niobrara-Codell in Colorado and Wyoming and the Granite Wash in Oklahoma and Texas (EIA, 2012).

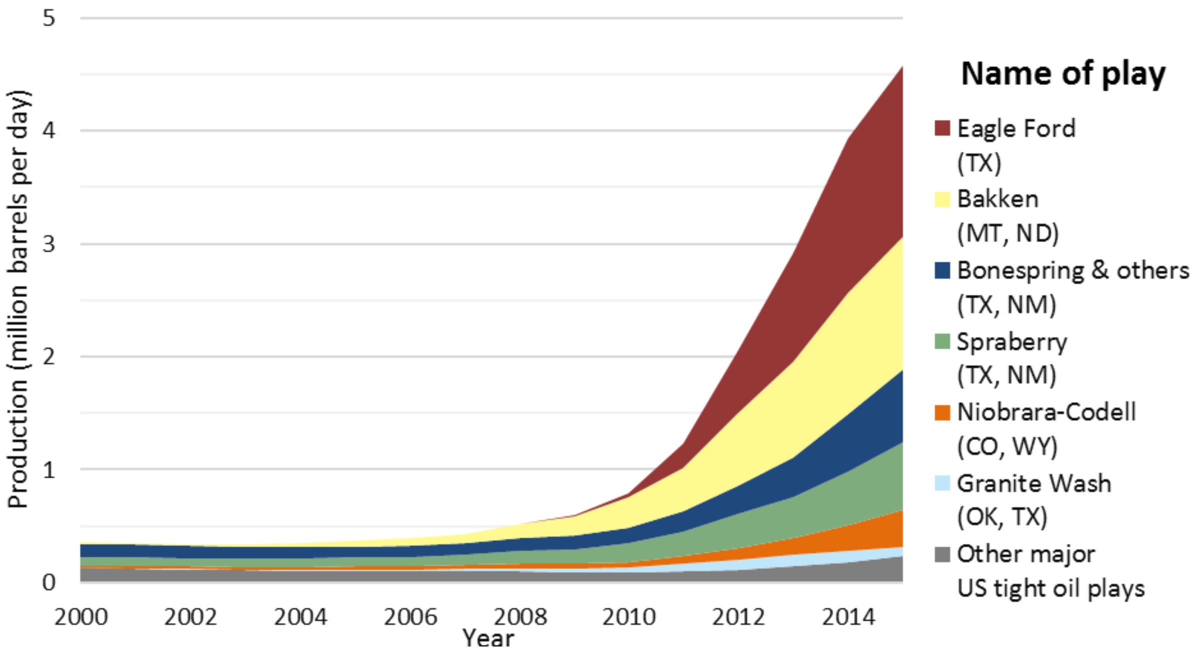

Figure 3-26. Production from U.S. tight oil plays, 2000-2014.

Source: EIA (2016g). The graph shows tight oil plays in the same vertical order as the legend.

3.6 Conclusions

Hydraulic fracturing is the injection of hydraulic fracturing fluids through the production well and into the subsurface oil or gas reservoir under pressures great enough to fracture the reservoir rock. The fractures allow for increased flow of oil and/or gas from the reservoir into the well. Water used in the hydraulic fracturing fluid is typically obtained from sources in the vicinity of the well. Water that naturally occurs in the oil and gas reservoir rocks often flows into the production well and through the well to the surface as a byproduct of the oil and gas production process. This byproduct water, commonly referred to as produced water, requires handling and management.

Many well site and operational activities are conducted to prepare a site and well for hydraulic fracturing and oil and/or gas production. The actual hydraulic fracturing event is of relatively short duration, usually several weeks or less, but it is also a phase of work with numerous complex operational activities to handle, mix, and inject the hydraulic fracturing fluid under pressure through the production well. The injected hydraulic fracturing fluid typically contains mostly water, includes a proppant (commonly sand) which ensures that the fractures remain propped open after injection, and contains less than two percent additives (chemicals) that improve the fluid properties for fracturing. These small percentages of additives, given the total volume of hydraulic fracturing fluids, mean that a typical hydraulic fracturing job can use tens of thousands of gallons of chemicals.

Since about 2005, the combination of hydraulic fracturing and directional drilling pioneered in the Barnett Shale in Texas has become widespread in the oil and gas industry. Hydraulic fracturing combined with directional drilling is now a standard industry practice. It has significantly contributed to the surge in United States oil and gas production, and accounted for slightly more than 50% of oil production and nearly 70% of gas production in 2015. Hydraulic fracturing has resulted in expanded production from unconventional shale and so-called tight oil or gas reservoirs that had previously been largely unused. This hydraulic fracturing-based production activity is geographically concentrated. About three-quarters of new hydraulic fracturing wells in 2011 and 2012 were located in five states (Texas, Colorado, Pennsylvania, North Dakota, and Oklahoma) with about half of all wells located in Texas.

There is no national database or complete national registry of wells that have been hydraulically fractured in the United States. Based on the data available from various commercial and public sources, we estimate that 25,000 to 30,000 new wells were drilled and hydraulically fractured in the United States annually between 2011 and 2014. In addition to these new wells, some existing wells not previously fractured were fractured, and some that had been fractured in the past were re-fractured. New drilling of hydraulic fracturing wells, influenced by oil and gas prices, peaked in the United States between 2005 and 2008 for gas and between 2011 and 2014 for oil. Following price declines, the number of new hydraulically fractured wells in 2015 was about 20,000. Future drilling and production will be influenced by future gas and oil prices. Despite recent declines in prices and new drilling, oil and gas production in the United States continues at historically high levels with projections of continued growth in the medium and long term led by hydraulic fracturing-based production from unconventional reservoirs.

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Chapter 4. Water Acquisition

Abstract

In this chapter, the EPA examined the potential impacts of water withdrawals for hydraulic fracturing on drinking water resource quantity and quality, and identified common factors affecting the frequency and severity of impacts. Groundwater and surface water resources used for hydraulic fracturing also currently serve or in the future may serve as drinking water sources, and water withdrawals for hydraulic fracturing can affect the quantity or quality of the remaining drinking water resource.

Hydraulic fracturing used a median of 1.5 million gallons (5.7 million liters) of water per well from 2011 through early 2013. Surface water supplies almost all water used for hydraulic fracturing in the eastern United States, whereas surface water or groundwater is used in the West. Reuse of hydraulic fracturing wastewater as a percentage of injected volume is generally low, with a median of 5% according to an EPA literature survey. Greater reuse occurs where disposal options are limited (e.g., the Marcellus Shale in Pennsylvania) and not necessarily where water availability is lowest.

Hydraulic fracturing generally uses and consumes a relatively small percentage of water when compared to total water use, water consumption, and water availability at the national, state, and county scale. There are exceptions, however. For example, EPA's analysis shows that counties in southern and western Texas have relatively high hydraulic fracturing water withdrawals and low water availability. These findings indicate where impacts are more likely to occur or be severe, but local information (i.e., at the scale of the drinking water resource) is needed to determine whether potential impacts have been realized. In some example cases (e.g., the Eagle Ford Shale in Texas, the Haynesville Shale in Louisiana), local impacts to drinking water resource quantity have occurred in areas with increased hydraulic fracturing activity. In these instances, hydraulic fracturing water withdrawals contributed to local impacts along with other water users and the lack of precipitation.

Drought or seasonal times of low water availability can increase the frequency and severity of impacts, while water management practices such as the establishment of low-flow criteria (termed passby flows), shifting from fresh to brackish water sources, or increasing the reuse of wastewater for hydraulic fracturing can help protect drinking water resources.

Uncertainty about the extent of impacts on drinking water resources stems from the lack of available data at the local scale. The EPA could assess the potential for impacts at the county scale, but often could not determine whether impacts occurred at drinking water withdrawal locations.

Overall, hydraulic fracturing uses and consumes a relatively small percentage of water at the county scale, but not always, and impacts can still occur depending on the local balance between withdrawals and availability. Regional or local-scale factors, such as drought or water management, can modify this balance to increase or decrease the frequency or severity of impacts.

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4. Water Acquisition

4.1 Introduction

Water is a crucial component of nearly all hydraulic fracturing operations, generally making up 90 – 97% of the total fluid volume injected into a well (Chapter 5).[1] Ground- and surface water resources that serve as sources of water for hydraulic fracturing also provide water for public water supplies or private drinking water wells. For this reason, water withdrawals for hydraulic fracturing can impact drinking water resources by changing the quantity or quality of the remaining resource.[2] In this chapter, we consider potential impacts of water acquisition for hydraulic fracturing on both drinking water resource quantity and quality, and, where possible, identify factors that affect the frequency or severity of impacts.[3]

We define impacts broadly in this assessment to include any change in the quantity or quality of drinking water resources; see Chapter 1 for more information. This definition applies reasonably well to the subsequent chapters (Chapters 5-8); however, by this definition, even the smallest water withdrawals would be considered impacts. Recognizing this, we focus on a smaller subset of potential impacts, specifically water withdrawals that have the potential to limit the availability of drinking water or alter its quality. Whether water withdrawals have this potential depends primarily on the balance between water use and availability at the local scale.[4,5] By “local” in this chapter, we refer to the scale at which impacts to drinking water resources are expected to occur. This usually means a given surface water (e.g., river or stream) or groundwater resource (i.e., aquifer), or a given watershed where we have detailed information about local water dynamics (e.g., case studies). We note the scale at which data are available and findings are reported.

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[1] This range is based on multiple sources that either present hydraulic fracturing fluid composition as a function of volume (e.g., 95% of the total volume injected) or as a function of mass (e.g., 90% of the total mass injected). See Chapter 5 for additional information.

[2] Surface water withdrawals can affect water quality by altering in-stream flow and decreasing the dilution of pollutants or changing water chemistry (Section 4.5.3). Groundwater withdrawals may alter water quality by inducing vertical mixing of fresh groundwater with contaminated water from the land surface or underlying formations, or by promoting changes in reduction-oxidation conditions and mobilizing chemicals from geologic sources (Section 4.5.1).

[3] Water acquired for use in other oil and gas development steps besides hydraulic fracturing is beyond the scope of this chapter, including the water used in well drilling and well pad preparation and water removal for the production of coalbed methane. Furthermore, water released to the atmosphere via gas combustion is also outside the scope of this chapter.

[4] Throughout this chapter we use the terms “water use” and “water withdrawals” interchangeably to refer to the water that is acquired for hydraulic fracturing operations.

[5] There is no standard definition for water availability, and it has not been assessed recently at the national scale (U.S. GAO, 2014). Instead, a number of water availability indicators have been suggested (e.g., Roy et al., 2005). Here, availability is most often used to qualitatively refer to the amount of a location’s water that could, currently or in the future, serve as a source of drinking water (U.S. GAO, 2014), which is a function of water inputs to a hydrologic system (e.g., rain, snowmelt, groundwater recharge) and water outputs from that system occurring either naturally or through competing demands of users. Where specific numbers are presented, we note the specific water availability indicator used.

A variety of factors can modify the balance between water use and availability. For example, multiple hydraulically fractured wells require more water than a single well, making it critical to assess the cumulative effects of multiple wells over a given area or time period. Furthermore, the combined effects of multiple water users pumping from the same aquifer can compound stress on already declining groundwater supplies. Alternatively, locally high rates of hydraulic fracturing wastewater reuse may help offset the need for fresh water withdrawals. These and other factors are discussed throughout the chapter.

This chapter proceeds roughly in two halves. In the first half, we address water use and consumption by hydraulic fracturing.[1] We provide an overview of the types of water used for hydraulic fracturing (Section 4.2); the amount of water used per well (Section 4.3); and then estimates of hydraulic fracturing water use and consumption at the national, state, and county scale, both in absolute terms and relative to total water use and consumption (Section 4.4). Although most available data and literature pertain to water use, we discuss water consumption because hydraulic fracturing consumes a substantial proportion of the water it uses, so that a proportion of the water is lost from the local hydrologic cycle. See Section 4.4 and Chapter 2 for more information.

In the second half of the chapter, we assess the potential for impacts by location in certain states (and major oil and gas regions within select states) where hydraulic fracturing currently occurs (Section 4.5; Appendix B.2). For each state and region, we discuss the water used and consumed by hydraulic fracturing, and then compare it to water availability. We do this using several lines of evidence: (1) literature information (both quantitative and qualitative) on state and regional hydraulic fracturing water use and availability; (2) comparisons between our county level estimates of hydraulic fracturing water use and an index of water availability; and (3) local case studies from the Eagle Ford play in Texas, the Upper Colorado River Basin in Colorado, and the Susquehanna River Basin in Pennsylvania.[2] The use of case studies provides insight into the local, sub-county scale, where impacts are most likely to be observed in both space and time.

Overall, this chapter provides a national assessment of where potential impacts to drinking water quantity and quality are most likely due to water acquisition for hydraulic fracturing. We utilize case studies where data are available to understand local dynamics and whether impacts are indeed realized. In the absence of case studies, we use county level data to assess where potential impacts are most likely. Finally, we identify the common factors affecting the frequency and severity of impacts. We provide a synthesis of our findings in Section 4.6.

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[1] We refer specifically to "water consumption" when data are available or it is explicitly noted in the scientific literature. However, when specific information is not available, we use "water use" or "water withdrawals" as general terms to refer to both water use and consumption by hydraulic fracturing.

[2] The EPA's *Review of Well Operator Files for Hydraulically Fractured Oil and Gas Production Wells* (i.e., the "Well File Review;" see Text Box 6-1) was originally planned to inform the water acquisition stage of the hydraulic fracturing water cycle, but did not yield any useable information on this topic, and is therefore not cited as a source of information in this chapter. Although information in some well files was of good quality, the well files generally contained insufficient or inconsistent information on nearby surface water and groundwater quality, injected water volumes, and wastewater volumes and disposition; therefore, these data were not summarized (U.S. EPA, 2015n).

4.2 Types of Water Used

The three major sources of water for hydraulic fracturing are surface water (i.e., rivers, streams, lakes, and reservoirs), groundwater, and reused hydraulic fracturing wastewater.[1,2,3] These sources often vary in their initial water quality and in how they are provisioned to hydraulic fracturing operations. In this section, we provide an overview of the sources (Section 4.2.1), water quality (Section 4.2.2), and provisioning of water (Section 4.2.3) required for hydraulic fracturing. Detailed information on the types of water used by state and locality is presented in Section 4.5.

4.2.1 Source

Whether water used in hydraulic fracturing originates from surface water or groundwater resources is largely determined by the type of locally available water sources. Water transportation costs can be high, so the industry tends to acquire water from nearby sources if available (Nicot et al., 2014; Mitchell et al., 2013a; Kargbo et al., 2010). Surface water supplies most of the water for hydraulic fracturing in the eastern United States, whereas surface water or groundwater is used in the more semi-arid to arid western states. In western states that lack available surface water resources, groundwater generally supplies the majority of water needed for fracturing (Table 4-1). Brackish sources of groundwater can be important for reducing demand on fresh groundwater resources in certain regions (e.g., the Permian Basin and Eagle Ford Shale in Texas; see Section 4.5.1).[4] Local policies also may direct the industry to seek withdrawals from designated sources (U.S. EPA, 2013a); for instance, some states have encouraged the industry to seek water withdrawals from surface water rather than groundwater due to concerns over aquifer depletion. See Section 4.5.4 and Section 4.5.5 for more information.

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[1] We use the term "hydraulic fracturing wastewater" to refer to produced water that is managed using practices that include, but are not limited to, reuse in subsequent hydraulic fracturing operations, treatment and discharge, and injection into disposal wells. The term is being used in this study as a general description of certain waters and is not intended to constitute a term of art for legal or regulatory purposes (see Chapter 8 and Appendix J, the Glossary, for more detail).

[2] Throughout this chapter we sometimes refer to "reused hydraulic fracturing wastewater" as simply "reused wastewater," because this is the dominant type of wastewater reused by the industry. When referring to other types of reused wastewater not associated with hydraulic fracturing (e.g., acid mine drainage, wastewater treatment plant effluent), we specify the source of the wastewater.

[3] We use the term "reuse" regardless of the extent to which the wastewater is treated (Nicot et al., 2014); we do not distinguish between reuse and recycling except when specifically reported in the literature.

[4] We use the term "fresh water" to qualitatively refer to water with relatively low TDS that is most readily and currently available for drinking water. We do not use the term to imply an exact TDS limit.

Table 4-1. Estimated proportions of hydraulic fracturing source water from surface water and groundwater.

Location	Surface water	Groundwater	Year or time period of estimate
Louisiana—Haynesville Shale	87%[a]	13%[a]	2009 - 2012
Oklahoma—Statewide	63%[b]	37%[b]	2011
Pennsylvania—Marcellus Shale, Susquehanna River Basin	92%[c]	8%[c]	2008 - 2013
Texas—Barnett Shale	50%[d]	50%[d]	2011 - 2013
Texas—Eagle Ford Shale	10%[e]	90%[e]	2011
Texas—TX-LA-MS Salt Basin[f]	30%[e]	70%[e]	2011
Texas—Permian Basin	0%[e]	100%[e]	2011
Texas—Anadarko Basin	20%[e]	80%[e]	2011
West Virginia—Statewide, Marcellus Shale	91%[g]	9%[g]	2012

[a] Percentages calculated from fracturing supply water usage data only. Rig supply water and other sources were excluded as they fall outside the scope of this assessment. Data from October 1, 2009, to February 23, 2012, for 1,959 Haynesville Shale natural gas wells (LA Ground Water Resources Commission, 2012).

[b] Proportion of surface water and groundwater permitted in 2011 by Oklahoma's 90-day provisional temporary permits for oil and gas mining. Temporary permits make up the majority of water use permits for Oklahoma oil and gas mining (Taylor, 2012).

[c] Calculated from SRBC (2016) data from July 2008 to December 2013.

[d] Nicot et al. (2014).

[e] Nicot et al. (2012).

[f] Nicot et al. (2012) refer to this region of Texas as the East Texas Basin.

[g] Estimated proportions are for 2012, the most recent estimate for a full calendar year available from West Virginia DEP (2014). Data from the West Virginia DEP show the proportion of water purchased from commercial brokers as a separate category and do not specify whether purchased water originated from surface water or groundwater. Therefore, we excluded purchased water in calculating the relative proportions of surface water and groundwater shown in Table 4-1 (West Virginia DEP, 2014).

The reuse of wastewater from past hydraulic fracturing operations reduces the need for withdrawals of fresh surface water or groundwater.[1] In a survey of literature values from 10 states, basins, or plays, we found a median of 5% of the water used in hydraulic fracturing comes from reused hydraulic fracturing wastewater, with this percentage varying by location (Table 4-2).[2,3]

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[1] Hydraulic fracturing wastewater may be stored on-site in open pits, which may also collect rainwater and runoff water. We do not distinguish between the different types of water that are collected on-site during oil and gas operations, and assume that most of the water collected on-site at well pads is hydraulic fracturing wastewater.

[2] Throughout this chapter, we preferentially report medians where possible because medians are less sensitive to outlier values than averages. Where medians are not available, averages are reported.

[3] This chapter examines reused wastewater as a percentage of injected volume because reused wastewater may offset total fresh water acquired for hydraulic fracturing. In contrast, Chapter 8 of this assessment discusses the total percentage of the generated wastewater that is reused rather than managed by different means (e.g., disposal in Class II wells). This distinction is sometimes overlooked, which can lead to a misrepresentation of the extent to which wastewater is reused to offset total fresh water used for hydraulic fracturing.

Table 4-2. Percentage of injected water volume that comes from reused hydraulic fracturing wastewater in various states, basins, and plays.

See Section 4.5 and Appendix B.2 for additional discussion of reuse practices by state and locality and variation over time where data are available.

State, basin, or play	Estimate of the percentage of injected water volume that comes from reused hydraulic fracturing wastewater[a]	Year or time period of estimate (NA = not available)
California—Monterey Shale	13%[b]	2014
Colorado—Wattenberg Field, Denver-Julesburg Basin	0%[c]	NA
Pennsylvania—Statewide	19%[d]	2014
Pennsylvania–Marcellus Shale, Susquehanna River Basin	16%[e]	2008 – 2013
Texas—Barnett Shale	5%[f]	2011
Texas—Eagle Ford Shale	0%[f]	2011
Texas—TX-LA-MS Salt Basin[g]	5%[f]	2011
Texas—Permian Basin (far west portion)	0%[f]	2011
Texas—Permian Basin (Midland portion)	2%[f]	2011
Texas—Anadarko Basin	20%[f]	2011
West Virginia—Statewide	15%[h]	2012
Overall Mean[i]	8%	
Overall Median[j]	5%	

[a] All estimates in this table refer to the percentage of injected water volume that comes from reused hydraulic fracturing wastewater. However, different literature sources used slightly different terminology when referring to this percentage. In the table footnotes below, we reference the terminology reported in the literature source cited.

[b] Produced water as a percentage of total water volume for 480 well stimulations according to completion reports between January 1, 2014, and December 10, 2014 (CCST, 2015a). All but two of these stimulations were conducted in Kern County, California (the remaining two were completed in Ventura County, California). Well stimulations mostly consisted of hydraulic fracturing operations, but also included smaller numbers of matrix acidizing and acid fracturing operations (CCST, 2015a).

[c] Reflects an assumption of reuse practices by Noble Energy in the Wattenberg Field of Colorado's Denver-Julesburg Basin, as reported by Goodwin et al. (2014).

[d] Percentage of recycled water used in hydraulic fracturing in 2014 based on data from the Pennsylvania Bureau of Topographic and Geologic Survey (Schmid and Yoxtheimer, 2015). This percentage was higher at 23% in 2013, but we present the most recent estimate available in the above table. The slight decline to 19% in 2014 may be explained by the fact that some completion reports had not yet been processed when these data were published, yet the data generally show an upward trend over time in reuse as a percentage of injected volume (Schmid and Yoxtheimer, 2015).

[e] Flowback water as a percentage of total water injected from July 2008 to December 2013 (SRBC, 2016). This percentage was 22% in 2013 alone (SRBC, 2016).

[f] Estimated percentage of recycling/reused water in 2011 (Nicot et al., 2012).

[g] Nicot et al. (2012) refer to this region of Texas as the East Texas Basin.

[h] Reused fracturing water as a percentage of total water used for hydraulic fracturing in 2012, calculated from data provided by the West Virginia DEP (2014).

[i] Calculated based on the values presented in Table 4-2, excluding the value for Pennsylvania's Susquehanna River Basin to avoid double counting with the statewide value. The overall mean is not weighted by the number of wells in a given state, basin, or play.

[j] Calculated based on the values presented in Table 4-2, excluding the value for Pennsylvania's Susquehanna River Basin to avoid double counting with the statewide value. The overall median is not weighted by the number of wells in a given state, basin, or play.

Available data on reuse trends indicate increased reuse as a percentage of injected volume over time in both Pennsylvania and West Virginia, likely due to the lack of nearby disposal options in Class II injection wells regulated by the Underground Injection Control (UIC) Program (Section 4.5.3).

The reuse of wastewater for hydraulic fracturing is limited by the amount of water that returns to the surface during production (Nicot et al., 2012). In the first 10 days of well production, 5% to almost 50% of the hydraulic fracturing fluid volume can be collected, with values varying across geologic formations (Chapter 7, Table 7-1). Longer duration measurements are rare, but between 10% and 30% of the hydraulic fracturing fluid volume has been collected in the Marcellus Shale in Pennsylvania over nine years of production, while over 100% has been collected in the Barnett Shale in Texas over six years of production (Chapter 7, Table 7-2).[1] Assuming that 10% of hydraulic fracturing fluid volume is collected in the first 30 days and 100% of the wastewater is reused, it would take 10 wells to produce enough water to hydraulically fracture a new well. As more wells are hydraulically fractured in a given area, the potential for wastewater reuse increases.

The decision to reuse hydraulic fracturing wastewater appears to be driven by economics and the quality of the wastewater, and not concerns over local water availability (Section 4.2.2). Water transportation costs (i.e., trucking, piping), the availability of Class II wells, and local regulations can play a role in determining whether hydraulic fracturing wastewater is reused to offset the need for fresh water withdrawals (Schmid and Yoxtheimer, 2015). Besides hydraulic fracturing wastewater, other wastewaters may be reclaimed for use in hydraulic fracturing. These include acid mine drainage, wastewater treatment plant effluent, and other sources of industrial and municipal wastewater (Nicot et al., 2014; Ziemkiewicz et al., 2013). Limited information is available on the extent to which these other wastewaters are used.

4.2.2 Quality

Water quality is an important consideration when sourcing water for hydraulic fracturing. Fresh water is most often used to maximize hydraulic fracturing fluid performance and to ensure compatibility with the geologic formation being fractured. This finding is supported by the EPA's analysis of disclosures to the FracFocus Chemical Disclosure Registry (version 1.0; hereafter, the EPA FracFocus report) (U.S. EPA, 2015b), as well as by regional analyses from Texas (Nicot et al.,

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[1] It is possible to collect over 100% of the hydraulic fracturing fluid volume because water from the formation returns to the surface along with the injected water.

2012) and the Marcellus Shale (Mitchell et al., 2013a).[1,2] Fresh water was the most commonly cited water source by companies included in an analysis of nine hydraulic fracturing service companies on their operations from 2005 to 2010 (U.S. EPA, 2013a). Three service companies noted that the majority of their water was fresh, because it required minimal testing and treatment (U.S. EPA, 2013a).[3] The majority of the nine service companies recommended testing for certain water quality parameters (pH and maximum concentrations of specific cations and anions) in order to ensure compatibility among the water, other fracturing fluid constituents, and the geologic formation (U.S. EPA, 2013a).

The reuse of hydraulic fracturing wastewater may be limited to an extent by water quality. Over the production life of a well, the quality of the wastewater produced begins to resemble the quality of the water naturally found in the geologic formation and may be characterized by high concentrations of total dissolved solids (TDS) (Goodwin et al., 2014). High concentrations of TDS and other individual dissolved constituents in wastewater, including specific cations (calcium, magnesium, iron, barium, strontium), anions (chloride, bicarbonate, phosphate, and sulfate), and microbial agents, can interfere with hydraulic fracturing fluid performance by producing scale in the borehole or by interfering with certain additives in the hydraulic fracturing fluid (e.g., high TDS may inhibit the effectiveness of friction reducers) (Gregory et al., 2011; North Dakota State Water Commission, 2010). Due to these limitations, wastewater can require treatment or blending with fresh water to meet the level of water quality desired in the hydraulic fracturing fluid formulation.[4]

Options for treating hydraulic fracturing wastewater to facilitate reuse are available and being used by the industry in some cases. For example, filter socks, centrifuge, dissolved air flotation, or settling technologies can remove suspended solids, and physical/chemical precipitation or electrocoagulation can remove dissolved metals (Schmid and Yoxtheimer, 2015). For more information on treatment of hydraulic fracturing wastewater, see Chapter 8.

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[1] The FracFocus Chemical Disclosure Registry (often referred to as FracFocus; www.fracfocus.org) is a national hydraulic fracturing chemical disclosure registry managed by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission. FracFocus was created to provide the public access to reported chemicals used for hydraulic fracturing within their area. It was originally established in 2011 (version 1.0) for voluntary reporting by participating oil and gas well operators. Six of the 20 states discussed in this assessment required disclosure to FracFocus at various points between January 1, 2011, and February 28, 2013, the time period analyzed by the EPA; another three of the 20 states offered the choice of reporting to FracFocus or the state during this same time period (see Appendix Table B-5 for states and disclosure start dates) (U.S. EPA, 2015b).

[2] Of all disclosures reviewed that indicated a source of water for the hydraulic fracturing base fluid, 68% listed “fresh” as the only source of water used. Note, 29% of all disclosures considered in the EPA’s FracFocus report included information on the source of water used for the base fluid (U.S. EPA, 2015b).

[3] Service companies did not provide data on the percentage of fresh water versus non-fresh water used for hydraulic fracturing (U.S. EPA, 2013a).

[4] The EPA FracFocus report suggests that fresh water makes up the largest proportion of the base fluid when blended with water sources of lesser quality (U.S. EPA, 2015b).

4.2.3 Provisioning

Water for hydraulic fracturing is typically either self-supplied by the industry or purchased from public water systems.[1] Self-supplied water for fracturing generally refers to permitted direct withdrawals from surface water or groundwater or the reuse of wastewater. Nationally, self-supplied water is more common, although there is much regional variation (U.S. EPA, 2015b; CCST, 2014; Mitchell et al., 2013a; Nicot et al., 2012). Water purchased from municipal public water systems can be provided either before or after treatment (Nicot et al., 2014). Water for hydraulic fracturing is also sometimes purchased from smaller private entities, such as local land owners (Nicot et al., 2014).

4.3 Water Use Per Well

In this section, we provide an overview of the amount of water used per well during hydraulic fracturing. We discuss water use in the life cycle of oil and gas operations (Section 4.3.1) and national per well estimates and associated variability (Section 4.3.2). More detailed locality-specific information on water use per well is provided in Section 4.5.

4.3.1 Hydraulic Fracturing Water Use in the Life Cycle of Oil and Gas

Water is needed throughout the life cycle of oil and gas production and use, including both at the well for processes such as well pad preparation, drilling, and fracturing (i.e., the upstream portion), and later for end uses such as electricity generation, home heating, or transportation (i.e., the downstream portion) (Jiang et al., 2014; Laurenzi and Jersey, 2013). Most of the upstream water usage and consumption occurs during hydraulic fracturing (Jiang et al., 2014; Clark et al., 2013; Laurenzi and Jersey, 2013).[2] Water use per well estimates in this chapter focus on hydraulic fracturing in the upstream portion of the oil and gas life cycle, as the downstream portion of the lifecycle is outside the scope of this assessment.[3]

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[1] According to Section 1401(4) of the Safe Drinking Water Act, a public water system is defined as system that provides water for human consumption from surface water or groundwater through pipes or other infrastructure to at least 15 service connections, or an average of at least 25 people, for at least 60 days per year. Public water systems may either be publicly or privately owned.

[2] Laurenzi and Jersey (2013) reported that hydraulic fracturing accounted for 91% of upstream water consumption, based on industry data for 29 wells in the Marcellus Shale. (91% was calculated from their paper by dividing hydraulic fracturing fresh water consumption (13.7 gal (51.9 L)/Megawatt-hour (MWh)) by total upstream fresh water consumption (15.0 gal (56.8 L)/MWh) and multiplying by 100). Similarly, Jiang et al. (2014) reported that 86% of water consumption occurred at the fracturing stage for the Marcellus Shale, based on Pennsylvania Department of Environmental Protection (PA DEP) data on 500 wells. The remaining water was used in several upstream processes (e.g., well pad preparation, well drilling, road transportation to and from the wellhead, and well closure once production ended). Clark et al. (2013) estimated lower percentages (30%−80%) of water use at the fracturing stage for multiple formations. Although their estimates for the fraction of water used at the fracturing stage may be low due to their higher estimates for transportation and processing, the estimates by Clark et al. (2013) similarly illustrate the importance of the hydraulic fracturing stage in water use, particularly in terms of the upstream portion of the life cycle.

[3] When the full life cycle of oil and gas production and use is considered (i.e., both upstream and downstream water use), most water is used and consumed downstream. For example, in a life cycle analysis of hydraulically fractured gas used for electricity generation, Laurenzi and Jersey (2013) reported that only 6.7% of water consumption occurred upstream (15.0 gal (56.8 L)/MWh), while 93.3% of fresh water consumption occurred downstream for power plant cooling via

4.3.2 National Estimates and Variability in Water Use Per Well for Hydraulic Fracturing

At its most basic level, the volume of water used per well for hydraulic fracturing equals the concentration of water in the hydraulic fracturing fluid multiplied by the total volume of the fluid injected. In turn, the total volume of fluid injected generally equals the volume of fluid in the fractures, plus the volume of the well itself, plus any fluid lost due to "leakoff" or other unintended losses.[1]

Nationally, most operators employ fracturing fluids with water as a base fluid, meaning the concentration of water in the fluid is high (U.S. EPA, 2015b; Yang et al., 2013; GWPC and ALL Consulting, 2009). The EPA inferred that more than 93% of reported disclosures to FracFocus used water as a base fluid (U.S. EPA, 2015b). The median reported concentration of water in the hydraulic fracturing fluid was 88% by mass, with 10th and 90th percentiles of 77% and 95%, respectively. Only roughly 2% of disclosures (761 wells) reported the use of non-aqueous substances as base fluids, typically either liquid-gas mixtures of nitrogen or carbon dioxide. Both of these formulations still contained substantial amounts of water, as water made up roughly 60% (median value) of the fluid in them (U.S. EPA, 2015b). Other formulations were rarely reported. Fluid formulations are discussed further in Chapter 5.

On average, hydraulic fracturing requires more than a million gallons (3.8 million liters) of water per well. Jackson et al. (2015) reported a national average of 2.4 million gal (9.1 million L) of water per well, calculated from FracFocus disclosures between 2010 and 2013. According to the EPA's project database of disclosures to FracFocus 1.0 (hereafter the EPA FracFocus 1.0 project database), the median volume of water used per well was 1.5 million gal (5.7 million L) between 2011 and early 2013, based on 37,796 disclosures nationally (U.S. EPA, 2015b, c).[2] Data on reported Information Handling Services well numbers and median volumes in Gallegos et al. (2015) show that overall per well volumes have increased in recent years from approximately 1.5 million gal (5.7 million L) in 2011 to 2.7 million gal (10.2 million L) in 2014.[3]

The recent increase in water use per well has been driven primarily by the proportional increase in horizontal wells (Gallegos et al., 2015) (Figure 4-1). Increases in horizontal well length affect total volumes injected primarily by allowing a larger fracture volume to be stimulated (Economides et al., 2013). As horizontal wells get longer, fracture, well, and total volumes all increase. Importantly, increases in the well length and water use per well do not necessarily mean an increase in water intensity (the amount of water used per unit energy extracted). Goodwin et al. (2014) found water

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evaporation (209.0 gal (791.2 L)/MWh). Similar results were found for gas extraction in the Eagle Ford Shale (Scanlon et al., 2014b).

[1] Leakoff is the fraction of the hydraulic fracturing fluid that infiltrates into the formation (e.g., through an existing natural fissure) and is not recovered during production. This water lost to the formation can be a substantial fraction of the water injected (O'Malley et al., 2015). See Chapter 6 for more information about leakoff and some recent findings related to the relationship between hydraulic fracturing fluid volume and fracture volume.

[2] All water use data included in the EPA's FracFocus 1.0 project database were obtained from disclosures made to FracFocus. Although disclosures were made on a per well basis, a small proportion of the wells were associated with more than one disclosure (i.e., 876 out of 37,114, based on unique API numbers) (U.S. EPA, 2015c). For the purposes of this chapter, we discuss water use per disclosure in terms of water use per well.

[3] Derived from supporting information in Gallegos et al. (2015). Calculated by multiplying the median volume by the number of wells for each well type, then summing volumes across well types, and dividing by the total number of wells.

intensity did not increase in the Denver Basin despite increases in well length and water use per well.

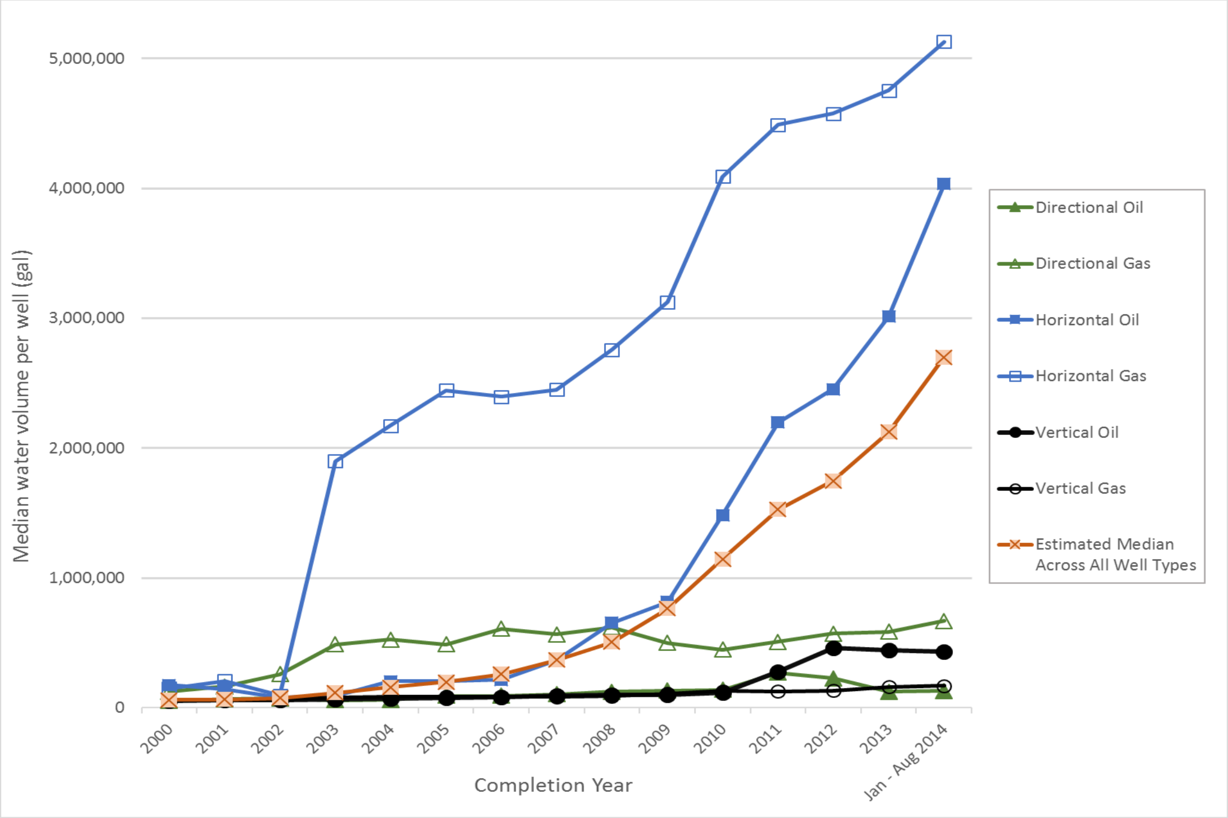

Figure 4-1. Median water volume per hydraulically fractured well nationally, expressed by well type and completion year.

Adapted using data from Gallegos et al. (2015). Note: shown in orange is the estimated median across all well types, derived from Gallegos et al. (2015) supporting information Tables S2 and S3. Calculated by multiplying the median volume by the number of wells for each well type, then summing volumes across well types, and dividing by the total number of wells for each year. This estimated median across all well types reflects the central tendency of the data, and was calculated because the individual data are proprietary and not published, preventing the calculation of an overall median.

There is substantial variation around these per well estimates. For instance, the 10th and 90th percentiles from the EPA FracFocus 1.0 project database are 74,000 gal and 6 million gal (280,000 L and 23 million L) per well, respectively.[1] Even in specific basins, plays, and within a single oil and gas field, water use per well varies widely. For example, Laurenzi and Jersey (2013) reported volumes ranging from 1 to 6 million gal (3.8 to 23 million L) per well (10th to 90th percentile) in the Wattenberg Field in Colorado.

Of the major unconventional formation types discussed in Chapter 2 (shales, tight formations-including tight sands or sandstones, and coalbeds), coalbeds generally require less water per well.

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[1] Although the EPA FracFocus report shows 5th and 95th percentiles, we report 10th and 90th percentiles throughout this chapter to further reduce the influence of outliers.

Coalbed methane (CBM) comes from coal seams that often have a high initial water content and tend to occur at much shallower depths (U.S. EPA, 2015k). In part because of the shallower depths, shorter well lengths result in lower water use per well, often by an order of magnitude or more compared to operations in shales or tight formations (e.g., Murray, 2013).

4.4 Hydraulic Fracturing Water Use and Consumption at the National, State, and County Scale

In this section, we provide an overview of water use and consumption for hydraulic fracturing at the national, state, and county scale. We then compare these values to total water use and consumption at these scales. We do this to contextualize hydraulic fracturing water use and consumption with total water use and consumption, and to illustrate whether hydraulic fracturing is a relatively large or small user and consumer of water at these scales. Later, we compare hydraulic fracturing water use to water availability estimates at the county scale (Text Box 4-2).

Water use is water withdrawn for a specific purpose, part or all of which may be returned to the local hydrologic cycle. Water consumption is water that is removed from the local hydrologic cycle following its use (e.g., via evaporation, transpiration, incorporation into products or crops, consumption by humans or livestock), and is therefore unavailable to other water users (Maupin et al., 2014). Hydraulic fracturing water consumption can occur through evaporation from storage ponds, the retention of water in the subsurface through imbibition, or disposal in Class II wells, among other means.

Hydraulic fracturing water use is a function of the water use per well and the total number of wells fractured at a given spatial scale during the time period analyzed, calculated from the EPA FracFocus 1.0 project database (U.S. EPA, 2015c). Water consumption estimates are derived from United States Geological Survey (USGS) water use data, and therefore both use and consumption are presented with the published water use numbers being first.

4.4.1 National and State Scale

Hydraulic fracturing uses and consumes billions of gallons of water each year in the United States, but at the national and state scales, it is a relatively small user and consumer of water compared to total water use and consumption. According to the EPA's FracFocus 1.0 project database, hydraulic fracturing used 36 billion gal (136 billion L) of water in 2011 and 52 billion gal (197 billion L) in 2012, yielding an average annually of 44 billion gal (167 billion L) of water in 2011 and 2012 across all 20 states in the project database (U.S. EPA, 2015b, c). National water use for hydraulic fracturing can also be estimated by multiplying the water use per well by the number of wells hydraulically fractured. If the median water use per well (1.5 million gal) (5.7 million L) from the EPA's FracFocus 1.0 project database is multiplied by 25,000 to 30,000 wells fractured annually (Chapter 3), national water use for hydraulic fracturing is estimated to range from 38 to 45 billion gal (142 to 170 billion L) annually. Other calculated estimates have ranged higher than this, including estimates of approximately 80 billion gal (300 billion L) (Vengosh et al., 2014) and 50 to 72 billion gal (190-273 billion L) (U.S. EPA, 2015e). These estimates are higher due to differences in the estimated water use per well and the number of wells used as multipliers. For example, Vengosh et al. (2014) derived the estimate of approximately 80 billion gal (300 billion L) by multiplying an average of 4.0 million gal (15 million L) per well (estimated for shale gas wells) by 20,000 wells (the approximate total number of fractured wells in 2012).[1]

All of these estimates of water use for hydraulic fracturing are small relative to total water use and consumption at the national scale. The USGS compiles national water use estimates every five years in the National Water Census, with the most recent census conducted in 2010 (Maupin et al., 2014).[2] The USGS publishes water use, not consumption estimates, yet by applying consumption factors for each use category in the 2010 National Water Census, we derived estimates of total water consumption. We also used a consumption factor to estimate hydraulic fracturing water consumption from values in the EPA FracFocus 1.0 project database.[3] Comparing these estimates, average annual hydraulic fracturing water use in 2011 and 2012 was less than 1% of total 2010 annual water use for all of the 20 states combined where operators reported water use to FracFocus in 2011 and 2012. Hydraulic fracturing water consumption followed the same pattern when compared to total water consumption (Appendix Table B-1).[4]

At the state scale, hydraulic fracturing also generally uses billions of gallons of water, but accounts for a low percentage of total water use or consumption. Of all states in the EPA FracFocus 1.0 project database, operators in Texas used the most water (47% of water use reported in the EPA FracFocus 1.0 project database) (U.S. EPA, 2015c) (Appendix Table B-1). This was due to the large number of wells in that state, since hydraulic fracturing water use is proportional to the number of wells. Over 94% of reported water use occurred in just seven of the 20 states in the EPA FracFocus 1.0 project database (listed in order of highest statewide hydraulic fracturing water use): Texas, Pennsylvania, Arkansas, Colorado, Oklahoma, Louisiana, and North Dakota (U.S. EPA, 2015c) (Appendix Table B-1). Hydraulic fracturing is a small percentage when compared to total water use (<1%) and consumption (<3%) in each individual state (Appendix Table B-1). Other studies have shown similar results, with hydraulic fracturing water use and consumption ranging from less than

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[1] This could result in an overestimation because the estimate of 20,000 wells was derived in part from FracFocus, and these wells are not necessarily specific to shale gas; they may include other types of wells that use less water (e.g., CBM). The estimate of 1.5 million gal (5.7 million L) per well based on the U.S. EPA (2015c) FracFocus 1.0 project database likely leads to a more robust estimate when used to calculate national water use for hydraulic fracturing because it includes wells from multiple formation types (i.e., shale, tight sand, and CBM), some of which use less water than shale gas wells on average.

[2] The National Water Census includes uses such as public supply, irrigation, livestock, aquaculture, thermoelectric power, industrial, and mining at the national, state, and county scale. The 2010 National Water Census included hydraulic fracturing water use in the mining category; there was no designated category for hydraulic fracturing alone.

[3] See footnotes for Appendix Table B-1 or for Table 4-3 for a description of the consumption estimate calculations.

[4] Water use percentages were calculated by averaging annual water use for hydraulic fracturing in 2011 and 2012 for a given state or county (U.S. EPA, 2015c), and then dividing by 2010 USGS total water use (Maupin et al., 2014) and multiplying by 100. Note, the annual hydraulic fracturing water use reported in FracFocus was not added to the 2010 total USGS water use value in the denominator, and is simply expressed as a percentage compared to 2010 total water use or consumption. This was done because of the difference in years between the two datasets, and because the USGS 2010 Water Census (Maupin et al., 2014) included hydraulic fracturing water use estimates in their mining category. This approach is consistent with that of other literature on this topic; see Nicot and Scanlon (2012). Consumption estimates were calculated in the same manner, except consumption, not use, values were employed. County level data from the USGS 2010 Water Census are available online at http://water.usgs.gov/watuse/data/2010/ (accessed November 11, 2014).

1% of total use in West Virginia (West Virginia DEP, 2013), Colorado (Colorado Division of Water Resources et al., 2014), and Texas (Nicot et al., 2014; Nicot and Scanlon, 2012), to approximately 4% in North Dakota (North Dakota State Water Commission, 2014).

4.4.2 County Scale

Water use and consumption for hydraulic fracturing is also relatively small in most, but not all, counties in the United States (Table 4-3; Figure 4-2; Figure 4-3a,b; and Appendix Table B-2). Based on the EPA FracFocus 1.0 project database, reported fracturing water use in 2011 and 2012 was less than 1% compared to 2010 USGS total water use in 299 of the 401 reporting counties (Figure 4-3a; Appendix Table B-2). However, hydraulic fracturing water use was 10% or more compared to total water use in 26 counties, 30% or more in nine counties, and 50% or more in four counties (Table 4-3; Figure 4-3a). McMullen County in Texas had the highest percentage at over 100% compared to 2010 total water use.[1] Total consumption estimates followed the same pattern, but with more counties in the higher percentage categories (hydraulic fracturing water consumption was 10% or more compared to total water consumption in 53 counties; 30% or more in 25 counties; 50% or more in 16 counties; and over 100% in four counties) (Table 4-3; Figure 4-3b).

Estimates based on the EPA's FracFocus 1.0 project database may form an incomplete picture of hydraulic fracturing water use in a given state or county, because the majority of states with data in the project database did not require disclosure to FracFocus during the time period analyzed (U.S. EPA, 2015b). We conclude that this likely does not substantially alter the overall patterns observed in Figure 4-3a,b. See Text Box 4-1 for further details. These percentages also depend both upon the absolute water use and consumption for hydraulic fracturing and the relative magnitude of other water uses and consumption in that state or county. For instance, a rural county with a small population might have relatively low total water use prior to hydraulic fracturing.[2] Also, just because water is used in a certain county does not necessarily mean it originated in that county. The cost of trucking water can be substantial (Slutz et al., 2012), and the industry tends to acquire water from nearby sources when possible (Section 4.2.1); however, water can also be piped in from more distant, regional supplies. Despite these caveats, it is clear that hydraulic fracturing is generally a relatively small user (and consumer) of water at the county level, with the exception of a small number of counties where water use and consumption for fracturing can be high relative to other uses and consumption.

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[1] Estimates of use or consumption exceeded 100% when hydraulic fracturing water use averaged for 2011 and 2012 exceeded total water use or consumption in that county in 2010.

[2] For example, McMullen County, Texas, mentioned above contains a small number of residents (707 people in 2010, according to the U.S. Census Bureau (2014).

Table 4-3. Average annual hydraulic fracturing water use and consumption in 2011 and 2012 compared to total annual water use and consumption in 2010, by county.

Only counties where hydraulic fracturing water was 10% or greater compared to 2010 total water use are shown (for full table, see Appendix Table B-2). Average annual hydraulic fracturing water use data in 2011 and 2012 from the EPA's FracFocus 1.0 project database (U.S. EPA, 2015c). Total annual water use data in 2010 from the USGS (Maupin et al., 2014). States listed by order of appearance in the chapter.

State	County	Total annual water use in 2010 (millions of gal)[a]	Average annual hydraulic fracturing water use in 2011 and 2012 (millions of gal)[b]	Hydraulic fracturing water use compared to total water use (%)[c]	Hydraulic fracturing water consumption compared to total water consumption (%)[c,d]
Texas	McMullen	657.0	745.9	113.5	350.4
	Karnes	1861.5	1055.2	56.7	120.1
	La Salle	2474.7	1288.7	52.1	93.7
	Dimmit	4073.4	1794.2	44.0	81.3
	Irion	1335.9	411.4	30.8	74.5
	Montague	3989.5	925.3	23.2	77.8
	De Witt	2394.4	546.6	22.8	48.6
	Loving	781.1	138.4	17.7	94.1
	San Augustine	1131.5	182.1	16.1	50.8
	Live Oak	1916.3	294.0	15.3	40.1
	Wheeler	6522.6	858.0	13.2	21.5
	Cooke	4533.3	454.3	10.0	29.9
Pennsylvania	Susquehanna	1617.0	751.3	46.5	123.4
	Sullivan	222.7	66.5	29.9	79.8
	Bradford	4354.5	1059.4	24.3	78.2
	Tioga	2909.1	566.3	19.5	47.3
	Lycoming	5854.6	704.6	12.0	33.8
West Virginia	Doddridge	405.2	78.5	19.4	69.4
Ohio	Carroll	1127.9	152.7	13.5	37.3
North Dakota	Mountrail	1248.3	449.4	36.0	98.3
	Dunn	1076.8	309.5	28.7	43.1
	Burke	394.2	63.6	16.1	40.8
	Divide	806.7	102.2	12.7	18.6

State	County	Total annual water use in 2010 (millions of gal)[a]	Average annual hydraulic fracturing water use in 2011 and 2012 (millions of gal)[b]	Hydraulic fracturing water use compared to total water use (%)[c]	Hydraulic fracturing water consumption compared to total water consumption (%)[c,d]
Arkansas	Van Buren	1587.8	899.6	56.7	168.8
Louisiana	Red River	1606.0	569.6	35.5	83.2
	Sabine	1522.1	395.2	26.0	76.6

[a] County level data accessed from the USGS website (http://water.usgs.gov/watuse/data/2010/) on November 11, 2014. Total water withdrawals per day were multiplied by 365 days to estimate total water use for the year (Maupin et al., 2014).

[b] Average of water used for hydraulic fracturing in 2011 and 2012 calculated from the EPA FracFocus 1.0 project database (U.S. EPA, 2015c).

[c] Percentages were calculated by averaging annual water use for hydraulic fracturing reported in FracFocus in 2011 and 2012 for a given state or county (U.S. EPA, 2015c), and then dividing by 2010 USGS total water use (Maupin et al., 2014) and multiplying by 100.

[d] Consumption values were calculated with use-specific consumption rates predominantly from the USGS, including 19.2% for public supply, 19.2% for domestic use, 60.7% for irrigation, 60.7% for livestock, 14.8% for industrial uses, 14.8% for mining (Solley et al., 1998), and 2.7% for thermoelectric power (Diehl and Harris, 2014). We used rates of 71.6% for aquaculture from Verdegem and Bosma (2009) ((evaporation per kg fish + infiltration per kg)/total water use per kg); and 82.5% for hydraulic fracturing (consumption value calculated by taking the median value for all reported produced water/injected water percentages in Tables 7-1 and 7-2 of this assessment and then subtracting from 100%). If a range of values was given, the midpoint was used. Note, this aspect of consumption is likely a low estimate since much of this produced water (injected water returning to the surface) is not subsequently treated and reused, but rather disposed of in Class II wells – see Chapter 8.

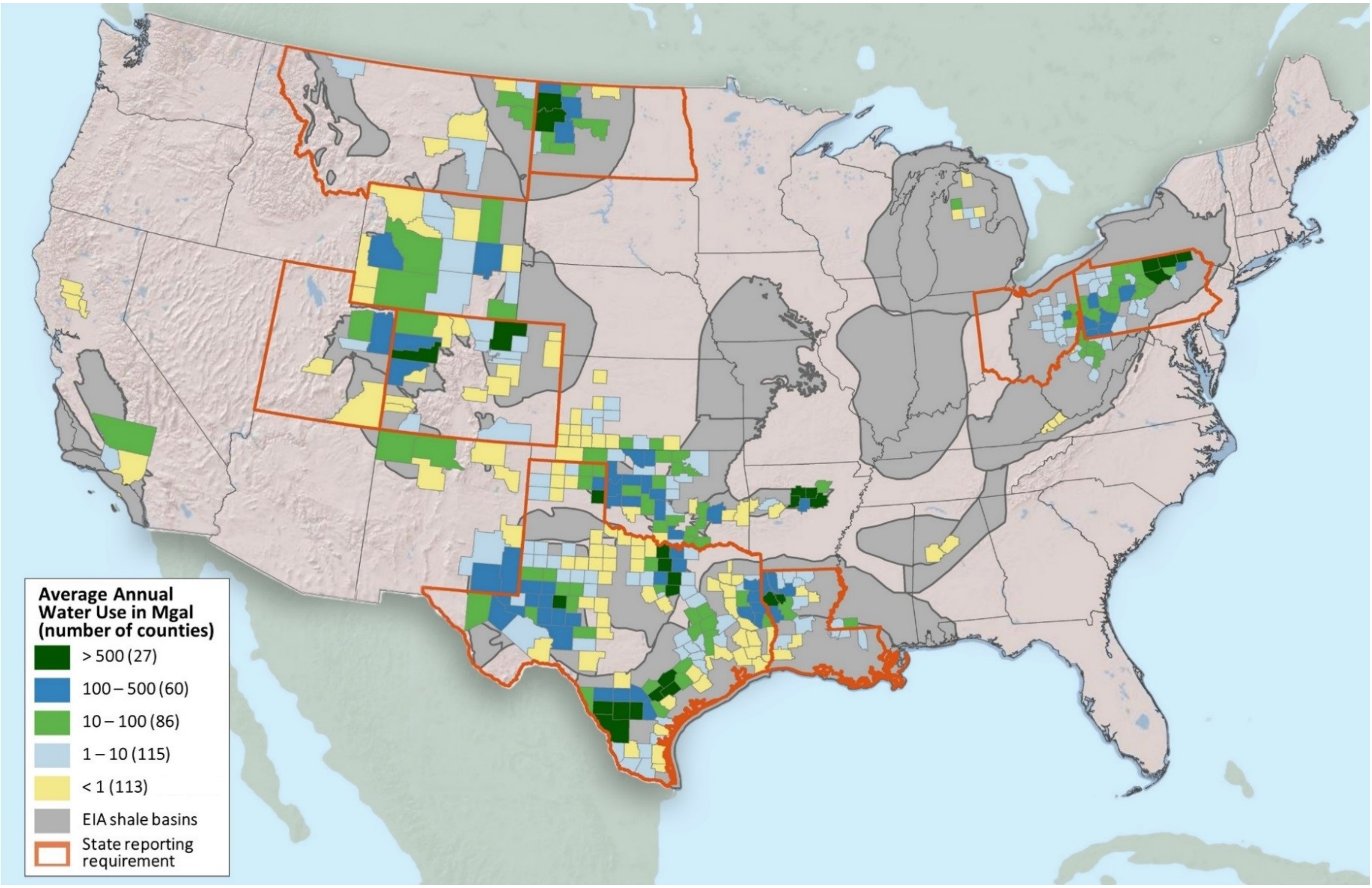
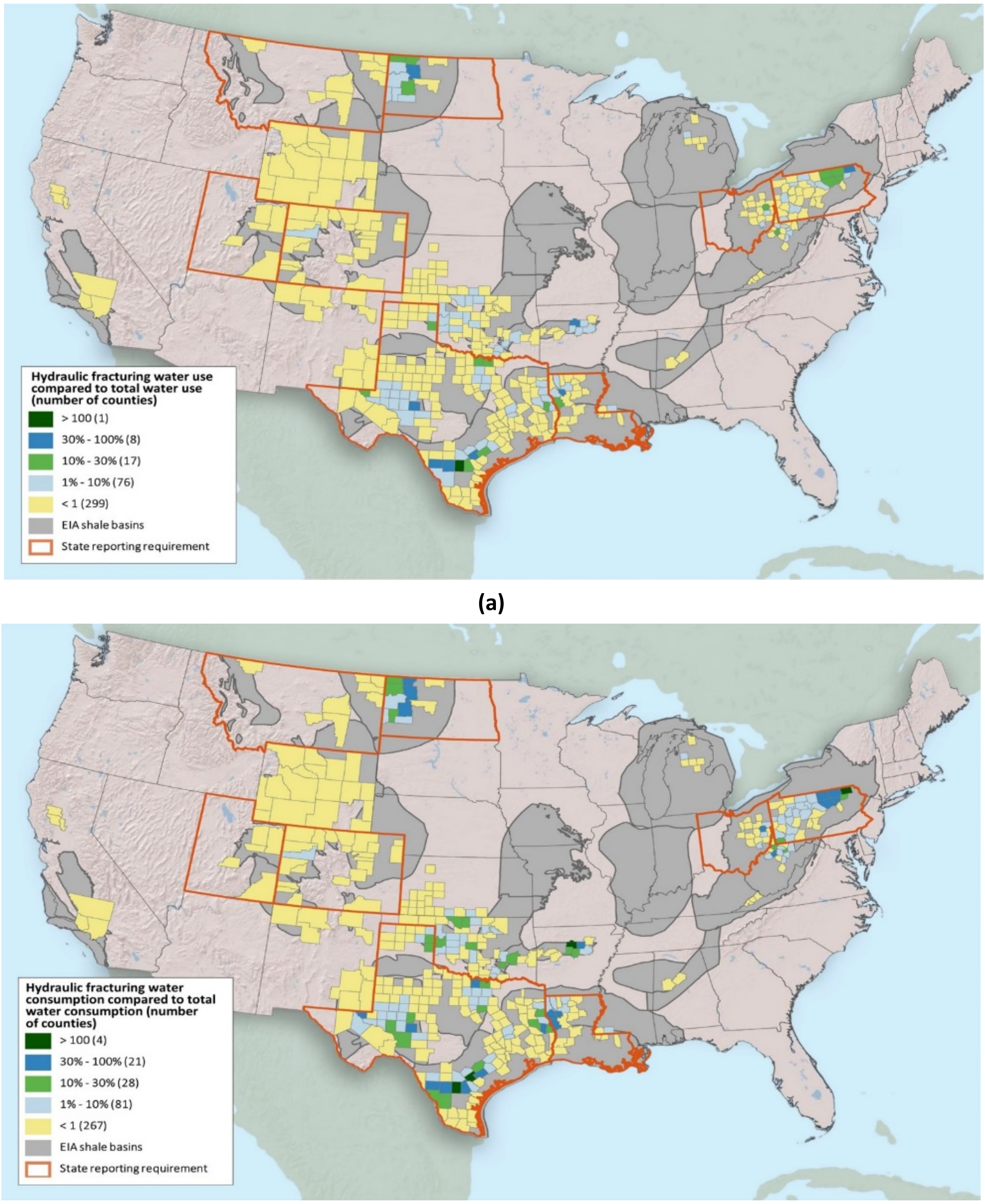


Figure 4-2. Average annual hydraulic fracturing water use in 2011 and 2012 by county.

Source: U.S. EPA (2015c). Water use in millions of gallons (Mgal). Counties shown with respect to major U.S. Energy Information Administration (EIA) shale basins (EIA, 2015). Orange borders identify states that required some degree of reporting to FracFocus in 2011 and 2012.



(a)

(b)

Figure 4-3. (a) Average annual hydraulic fracturing water use in 2011 and 2012 compared to total annual water use in 2010, by county, expressed as a percentage; (b) Average annual hydraulic fracturing water consumption in 2011 and 2012 compared to total annual water consumption in 2010, by county, expressed as a percentage.

Average annual hydraulic fracturing water use data in 2011 and 2012 from the EPA's FracFocus 1.0 project database (U.S. EPA, 2015c). Total annual water use data in 2010 from the USGS (Maupin et al., 2014). See Table 4-3 for descriptions of calculations for estimating consumption. Counties shown with respect to major U.S. EIA shale basins (EIA, 2015). Orange borders identify states that required some degree of reporting to FracFocus in 2011 and 2012. Note: Values over 100% denote counties where the average annual hydraulic fracturing water use or consumption in 2011 and 2012 exceeded the total annual water use or consumption in that county in 2010.

Text Box 4-1. Using the EPA's FracFocus 1.0 Project Database to Estimate Water Use for Hydraulic Fracturing.

The FracFocus Chemical Disclosure Registry (often referred to as FracFocus; www.fracfocus.org) is a national hydraulic fracturing chemical disclosure registry managed by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission. FracFocus was created to provide the public access to reported chemicals used for hydraulic fracturing within their area. It was originally established in 2011 (version 1.0) for voluntary reporting by oil and gas well operators. The EPA used the data available from FracFocus between January 1, 2011 and February 28, 2013 to develop the EPA FracFocus 1.0 project database; the database and a related EPA report were both peer reviewed and published (U.S. EPA, 2015b, c). Six of the 20 states discussed in this assessment required disclosure to FracFocus at various points during this time; another three of the 20 states offered the choice of reporting to FracFocus or the state during this same time period (U.S. EPA, 2015b). Estimates based on the EPA's FracFocus 1.0 project database could form an incomplete picture of hydraulic fracturing water use, because most states with data in the project database (14 out of 20) did not require disclosure to FracFocus during the time period analyzed (U.S. EPA, 2015b).

Water use for fracturing is a function of the water use per well and the total number of wells fractured over a given spatial area or a given period of time. For water use per well, we found seven literature values for comparison with values from the EPA's FracFocus 1.0 project database. On average, water use estimates per well in the project database were 77% of literature values (the median was 86%); Colorado's Denver Basin was the only location where the project database estimate as a percentage of the literature estimate was low (14%) (Appendix Table B-3). In general, water use per well estimates from the EPA's FracFocus 1.0 project database appear to align closely with the literature estimates for most areas for which we have data, with the exception of the Denver Basin of Colorado.

For the number of wells, we compared data in the EPA's FracFocus 1.0 project database to numbers available in state databases from North Dakota, Pennsylvania, and West Virginia (Appendix Table B-4). These were the state databases from which we could distinguish hydraulically fractured wells from other oil and gas wells. On average, we found that the EPA FracFocus 1.0 project database included 67% of the wells listed in state databases for 2011 and 2012 (Appendix Table B-4). Unlike North Dakota and Pennsylvania, West Virginia did not require operators to report fractured wells to FracFocus during this time period, possibly explaining its lower reporting rate. Multiplying the average EPA FracFocus 1.0 project database values of 77% for water use per well and 67% for well counts yields 52%. Thus, the EPA FracFocus 1.0 project database estimates for water use could be slightly over half of the estimates from these three state databases during this time period. These values are based on small sample sizes (seven literature values and three state databases) and should be interpreted with caution. Nevertheless, these numbers suggest that estimates based on the EPA's FracFocus 1.0 project database likely form an incomplete picture of hydraulic fracturing water use during this time period.

To assess how this might affect hydraulic fracturing water use estimates in this chapter, we doubled the water use value in the EPA's FracFocus 1.0 project database for each county, an adjustment much higher than any likely underestimation. Even with this adjustment, fracturing water use was still less than 1% compared to 2010 total water use in the majority of the 401 U.S. counties represented in the EPA FracFocus 1.0 project database (299 counties without adjustment versus 280 counties with adjustment). The number of counties where hydraulic fracturing water use was 30% or more of 2010 total county water use increased from nine to 21 with the adjustment.

These results indicate that most counties have relatively low hydraulic fracturing water use relative to total water use, even when accounting for likely underestimates. Since consumption estimates are derived from use, these will also follow the same pattern. Thus, potential underestimates based on the EPA's FracFocus 1.0 project database likely do not substantially alter the overall pattern shown in Figure 4-3. Rather, underestimates of hydraulic fracturing water use would mostly affect the percentages in the small number of counties where fracturing already constitutes a higher percentage of total water use and consumption.

4.5 Potential for Impacts by Location

The potential for hydraulic fracturing water acquisition to impact drinking water availability or alter its quality depends on the balance between water withdrawals and water availability at a given location. Where water availability is high compared to the volume of water withdrawn for hydraulic fracturing, this water use can be accomodated. However, where water availability is low and hydraulic fracturing water use is high, these withdrawals are more likely to impact drinking water resources. The balance between withdrawals and availability can vary greatly by geographic location. Moreover, a combination of regional or site-specific factors can alter this balance, making impacts more or less likely, or more or less severe. For these reasons, we discuss the various factors and potential for impacts by geographic location in the following section.

We organize this discussion by state, addressing 15 states accounting for almost all disclosures reported in the EPA FracFocus 1.0 project database (U.S. EPA, 2015c): Texas (Section 4.5.1); Colorado and Wyoming (Section 4.5.2); Pennsylvania, West Virginia, and Ohio (Section 4.5.3); North Dakota and Montana (Section 4.5.4); Arkansas and Louisiana (Section 4.5.5), Oklahoma and Kansas (Appendix B.2.1); and Utah, New Mexico, and California (Appendix B.2.2). We highlight the states that best illustrate concepts relating to the potential for impacts, or factors that affect the frequency or severity of these impacts in Section 4.5; the remaining states are discussed in Appendix B.2. Within Section 4.5 and Appendix B, we address each state in order of most hydraulically fractured wells to least, and combine states with similar geographies or activity. For certain states, we address major oil and gas regions separately (e.g., the Permian Basin in Texas). Each section describes the number of fractured wells in that state or region, the type of water used, water use per well, and water use estimates at the county scale. We then discuss the potential for impacts by comparing water use and water availability and addressing factors (e.g., drought or the amount of water reused to offset fresh water use) that might alter the frequency or severity of impacts. As noted in the chapter introduction, we use several lines of evidence to evaluate the potential for impacts and factors for each location. We use the scientific literature, county level assessments, and local case studies where available.

4.5.1 Texas

Hydraulic fracturing in Texas accounts for the bulk of the activity reported nationwide, comprising 48% of the disclosures in the EPA FracFocus 1.0 project database (U.S. EPA, 2015c) (Figure 4-4; Appendix Table B-5). There are five major basins in Texas: the Permian, Western Gulf (includes the Eagle Ford play), Fort Worth (includes the Barnett play), TX-LA-MS Salt (includes the Haynesville play), and the Anadarko (Figure 4-5); together, these five basins contain 99% of Texas' reported wells (Appendix Table B-5).

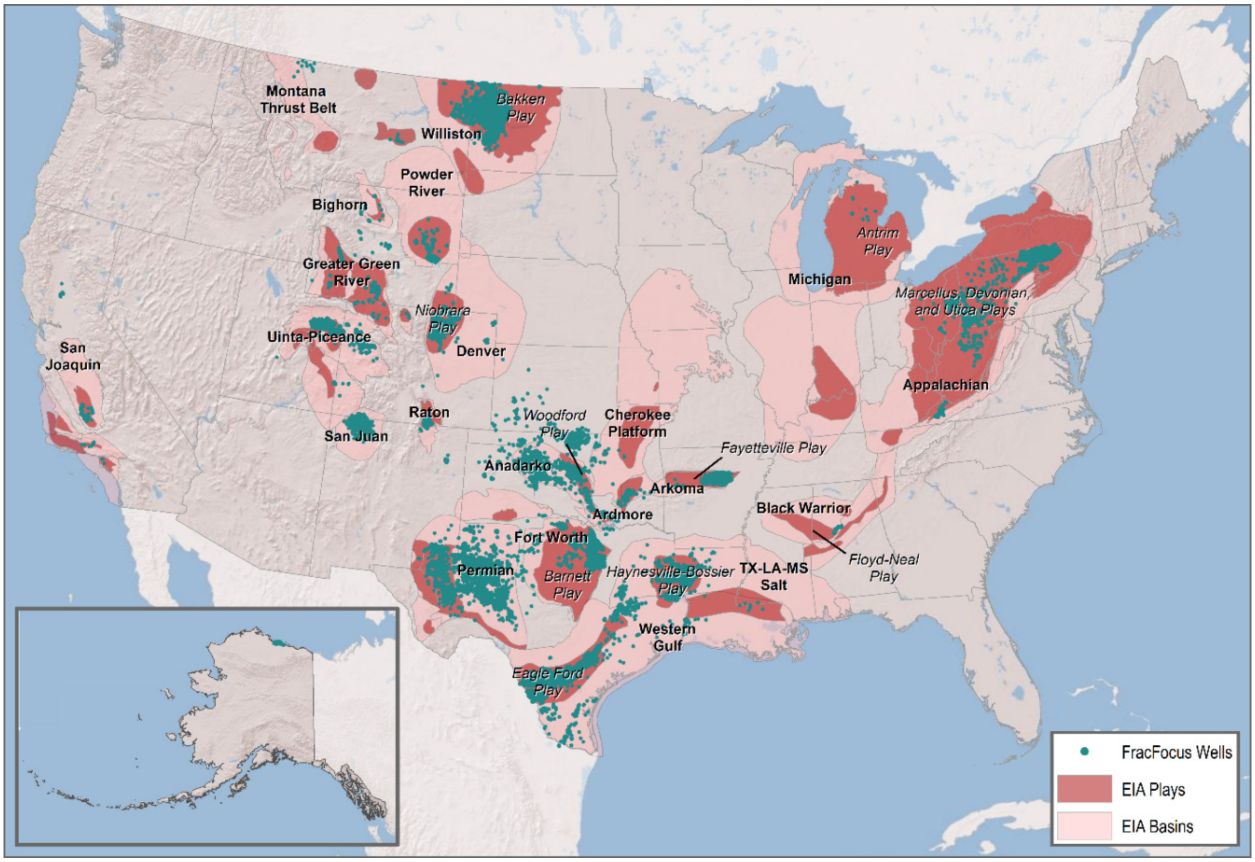


Figure 4-4. Locations of wells in the EPA FracFocus 1.0 project database, with respect to U.S. EIA shale plays and basins.

Note: Hydraulic fracturing can be conducted in geologic settings other than shale; therefore, some wells on this map are not associated with any EIA shale play or basin (EIA, 2015; U.S. EPA, 2015c).

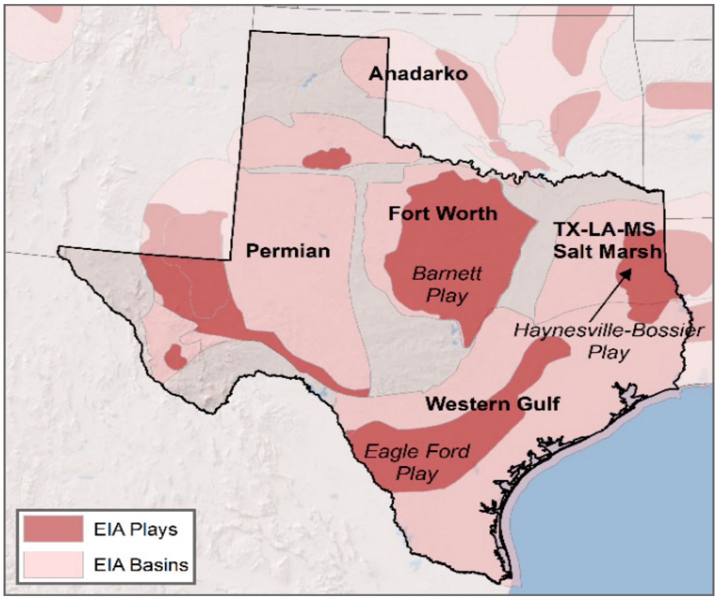


Figure 4-5. Major U.S. EIA shale plays and basins for Texas.

Source: EIA (2015).

Types of water used: What is known about water sources in Texas largely comes from direct surveys and interviews with industry operators and water suppliers (Nicot et al., 2014; Nicot et al., 2012). Overall, groundwater is the dominant source throughout most of the state (Nicot et al., 2014; Nicot et al., 2012) (Table 4-1). The exception is the Barnett Shale, where both surface water and groundwater are used in approximately equal proportions.

Hydraulic fracturing in Texas uses mostly fresh water (Nicot et al., 2012).[1] The exception is the far western portion of the Permian Basin, where brackish water makes up an estimated 80% of total hydraulic fracturing water use. Brackish water is used to a lesser extent in the Anadarko Basin, the Midland portion of the Permian Basin, and the Eagle Ford Shale (Table 4-4). Reuse of wastewater as a percentage of total water use is generally low (5% or less) in all major basins and plays in Texas, except for the Anadarko Basin in the Texas Panhandle, where it is 20% (Nicot et al., 2012) (Table 4-2).

Table 4-4. Estimated brackish water use as a percentage of total hydraulic fracturing water use in the main hydraulic fracturing areas of Texas, 2011.[a]

Adapted from Nicot et al. (2012).[b]

Play	Percentage
Barnett Shale	3%
Eagle Ford Shale	20%
Texas portion of the TX-LA-MS Salt Basin[c]	0%
Permian Basin—Far West	80%
Permian Basin—Midland	30%
Anadarko Basin	30%

[a] Nicot et al. (2012) define brackish water as any water with a total dissolved solids (TDS) content of >1,000 mg/L, but <35,000 mg/L, although they often limit that range to between 1,000 and 10,000 mg/L.

[b] Nicot et al. (2012) present the estimated percentages of brackish, recycled/reused, and fresh water relative to total hydraulic fracturing water use so that the percentages of the three categories sum to 100%.

[c] Nicot et al. (2012) refer to this region of Texas as the East Texas Basin.

The majority of water used in Texas for hydraulic fracturing is self-supplied via direct ground or surface water withdrawals (Nicot et al., 2014). Less often, water is purchased from local landowners, municipalities, larger water districts, or river authorities (Nicot et al., 2014).

Water use per well: Water use per well varies across Texas basins, with reported medians from 2011 to early 2013 of 3.9 million gal (14.8 million L) in the Fort Worth Basin, 3.8 million gal (14.4 million L) in the Western Gulf, 3.3 million gal (12.5 million L) in the Anadarko, 3.1 million gal (11.7 million L) in the TX-LA-MS Salt, and 840,000 gal (3.2 million L) in the Permian (Appendix

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[1] The EPA FracFocus report shows that "fresh" was the only source of water listed in 91% of all disclosures reporting a source of water in Texas (U.S. EPA, 2015b). Nineteen percent of Texas disclosures included information related to water sources (U.S. EPA, 2015b).

Table B-5). Relatively low water use in the Permian Basin, which contains roughly half the reported wells in the state, is due to the abundance of vertical wells, mostly for oil extraction (Nicot et al., 2012).

Water use per well is increasing in most locations in Texas. In the Barnett Shale, water use per well increased from approximately 3 million gal (11 million L) in the mid-2000's to approximately 5 million gal (19 million L) in 2011 as the horizontal lengths of wells increased (Nicot et al., 2014). Similar increases in lateral length and water use per well were reported for the Texas-Haynesville, East Texas, and Anadarko basins, and most of the Permian Basin (Nicot et al., 2012; Nicot and Scanlon, 2012).[1]

Water use/consumption at the county scale: Water use and consumption for hydraulic fracturing can be significant in some Texas counties. Texas contains five of nine counties nationwide where operators used more than 1 billion gal (3.8 billion L) of water annually for hydraulic fracturing, and five of nine counties where fracturing water use in 2011 and 2012 was 30% or more compared to total water use in those counties in 2010 (Table 4-3, Figure 4-3a; Appendix Table B-2).[2]

According to detailed county level projections, water use for hydraulic fracturing is expected to increase with oil and gas production in the coming decades, peaking around the year 2030 (Nicot et al., 2012). These projections were made before the recent decline in oil and gas prices, and so are highly uncertain. If these projections hold, the majority of counties are expected to have relatively low water use for fracturing in the future, but hydraulic fracturing water use could equal or exceed 10%, 30%, and 50% compared to 2010 total county water use in 30, nine, and three counties, respectively, by 2030 (Appendix Table B-7).

Potential for impacts: Of all locations surveyed in this chapter, the potential for water quantity and quality impacts due to hydraulic fracturing water acquisition appears to be highest in southern and western Texas. This area includes the Anadarko, the Western Gulf (Eagle Ford play), and the Permian Basins. According to Ceres (2014), 28% and 87% of the wells fractured in the Eagle Ford play and Permian Basin, respectively, are in areas of high to extremely high water stress.[3] A comparison of hydraulic fracturing water use to water availability at the county scale also suggests the potential for impacts in this region (Text Box 4-2).

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[1] It should be noted that energy production also increases with lateral lengths, and therefore, water use per unit energy produced—typically referred to as water intensity—may remain the same or decline despite increases in per-well water use (Nicot et al., 2014; Laurenzi and Jersey, 2013).

[2] Texas also contains 10 of the 25 counties nationwide where hydraulic fracturing water consumption was greater than or equal to 30% of 2010 total water consumption (Table 4-3). Nicot and Scanlon (2012) found similar variation among counties when they compared hydraulic fracturing water consumption to total county water consumption for the Barnett play. Their consumption estimates ranged from 581 million gal (2.20 billion L) in Parker County to 2.7 billion gal (10.2 billion L) in Johnson County, representing 10.5% and 29.7% compared to total water consumption in those counties, respectively. Fracturing in Tarrant County, part of the Dallas Fort-Worth area, consumed 1.6 billion gal (6.1 billion L) of water, 1.4% compared to total county water consumption (Nicot and Scanlon, 2012).

[3] Ceres (2014) compared well locations to areas categorized by a water stress index, characterized as follows: extremely high (defined as annual withdrawals accounting for greater than 80% of surface flows); high (40–80% of surface flows); or medium-to-high (20–40% of surface flows).

Text Box 4-2. Hydraulic Fracturing Water Use as a Percentage of Water Availability Estimates.

Researchers at Sandia National Laboratories assessed county level water availability across the continental United States (Tidwell et al., 2013). Assessments of water availability in the United States are generally lacking at the county scale, and this analysis—although undertaken for siting new thermoelectric power plants—can be used to assess potential impacts of hydraulic fracturing water withdrawals.

The authors generated annual water availability estimates for five categories of water: unappropriated surface water, unappropriated groundwater, appropriated water potentially available for purchase, brackish groundwater, and wastewater from municipal treatment plants (Tidwell et al., 2013). In the western United States, water is generally allocated by the principle of prior appropriation—that is, first in time of use is first in right. New development must use unappropriated water or purchase appropriated water from vested users. In their analysis, the authors assumed 5% of appropriated irrigated water could be purchased; they also excluded wastewater required to be returned to streams and the wastewater fraction already reused.

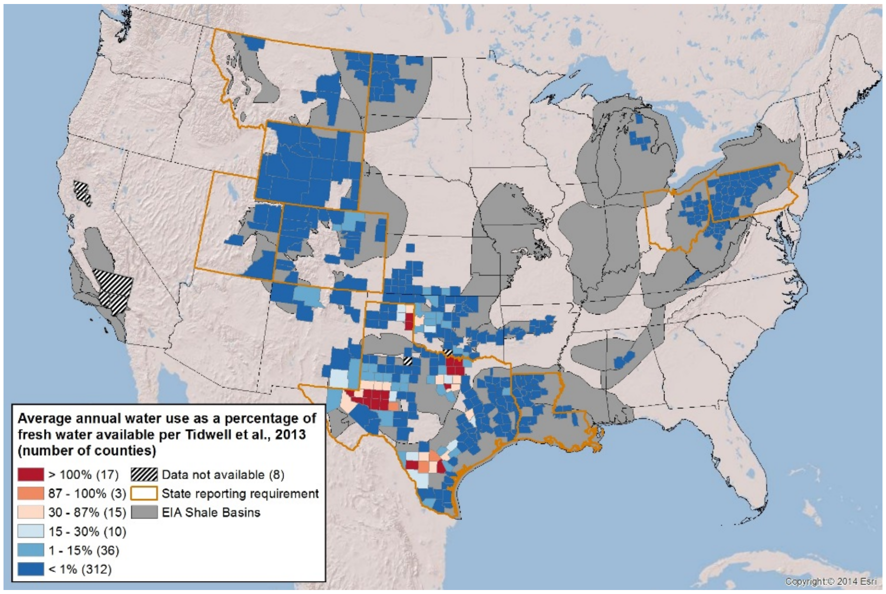
Given regulatory restrictions, they considered no fresh water to be available in California for new thermoelectric plants. Their definition of brackish water ranged from 3,000 to 10,000 ppm TDS, and from 50 to 2,500 ft (15-760 m) below the surface.

Combining their estimates of unappropriated surface water and groundwater and appropriated water potentially available for purchase, we derived a fresh water availability estimate for each county (except for those in California) and then compared this value to reported water use for hydraulic fracturing in 2011 and 2012 (U.S. EPA, 2015c). We also added the estimates of brackish groundwater and wastewater from municipal treatment plants to fresh water estimates to derive estimates of total water availability and did a similar comparison. Since the water availability estimates already take into account current water use for oil and gas operations, these results should be used only as indicator of areas where shortages might arise in the future. Here we focus on hydraulic fracturing water use compared to water availability. If we compared hydraulic fracturing water consumption to water availability, consumption would be lower relative to availability since by definition, water consumption is less than water use. Hence, water use versus availability acts as an upper-bound estimate, and includes consumption.

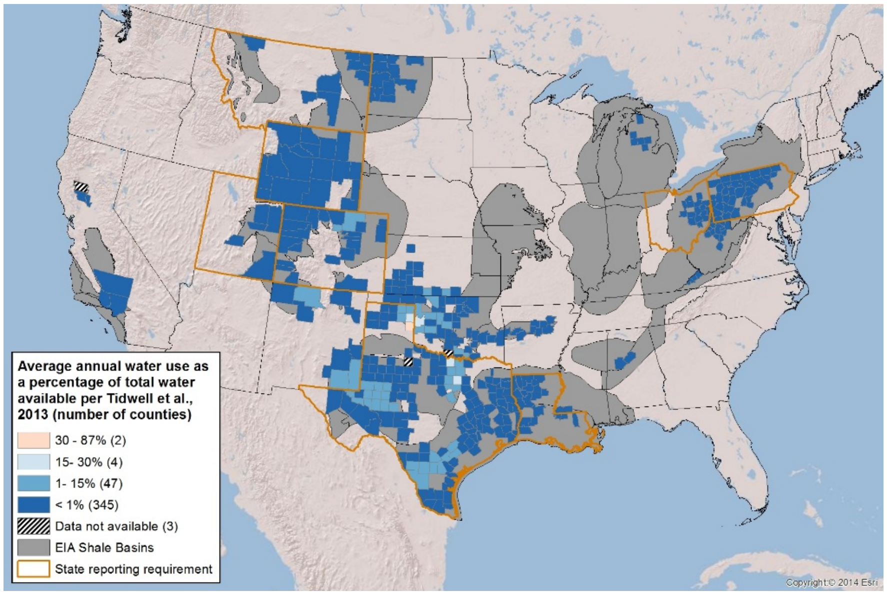
Overall, hydraulic fracturing water use represented less than 1% of fresh water availability in over 300 of the 395 counties analyzed (Figure 4-6a). This result suggests that there is ample water available at the county scale to accommodate hydraulic fracturing in most locations. However, there was a small number of counties where hydraulic fracturing water use was a relatively high percentage of fresh water availability. In 17 counties, fracturing water use actually exceeded the index of fresh water available; all of these counties were located in the state of Texas and were associated with the Anadarko, Barnett, Eagle Ford, and Permian basins/plays (Figure 4-5). In Texas counties with relatively high brackish water availability, hydraulic fracturing water use represented a much smaller percentage of total water availability (fresh + brackish + wastewater) (Figure 4-6b). This finding illustrates that potential impacts can be avoided or reduced in these counties through the use of brackish water or wastewater for hydraulic fracturing; a case study in the Eagle Ford play in southwestern Texas echoes this finding (Text Box 4-3).

(Text Box 4-2 is continued on the following page.)

Text Box 4-2 (continued). Hydraulic Fracturing Water Use as a Percentage of Water Availability Estimates.



(a)



(b)

Figure 4-6. Average annual hydraulic fracturing water use in 2011 and 2012 compared to (a) fresh water available and (b) total water (fresh, brackish, and wastewater) available, by county, expressed as a percentage. Counties shown with respect to major U.S. EIA shale basins (EIA, 2015). Orange borders identify states that required some degree of reporting to FracFocus in 2011 and 2012. Data from U.S. EPA (2015c) and Tidwell et al. (2013); data from Tidwell et al. (2013) supplied from the U.S. Department of Energy (DOE) National Renewable Energy Laboratory on January 28, 2014 and available upon request from the U.S. DOE Sandia National Laboratories. The analysis by Tidwell et al. (2013) was done originally for thermoelectric power generation. As such, it was assumed that no fresh water could be used in California for this purpose due to regulatory restrictions, and therefore no fresh water availability data were given for California. The total water available for California is the sum of brackish water plus wastewater only.

Surface water availability is generally low in southern and western Texas (Figure 4-7a), and both fracturing operations and residents rely heavily on groundwater (Figure 4-7b). Similar to trends nationally, groundwater aquifers in Texas have experienced substantial declines caused by withdrawals (Konikow, 2013; TWDB, 2012; George et al., 2011). Groundwater in the Pecos Valley, Gulf Coast, and Ogallala aquifers in southern and western Texas is estimated to have declined by roughly 5, 11, and 44 mi^3 (21, 45.5, and 182 km^3), respectively, between 1900 and 2008 (Konikow, 2013).[1]

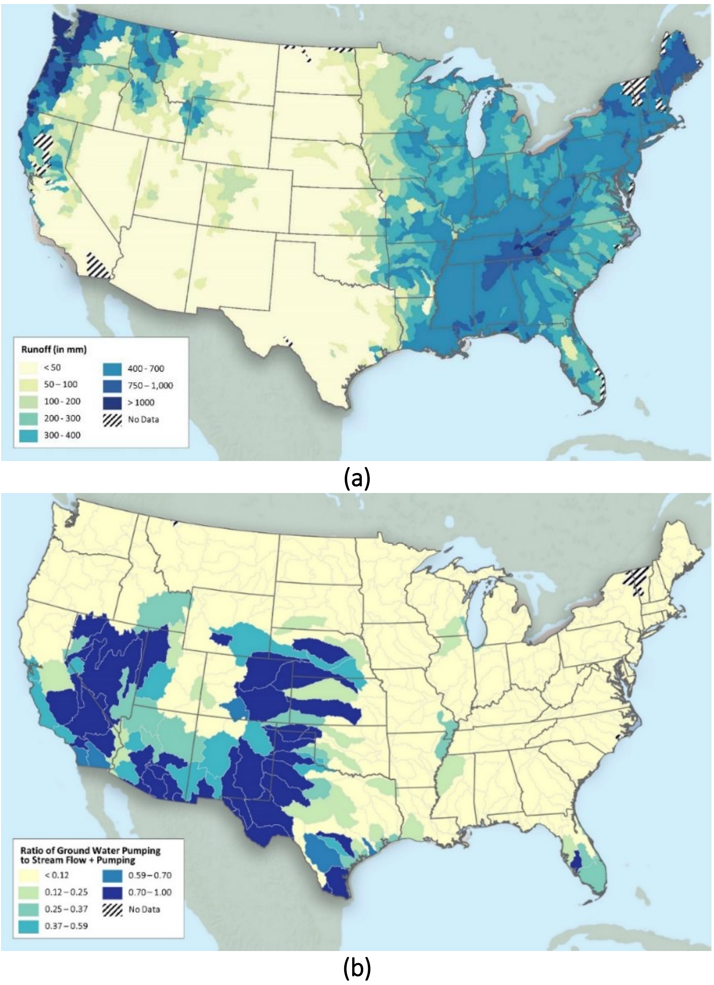


Figure 4-7. (a) Estimated annual surface water runoff from the USGS; (b) Reliance on groundwater as indicated by the ratio of groundwater pumping to stream flow and pumping. Estimates for Figure 4-7a were calculated at the 8-digit hydrological unit code (HUC) scale by dividing annual average daily stream flow (from October 1, 2012, to September 30, 2013) by HUC area. Data accessed from the USGS (USGS, 2014c). Higher ratios (darker blues) in Figure 4-7b indicate greater reliance on groundwater. Figure adapted from Tidwell et al. (2012), using data provided by the U.S. Department of Energy's Sandia National Laboratories on December 12, 2014.

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[1] The estimate of total net volumetric groundwater depletion for the Gulf Coast aquifer is the sum of the individual depletion estimates for the north (Houston area), central, and southern (Winter Garden area) parts of the Texas Gulf Coast aquifer. Groundwater depletion from the Carrizo-Wilcox aquifer is included in the estimate for the southern portion of the Gulf Coast aquifer (Konikow, 2013).

Groundwater quality degradation associated with aquifer pumping and the cumulative effects of all water users is well documented in the southern portion of the Ogallala aquifer. The quality of groundwater used by many private, public supply, and irrigation wells is poorest in the aquifer's southern portion, with elevated concentrations of TDS, chloride, nitrate, fluoride, manganese, arsenic, and uranium (Chaudhuri and Ale, 2014a; Gurdak et al., 2009; McMahon et al., 2007).[1] Extensive groundwater pumping can alter the quality of drinking water resources by inducing vertical mixing of high-quality groundwater with recharge water from the land surface that has been contaminated by nitrate or pesticides, or with lower-quality groundwater from underlying geologic formations (Gurdak et al., 2009; Konikow and Kendy, 2005). Pumping can also promote changes in reduction-oxidation (redox) conditions and thereby mobilize chemicals from geologic sources (e.g., uranium) (DeSimone et al., 2014). Similar patterns of groundwater quality degradation associated with prolonged aquifer depletion (i.e., salinization and contamination) have also been observed in other Texas aquifers, notably the northwest Edwards-Trinity (plateau), Pecos Valley, Carrizo-Wilcox, and southern Gulf Coast aquifers.[2]

The Texas Water Development Board (TWDB) estimates that overall demand for water (including water for hydraulic fracturing) out to the year 2060 will outstrip supply in southern and western Texas (TWDB, 2012). Furthermore, the TWDB expects groundwater supply in the major aquifers to decline by 30% between 2010 and 2060, mostly due to declines in the Ogallala aquifer (TWDB, 2012).[3,4] Irrigated agriculture is by far the dominant user of water from the Ogallala aquifer (Gurdak et al., 2009), but fracturing operations, along with other uses, now contribute to the aquifer's depletion.

The state has also experienced moderate to extreme drought conditions for much of the last decade, and the second-worst and longest drought in Texas history between March 2010 and November 2014 (TWDB, 2016; National Drought Mitigation Center, 2015) (Figure 4-8). Sustained drought conditions compound water availability concerns, and climate change is expected to place further stress on groundwater both now and in the future (Aghakouchak et al., 2014; Melillo et al., 2014) (Chapter 2). In their evaluation of the potential impact of climate change on groundwater recharge in the western United States, Meixner et al. (2016) show the largest declines in recharge are expected in specific aquifers in the southwestern United States, including the southern portion of the Ogallala aquifer, which is expected to receive 10% less recharge through the year 2050.

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[1] Elevated levels of these constituents result from both natural processes and human activities, such as groundwater pumping (Chaudhuri and Ale, 2014a; Gurdak et al., 2009).

[2] Persistent salinity has been observed in west Texas, specifically in the southern Ogallala, northwest Edwards-Trinity (plateau), and Pecos Valley aquifers, largely due to prolonged irrigational groundwater pumping and ensuing alteration of hydraulic gradients leading to groundwater mixing (Chaudhuri and Ale, 2014b). High levels of groundwater salinization associated with prolonged aquifer depletion have also been documented in the Carrizo-Wilcox and southern Gulf Coast aquifers, underlying the Eagle Ford Shale in south Texas (Chaudhuri and Ale, 2014b; Konikow, 2013; Boghici, 2009). Further, elevated levels of constituents, including nitrate, lead, fluoride, chloride, sulfate, iron, manganese, and TDS, have been reported in the Carrizo-Wilcox aquifer (Boghici, 2009).

[3] TWDB (2012) defines groundwater supply as the amount of groundwater that can be produced given current permits and existing infrastructure. By contrast, TWDB (2012) defines groundwater availability as the amount of groundwater that is available regardless of legal or physical availability. Total groundwater availability in Texas is expected to decline by approximately 24% between 2010 and 2060 (TWDB, 2012).

[4] This message is echoed in the 2017 Texas State Water Plan (TWDB, 2016).

Groundwater moves slowly, and natural recharge rates are lower during times of drought (DeSimone et al., 2014). Consequently, as water withdrawals continue to outpace the rate of recharge, aquifer storage will decline further (USGS, 1999), potentially impacting both drinking water resource quantity and quality. For example, research from Steadman et al. (2015) in the Eagle Ford play shows that hydraulic fracturing groundwater consumption exceeds estimated recharge rates in the seven most active counties for drilling.

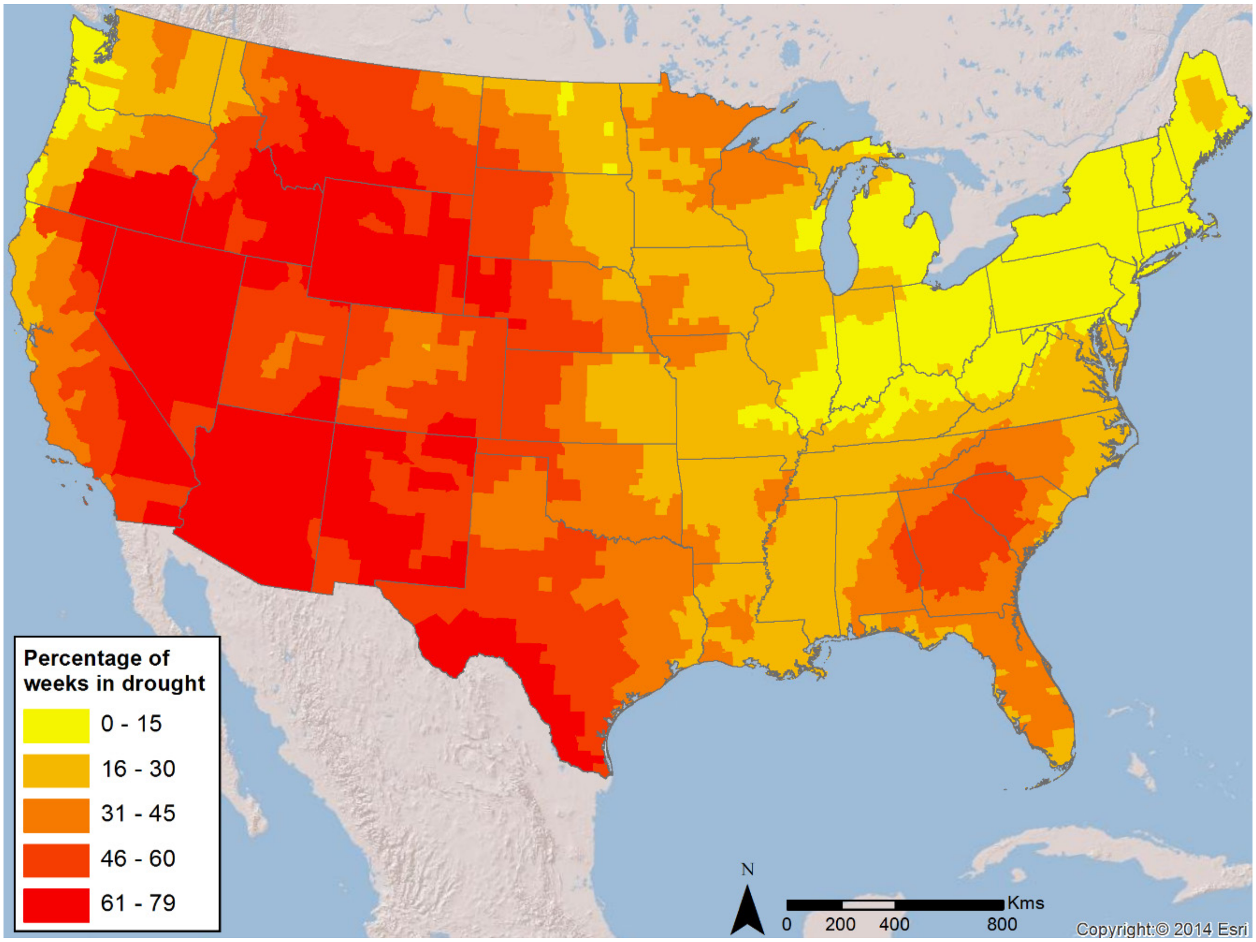

Figure 4-8. Percentage of weeks in drought between 2000 and 2013 by county.

Drought for a given week is defined as any portion of a given U.S. county having a weekly classification of moderate to exceptional drought (D1-D4 categorization) according to the National Drought Mitigation Center (http://droughtmonitor.unl.edu); number of weeks = 731.

A case study in the Eagle Ford play in southwestern Texas compared water demand for hydraulic fracturing with water supplies at the scale of the play, county, and 1 mi^2 (2.6 km^2) (Scanlon et al., 2014b). The authors observed generally adequate water supplies for hydraulic fracturing, except in specific locations, where they found excessive drawdown of groundwater locally in ~6% of the play area, with estimated declines of ~100-200 ft (31-61 m) after hydraulic fracturing activity increased in 2009 (Text Box 4-3).

Text Box 4-3. Case Study: Water Profile of the Eagle Ford Play, Texas.

Researchers from the University of Texas published a detailed case study of water supply and demand for hydraulic fracturing in the Eagle Ford play in southwestern Texas (Scanlon et al., 2014b). This effort assembled detailed information from state and local water authorities, and proprietary industry data on hydraulic fracturing, to develop a portrait of water resources in this 16-county area.

Scanlon et al. (2014b) compared water demand for hydraulic fracturing currently and over the projected play life (20 years) relative to water supply from groundwater recharge, groundwater storage (brackish and fresh), and stream flow. Using groundwater availability models developed by the Texas Water Development Board, they reported that water demand for hydraulic fracturing in 2013 was 30% of annual groundwater recharge in the play area, and over the 20-year play lifespan it was projected to be 26% of groundwater recharge, 5-8% of fresh groundwater storage, and 1% of brackish groundwater storage. The dominant water user in the play is irrigation (57 to 61% of water use, 62 to 65% of consumption), as compared with hydraulic fracturing (13% of water use and 16% of consumption). At the county level, projected water demand for hydraulic fracturing over the 20-year period was low relative to freshwater supply (ranging from 0.6-27% by county, with an average of 7.3%). Similarly, projected total water demand from all uses was low relative to supply, excluding two counties with high irrigation demands (Frio, Zavala), and one county with no known groundwater supplies (Maverick).

Although supply was found to be sufficient even in this semi-arid region, there were important exceptions, especially at sub-county scales. The researchers found no water level declines over much of the play area assessed (69% of the play area), yet in some areas they estimated groundwater drawdowns of 50 ft (15 m) or more (19% of the play area), 100 ft (31 m) or more (6% of the play area), and 200 ft (60 m) or more (approximately 2% of the play area). This was corroborated with well monitoring data that showed a sharp decline in water levels in several groundwater monitoring wells after hydraulic fracturing activity increased in 2009.

The researchers further concluded that shifting toward brackish groundwater is feasible, as evidenced by operators already doing so. This shift could further reduce impacts on fresh water resources and provide a large source of water for future hydraulic fracturing. In a 2011 estimate, approximately 20% of water used in the play came from brackish sources (Table 4-4), and anecdotal evidence suggests this practice has increased since then (Scanlon et al., 2014b). Projected hydraulic fracturing water use represents less than 1% of total brackish groundwater storage in the play area. By contrast, Scanlon et al. (2014b) concluded there is limited potential for reuse of wastewater in this play because of the small volumes that return to the surface during production (less than or equal to 5% of hydraulic fracturing water requirements).

In contrast to southern and western Texas, the potential for water quantity and quality effects appears to be lower in the north-central and eastern parts of the state, in areas including the Barnett and Haynesville plays. Residents obtain water for domestic use—which includes use of water for drinking—from a mixture of groundwater and surface water sources (Appendix Table B-6). Counties encompassing Dallas and Fort Worth rely mostly on publicly-supplied surface water (TWDB, 2012) (Appendix Table B-6). The Trinity aquifer in northeast Texas is projected to decline only slightly between 2010 and 2060 (TWDB, 2012). Nevertheless, Bene et al. (2007) estimate that hydraulic fracturing groundwater withdrawals will increase from 3% of total groundwater use in 2005 to 7%–13% in 2025, suggesting the potential for localized aquifer drawdown. Groundwater quality degradation associated with aquifer drawdown has been documented in the Trinity and Woodbine aquifers overlying much of the Barnett play, with both aquifers showing high levels of salinization (Chaudhuri and Ale, 2013).

Overall, the potential for impacts appears higher in western and southern Texas, compared to the northeast part of the state. Groundwater withdrawals for hydraulic fracturing, along with irrigation and other uses, may contribute to water quality degradation associated with intensive aquifer pumping in western and southern Texas. Areas with numerous high-capacity wells and large amounts of sustained groundwater pumping are most likely to experience groundwater quality degradation associated with withdrawals (Gurdak et al., 2009; McMahon et al., 2007). Further, given that Texas is prone to drought conditions and groundwater recharge is limited, the already declining aquifers in southern and western Texas are especially vulnerable to further groundwater depletion and resulting impacts to groundwater quantity and quality (Gurdak et al., 2009; Jackson et al., 2001). Impacts are likely to be localized drawdowns of groundwater, as shown by a detailed case study of the Eagle Ford play (Text Box 4-3). Scanlon et al. (2014b) suggested that a shift toward brackish water use could minimize potential future impacts to fresh water resources. This finding is consistent with our county level data (Text Box 4-2).

4.5.2 Colorado and Wyoming

Colorado had the second highest number of disclosures in the EPA FracFocus 1.0 project database, (13% of disclosures) (Figure 4-4 and Appendix Table B-5). We combine Colorado and Wyoming because of their shared geology of the Denver Basin (including the Niobrara play) and the Greater Green River Basin (Figure 4-9). There are three major basins reported for Colorado: the Denver Basin; the Uinta-Piceance Basin; and the Raton Basin. Together these basins contain 99% of reported wells in the state, although the bulk of the activity in Colorado is in the Denver Basin (Appendix Table B-5). Fewer wells (roughly 4% of disclosures in the EPA FracFocus 1.0 project database) are reported in Wyoming. There are two major basins reported for Wyoming (Greater Green River and Powder River) that together contain 86% of activity in the state (Appendix Table B-5).

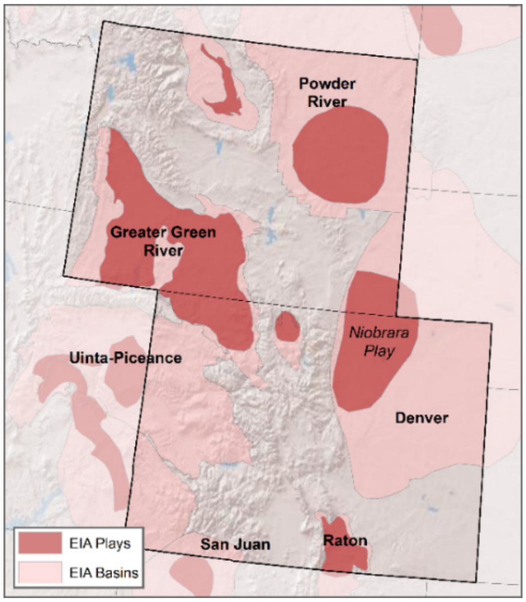

Figure 4-9. Major U.S. EIA shale plays and basins for Colorado and Wyoming.
Source: EIA (2015).

Types of water used: Water for hydraulic fracturing in Colorado and Wyoming comes from both groundwater and surface water, as well as reused wastewater (Colorado Division of Water Resources et al., 2014; BLM, 2013). Publicly available information on water sources for each state generally comes in the form of a list of potential sources, and detailed information on the types of water used for hydraulic fracturing is not readily accessible.[1] In northwestern Colorado's Garfield County (Uinta-Piceance Basin), the U.S. EPA (2015e) reports that any fresh water used for fracturing comes from surface water sources. In the Denver Basin (Niobrara play) of southeastern Wyoming, qualitative information suggests that groundwater supplies much of the water used for fracturing, although no data were available to characterize the ratio of groundwater to surface water withdrawals (AMEC Environment & Infrastructure, 2014; BLM, 2013; Tyrrell, 2012).

Non-fresh water sources, including industrial and municipal wastewater, brackish groundwater, and reused hydraulic fracturing wastewater, are sometimes listed as potential alternatives to fresh water for fracturing in both Colorado and Wyoming (Colorado Division of Water Resources et al., 2014; BLM, 2013); no data are available to show the extent to which these non-fresh water sources are used at the state or basin level. Based on discussions with industry, the U.S. EPA (2015e) reports that fresh water is used solely for drilling and reused wastewater supplies nearly all the water for hydraulic fracturing in Colorado's Garfield County. This estimate of reused wastewater as a percentage of injected volume is markedly higher than in other locations and likely results from the geologic characteristics of the Piceance tight sand formation, which has naturally high water content and produces large volumes of relatively high-quality wastewater (U.S. EPA, 2015e).

In contrast, a study by Goodwin et al. (2014) assumed no reuse of wastewater for hydraulic fracturing operations by Noble Energy in the Denver-Julesburg Basin of northeastern Colorado (Table 4-2). It is unclear whether this assumption is indicative of reuse practices of other companies in the Denver-Julesburg Basin. The difference in reused wastewater rates reported by the U.S. EPA (2015e) and Goodwin et al. (2014) may indicate an east-west divide in Colorado (i.e., low reuse in the east versus high reuse in the west), due at least in part to differences in wastewater volumes available for reuse. However, further information is needed to adequately characterize reuse patterns in Colorado.

Water use per well: Water use per well varies across Colorado, with median values of 1.8 million, 400,000, and 96,000 gal (6.8 million, 1.5 million, and 360,000 L) in the Uinta-Piceance, Denver, and Raton Basins, respectively, according to the EPA FracFocus 1.0 project database (Appendix Table B-5). Relatively low water volumes per well are reported in Wyoming (Appendix Table B-5). Low volumes reported for the Raton Basin of Colorado and the Powder River Basin of Wyoming are likely due to the prevalence of CBM extraction in these locations (U.S. EPA, 2015k; Sando et al., 2014).

More difficult to explain are the low volumes reported for the Denver Basin in the EPA FracFocus 1.0 project database. These values are lower than volumes reported in other non-CBM basins

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[1] The Colorado Oil and Gas Conservation Commission collects information on the sources and quality of water used for hydraulic fracturing, including reused wastewater, with Form 5A, and has done so since June 2012; however, these data are in PDFs linked to individual wells and are not aggregated into a searchable database.

included in Appendix Table B-5. Goodwin et al. (2014) report much higher water use per well in the Denver Basin from 2010 to 2013, with a median of 2.8 million gal (10.6 million L) (although only usage for the Wattenberg Field was reported). Indeed, the 10th–90th percentiles (2.4-3.8 million gal) (9.1-14.4 million L) from Goodwin et al. (2014) are almost completely above those from the EPA FracFocus 1.0 project database for the Denver Basin (Appendix Table B-5).[1] However, it is difficult to draw clear conclusions because of differences in scale (i.e., field in Goodwin et al. (2014) versus basin in the EPA FracFocus 1.0 project database) and operators (i.e., Noble Energy in Goodwin et al. (2014) versus all in the EPA FracFocus 1.0 project database).

Trends in water use per well are generally lacking for Colorado, with the exception of those reported by Goodwin et al. (2014). They found that water use per well is increasing with well length in the Denver Basin; however, they also observed that water intensity (gallons of water per unit energy extracted) did not change, since energy recovery increased along with water use.

Water use/consumption at the county scale: Hydraulic fracturing operations in Colorado use billions of gallons of water, but this amount is a small percentage compared to total water used or consumed at the county scale. In both Garfield and Weld Counties, located in the Uinta-Piceance and Denver Basins, respectively, hydraulic fracturing used more than 1 billion gal (3.8 billion L) annually. Fracturing water use and consumption in these counties exceeded those in all other Colorado counties combined (Appendix Table B-2), but the water used for hydraulic fracturing in Garfield and Weld counties was less than 2% and 3% compared to 2010 total water use and consumption, respectively. In comparison, irrigated agriculture accounts for over 90% of the water used in both counties (Maupin et al., 2014). Overall, hydraulic fracturing accounts for less than 2% compared to 2010 total water use in all Colorado counties represented in the EPA FracFocus 1.0 project database (Appendix Table B-2). Water use estimates based on the EPA FracFocus 1.0 project database may be low relative to literature and state estimates (Text Box 4-1), but even if estimates from the project database were doubled, hydraulic fracturing water use and consumption would still be less than 4% and 6% compared to 2010 total water use and consumption, respectively, in each Colorado county.

In Wyoming, reported water use for hydraulic fracturing is small compared to Colorado (Appendix Table B-1). Fracturing water use and consumption did not exceed 1% of 2010 total water use and consumption, respectively, in any county (Appendix Table B-2). Unlike Colorado, Wyoming did not require disclosure to FracFocus during the time period analyzed by the EPA (U.S. EPA, 2015b) (Appendix Table B-5).

Colorado Division of Water Resources et al. (2014) projected that annual water use for hydraulic fracturing in the state would increase by approximately 16% between 2012 and 2015, but demand in later years is unclear. Even with an increase of 16% or more, hydraulic fracturing would still remain a relatively small user of water at the county scale in Colorado.

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[1] Different spatial extents might explain these differences, since Goodwin et al. (2014) focus on 200 wells in the Wattenberg Field of the Denver Basin; however, Weld County is the center of activity in the Wattenberg Field, and the EPA FracFocus 1.0 project database contains 3,011 disclosures reported in Weld County, with a median water use per of 407,442 gal (1,542,340 L), similar to that for the basin as a whole.

Potential for impacts: The potential for water quantity and quality impacts due to hydraulic fracturing water withdrawals appears to be low at the county scale in Colorado and Wyoming because fracturing accounts for a low percentage of total water use and consumption (Figure 4-3a,b). This conclusion is also supported by the comparison of hydraulic fracturing water use to water availability at the county scale (Text Box 4-2; Figure 4-6a,b). However, counties in Colorado and Wyoming are large in their spatial extents, and any potential impacts will depend on site-specific factors affecting the balance between water use and availability at the local scale (i.e., at a given withdrawal point). In a multi-scale case study in the Upper Colorado River Basin, the U.S. EPA (2015e) did not identify any locations where fracturing currently contributed to locally high water use intensity due to the high rates of wastewater reuse reported. They did conclude, however, that future effects may be possible (Text Box 4-4).

Text Box 4-4. Case Study: Impact of Water Acquisition for Hydraulic Fracturing on Local Water Availability in the Upper Colorado River Basin.

The U.S. EPA (2015e) conducted a case study to explore the impact of hydraulic fracturing water demand on water availability at the river basin, county, and local scales in the semi-arid Upper Colorado River Basin (UCRB) of western Colorado. The study area overlies the Piceance geologic basin with natural gas in tight sands. Water withdrawal impacts were quantified using a water use intensity index (i.e., the ratio between the volume of water withdrawn at a site for hydraulic fracturing and the volume of available water). Researchers obtained detailed site-specific data on hydraulic fracturing water usage from state and regional authorities, and estimated available water supplies using observations at USGS gage stations and empirical and hydrologic modeling.

They found that water supplies accessed for oil and gas demand were concentrated in Garfield County, and most fresh water withdrawals were concentrated within the Parachute Creek watershed (198 mi^2). However, fresh water makes up a small proportion of the total water used for fracturing due to large quantities of high-quality wastewater produced from the Piceance tight sands. Based on discussions with industry, the U.S. EPA (2015e) reports that fresh water is used solely for drilling and reused wastewater supplies nearly all the water for hydraulic fracturing in Garfield County. Due to the high reuse rate, the U.S. EPA (2015e) did not identify any locations in the Piceance play where fracturing contributed to locally high water use intensity.

Scenario analyses demonstrated a pattern of increasing potential impact with decreasing watershed size in the UCRB. The U.S. EPA (2015e) examined hydraulic fracturing water use intensity under the current rates of both directional (S-shaped) and horizontal drilling. They showed that for the more water-intensive horizontal drilling, watersheds had to be larger to meet the same index of water use intensity (0.4) as that for directional drilling (100 mi^2 for horizontal drilling, as compared to 30 mi^2 for directional drilling). To date, most wells have been drilled directionally into the Piceance tight sands, although a trend toward horizontal drilling is expected to increase annual water use per well by about four times. Despite this increase, total hydraulic fracturing water use is expected to remain small relative to other users. Currently, irrigated agriculture is the largest water user in the UCRB.

Greater water demand could occur in the future if the water-intensive oil shale extraction industry becomes economically viable in the region. Projections for oil shale water demand indicate that the industry could increase water use for energy extraction in Garfield and Rio Blanco counties.

East of the Rocky Mountains in the Denver Basin, the potential for localized impacts exists given the combination of high hydraulic fracturing activity and low water availability (e.g., Weld County, Colorado), but lack of available data and literature at the local scale limits our ability to assess the potential for impacts in this location. Ceres (2014) concludes that all fractured wells in the Denver Basin are in high or extremely high water-stressed areas. Furthermore, the development of the Niobrara Shale in southeast Wyoming occurs in areas already impacted by high agricultural water use from the Ogallala aquifer, including the state's only three groundwater control areas, which were established as management districts in the southeast portion of the state in response to declining groundwater levels (AMEC Environment & Infrastructure, 2014; Wyoming State Engineer's Office, 2014; Tyrrell, 2012; Bartos and Hallberg, 2011). Groundwater withdrawals for hydraulic fracturing may have the potential to contribute to water quality degradation in these areas, depending on site-specific factors that may alter the balance between water use and availability.

Overall, the potential for impacts appears low at the county scale in Colorado and Wyoming, but local effects are certainly possible particularly east of the Rocky Mountains in the Denver Basin. Lack of available data and literature at the local scale limits our ability to assess the potential for impacts in this location.

4.5.3 Pennsylvania, West Virginia, and Ohio

Pennsylvania had the third most disclosures in the EPA FracFocus 1.0 project database (6.5% of disclosures) (Appendix Table B-5; Figure 4-4). We combine West Virginia and Ohio with Pennsylvania because they share similar geology overlying the Appalachian Basin (including the Marcellus, Devonian, and Utica stacked plays) (Figure 4-10); however, much less activity is reported in these two states (Appendix Table B-5).

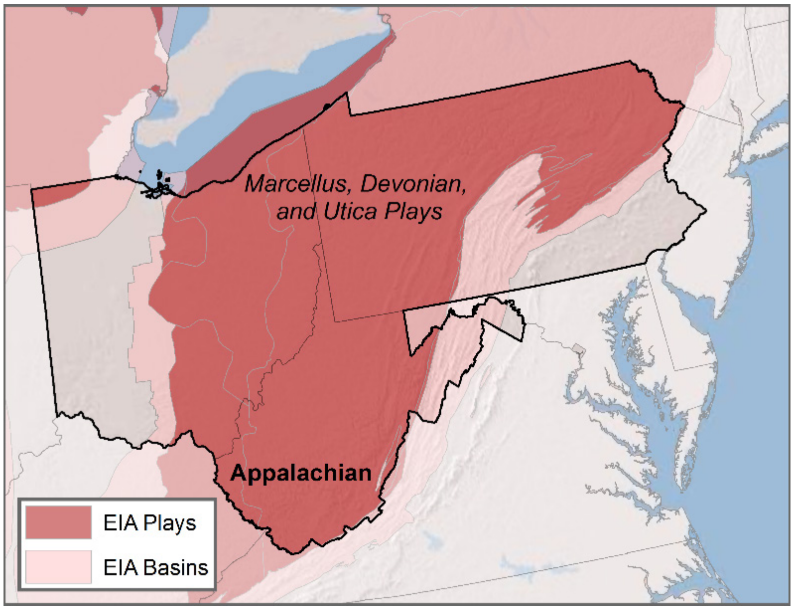

Figure 4-10. Major U.S. EIA shale plays and basins for Pennsylvania, West Virginia, and Ohio.
Source: EIA (2015).

Types of water used: Surface water is the primary water source for hydraulic fracturing in Pennsylvania, West Virginia, and Ohio (SRBC, 2016; Schmid and Yoxtheimer, 2015; West Virginia DEP, 2014; Mitchell et al., 2013a; West Virginia DEP, 2013; Ohio EPA, 2012b; STRONGER, 2011b) (Table 4-1). Further, the water used for hydraulic fracturing is most often fresh water in all three states. In both Pennsylvania's Susquehanna River Basin and throughout West Virginia, most water for hydraulic fracturing is self-supplied via direct withdrawals from surface water and groundwater (U.S. EPA, 2015e; West Virginia DEP, 2013). Operators also purchase water from public water systems, which may include a variety of commercial water brokers (West Virginia DEP, 2014; SRBC, 2013; West Virginia DEP, 2013). Municipal supplies are also used, particularly in urban areas of Ohio (STRONGER, 2011b).

Reused hydraulic fracturing wastewater as a percentage of total water used for fracturing was 19% in 2014 in Pennsylvania, and 15% in 2012 in West Virginia (Schmid and Yoxtheimer, 2015; West Virginia DEP, 2014) (Table 4-2). Available data indicate an increasing trend in reuse of wastewater over time in this region, likely due to the lack of nearby disposal options in Class II wells. Reused wastewater as a percentage of injected water volume ranged from approximately 2% to 19% in Pennsylvania (statewide) from 2009-2014 (Schmid and Yoxtheimer, 2015). This upward trend is also shown in Pennsylvania's SRB, where reuse as a percentage of total water injected reached 22% in 2013; the average reuse rate for 2008-2013 in the SRB was 16% (SRBC, 2016) (Table 4-2). In West Virginia, reuse as a percentage of injected volume ranged from 6% to 15% from 2010-2012 (West Virginia DEP, 2014). In Ohio's Marcellus and Utica Shales, reuse of wastewater is reportedly uncommon (STRONGER, 2011b), likely due to the prevalence of disposal wells in Ohio. See Chapter 8 for more information.

Aside from reused hydraulic fracturing wastewater, other types of wastewaters reused for hydraulic fracturing may include wastewater treatment plant effluent, treated acid mine drainage, and rainwater collected at various well pads (West Virginia DEP, 2014; SRBC, 2013; West Virginia DEP, 2013; Ziemkiewicz et al., 2013; Ohio EPA, 2012b). No data are available on the frequency of use of these other wastewaters.

Water use per well: Operators in these three states reported the third, fourth, and fifth highest median water use per well of the states we considered from the EPA FracFocus 1.0 project database, with 5.0, 4.2, and 3.9 million gal (18.9, 15.9, and 14.8 million L) in West Virginia, Pennsylvania, and Ohio, respectively (Appendix Table B-5). Hansen et al. (2013) report similar water use estimates for Pennsylvania and West Virginia for 2011 and 2012 (Appendix Table B-5). This correspondence is not surprising, as these estimates are also based on FracFocus data (via Skytruth). For 2011, the year overlapping with the time frame of the EPA FracFocus report (U.S. EPA, 2015b), Mitchell et al. (2013a) report an average of 2.3 million gal (8.7 million L) for vertical wells (54 wells) and 4.6 million gal (17.4 million L) for horizontal wells (612 wells) in the Pennsylvania portion of the Upper Ohio River Basin, based on records from PA DEP. The weighted average water use per well was 4.4 million gal (16.7 million L), similar to results based on the EPA FracFocus 1.0 project database listed above. In Pennsylvania's SRB, the long-term average water use per well from 2008-2013 was 4.3 million gal (16.3 million L). In 2013, the average water use per well increased to approximately 5.1 to 6.5 million gal (19.3 to 24.6 million L) due to increasing lengths of laterals in horizontal drilling (SRBC, 2016). Across the entire state of Pennsylvania, water use per well has increased over time, which may be explained by increasing horizontal well length, depth, and length of the completed interval (Schmid and Yoxtheimer, 2015).

Water use/consumption at the county scale: In this tri-state region, the highest water use for hydraulic fracturing is in northeastern Pennsylvania counties. On average, operators in Bradford County reported over 1 billion gal (3.8 billion L) used annually in 2011 and 2012 for fracturing; operators in three other counties (Susquehanna, Lycoming, and Tioga Counties) reported 500 million gal (1.9 billion L) or more used annually in each county (Table 4-3). On average, hydraulic fracturing water use is 3.2% compared to 2010 total water use for counties with disclosures in the EPA FracFocus 1.0 project database in these three states (Table 4-3; Appendix Table B-2). Susquehanna County in Pennsylvania has the highest percentages relative to 2010 total water use (47%) and consumption (123%).

Potential for impacts: Water availability is higher in Pennsylvania, West Virginia, and Ohio than in many western states, reducing the likelihood of impacts to drinking water resource quantity and quality. At the county scale, water supplies appear adequate to accommodate this use (Text Box 4-2; Figure 4-6a,b). However, impacts could still occur at the local scale (i.e., specific withdrawal points) as high water availability in a region does not preclude water stress, particularly if water withdrawals occur during seasonal low-flow periods (Entrekin et al., 2015). Without management of the rate and timing of withdrawals, surface water withdrawals for hydraulic fracturing have the potential to affect both drinking water quantity and quality (Mitchell et al., 2013a). For instance, withdrawals may alter natural stream flow regimes, potentially decreasing a stream's capacity to dilute contaminants (Gallegos et al., 2015; Mitchell et al., 2013a; Entrekin et al., 2011; NYSDEC, 2011; van Vliet and Zwolsman, 2008; IPCC, 2007; Environment Canada, 2004; Murdoch et al., 2000).

In a second, multi-scale case study, EPA showed that the potential for water acquisition impacts to drinking water resource quantity and quality increases at finer temporal and spatial resolutions (U.S. EPA, 2015e). They concluded that individual streams in Pennsylvania's SRB can be vulnerable to typical hydraulic fracturing water withdrawals depending on stream size, as defined by contributing basin area (U.S. EPA, 2015e) (Text Box 4-5). They observed infrequent (in less than 1% of withdrawals) high ratios of hydraulic fracturing water consumption to stream flow (high consumption-to-stream flow events). Further research from Barth-Naftilan et al. (2015) in Pennsylvania's Marcellus Shale (SRB and Ohio River Basin (ORB)) confirmed that stream flow alteration due to hydraulic fracturing surface water withdrawals increases at finer spatial scales (i.e., smaller watershed area). They showed that streams with drainage areas under 50 mi^2 (130 km^2) are the most vulnerable to stress induced by flow alteration (Barth-Naftilan et al., 2015).

Text Box 4-5. Case Study: Impact of Water Acquisition for Hydraulic Fracturing on Local Water Availability in the Susquehanna River Basin.

The U.S. EPA (2015e) conducted a second case study analogous to that in the UCRB (Text Box 4-4), to explore the impact of hydraulic fracturing water demand on water availability at the river basin, county, and local scales in the SRB in northeastern Pennsylvania. The study area overlies the Marcellus Shale gas reservoir. Water withdrawal impacts were quantified using a water use intensity index (Text Box 4-4). Researchers obtained detailed site-specific data on hydraulic fracturing water usage from state and regional authorities, and estimated available water supplies using observations at USGS gage stations and empirical and hydrologic modeling.

Most water for fracturing in the SRB is self-supplied by operators from rivers and streams with withdrawal points distributed throughout a wide geographic area. Public water systems provide a relatively small proportion of the water needed. Reuse of wastewater as a percentage of hydraulic fracturing fluid volume averaged 16% from 2008-2013, and has increased over time, reaching 22% in 2013 (SRBC, 2016) (Table 4-2). The Susquehanna River Basin Commission (SRBC) regulates water acquisition for hydraulic fracturing and issues permits that set limits on the volume, rate, and timing of withdrawals at individual withdrawal points; passby flow thresholds (hereafter, passby flows) halt water withdrawals during low flows.

The U.S. EPA (2015e) demonstrated that streams can be vulnerable from hydraulic fracturing water withdrawals depending on their size, as defined by contributing basin area. Small streams have the potential for impacts (i.e., high water use intensity) for all or most of the year. The U.S. EPA (2015e) showed an increased likelihood of impacts in small watersheds in the SRB (less than 10 mi^2 or 26 km^2). Furthermore, they showed that in the absence of passby flows, even larger watersheds (up to 600 mi^2 or 1,554 km^2) could be vulnerable during maximum withdrawal volumes and infrequent droughts. However, high water use intensity calculated from observed hydraulic fracturing withdrawals occurred at only a few withdrawal locations in small streams; local high water use intensity was not found at the majority of withdrawal points.

Detailed studies and state reports available throughout the Marcellus Shale region help provide an understanding of the potential impacts of hydraulic fracturing water withdrawals in both space and time at the local scale (SRBC, 2016; Barth-Naftilan et al., 2015; U.S. EPA, 2015e). In the SRB and ORB, water for hydraulic fracturing is taken from both large rivers and small headwater streams, with a considerable fraction of the water taken from small streams of small watersheds (Barth-Naftilan et al., 2015). The SRBC reports that most natural gas development in the SRB is focused in rural, headwater areas, where withdrawals have the potential to alter natural stream flow regimes (SRBC, 2016). In an analysis of the effects of water withdrawals on twelve streams in the SRB, Shank and Stauffer (2015) found that the largest withdrawals relative to stream size were from headwater streams, where daily withdrawals averaged 6.8% of average daily flows. However, they found water management in the form of low flow protections helped limit the potential for impacts.

Compared to conventional energy extraction, hydraulic fracturing consumes more water in a highly concentrated period of time (Patterson et al., 2016); thus, the cumulative impact of multiple wells withdrawing water from small streams, particularly during drought or seasonal low flows, has the potential to impact the quantity and quality of drinking water resources (Patterson et al., 2016). For instance, in modeling the potential future impact of hydraulic fracturing in the Delaware River Basin (DRB), Habicht et al. (2015) showed that under maximum well development, hydraulic fracturing water withdrawals from small streams could remove up to 70% of water during periods of low stream flow, and less than 3% during periods of normal stream flow.[1] Unlike groundwater withdrawals, any impacts to drinking water resource quantity and quality associated with surface water withdrawals are likely to persist for a shorter time period since the rate of replenishing water removed from the system is greater in surface water than groundwater (Alley et al., 1999) (Section 4.5.1).

The potential for water acquisition impacts to drinking water resource quality in this region is also greatest in small, unregulated streams, particularly under drought conditions or during seasonal low flows (U.S. EPA, 2015e; Vengosh et al., 2014; Mitchell et al., 2013a; Vidic et al., 2013; Rahm and Riha, 2012; Rolls et al., 2012; Kargbo et al., 2010; McKay and King, 2006). Surface water quality impacts may be of concern if a pollution discharge point (e.g., sewage treatment plant, agricultural runoff, or chemical spill) is immediately downstream of a hydraulic fracturing withdrawal point (U.S. EPA, 2015e; NYSDEC, 2011).[2] Potential water quality impacts associated with reduced water levels may also include possible interference with the efficiency of drinking water treatment plant operations, as increased contaminant concentrations in drinking water sources may necessitate additional treatment and ultimately impact drinking water quality (Water Research Foundation, 2014; Benotti et al., 2010).[3]

Water management policies in place in this region can help reduce the potential for impacts associated with hydraulic fracturing water withdrawals, including excessive lowering of water levels, unreliable water supplies, and degradation of water quality (SRBC, 2016; Barth-Naftilan et al., 2015; U.S. EPA, 2015e) (Text Box 4-5). For instance, the SRBC manages the quantity, location, and timing of withdrawals, using site-specific information to set instantaneous and daily withdrawal limits for all approved surface water and groundwater withdrawals. They also set low flow protections, known as passby flows, for most approved surface water withdrawals that require withdrawals to cease when stream flow drops below a prescribed threshold level (SRBC, 2016). Passby flows can reduce the frequency of high consumption-to-stream flow events, particularly in the smallest streams (Shank and Stauffer, 2015; U.S. EPA, 2015e).

Overall, there appears to be adequate surface water for hydraulic fracturing in Pennsylvania, West Virginia, and Ohio, but there is still the potential for impacts to both drinking water resource quantity and quality, particularly in small streams, if the rate and timing of withdrawals are not managed (U.S. EPA, 2015e). These potential impacts are expected to be localized in space (i.e.,

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[1] Presently there is a moratorium on hydraulic fracturing in the DRB, which spans Pennsylvania, Delaware, New Jersey, and New York. Habicht et al. (2015) modeled the potential future environmental impact of hydraulic fracturing in the DRB should the moratorium be lifted, allowing hydraulic fracturing to expand into this region in the future.

[2] Aside from direct surface water withdrawals, unmanaged withdrawals from public water systems can cause cross-contamination if there is a loss of pressure, allowing the backflow of pollutants from tank trucks into the distribution system. The state of Ohio has issued a fact sheet relevant to this potential concern, intended specifically for public water systems providing water to oil and gas companies (Ohio EPA, 2012a). To prevent potential cross-contamination, Ohio requires a backflow prevention device at cross-connections. For example, bulk loading stations that provide public supply water directly to tank trucks are required to have an air-gap device at the cross-connection to prevent the backflow of contaminants into the public water system (Ohio EPA, 2012a).

[3] For instance, an increased proportion of organic matter entering a treatment plant may increase the formation of trihalomethanes, byproducts of the disinfection process formed as chlorine reacts with organic matter in the water being treated (Water Research Foundation, 2014).

occurring at specific withdrawal points), and time (e.g., low flow periods). Passby flows appear to be an effective water management tool for reducing the potential for impacts from surface water withdrawals.

4.5.4 North Dakota and Montana

North Dakota was fourth in the number of disclosures in the EPA FracFocus 1.0 project database (5.9% of disclosures) (Appendix Table B-5; Figure 4-4). We combine Montana with North Dakota, because both overlie the Williston Basin (which contains the Bakken play, shown in Figure 4-11), although many fewer wells are reported for Montana (Appendix Table B-5). The Williston Basin is the only basin with significant activity reported for either state, though other basins are also present in Montana (e.g., the Powder River Basin).

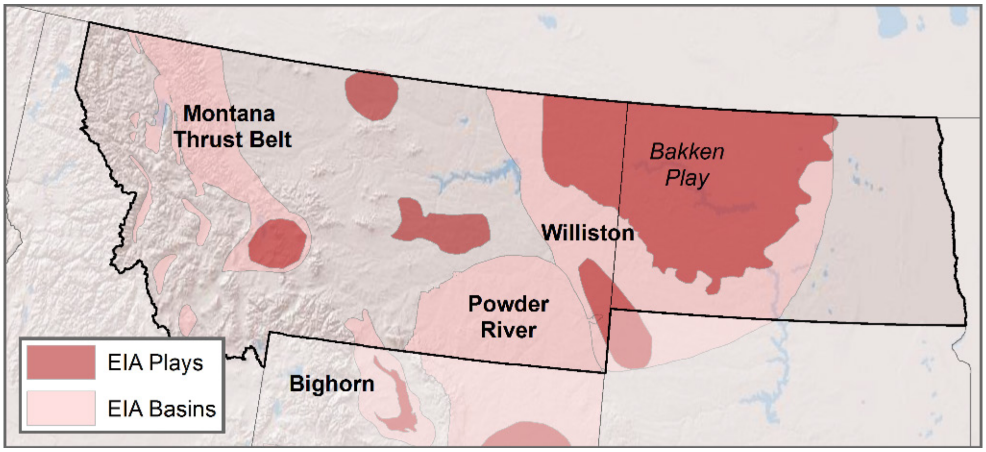

Figure 4-11. Major U.S. EIA shale plays and basins for North Dakota and Montana.
Source: EIA (2015).

Types of water used: Hydraulic fracturing in the Bakken play depends on both ground and surface water resources. Surface water from the Missouri River system provides the largest source of fresh water in the center of Bakken oil development (North Dakota State Water Commission, 2014; EERC, 2011, 2010; North Dakota State Water Commission, 2010). Apart from the Missouri River system, regional surface waters (e.g., smaller streams) do not provide a consistent supply of water for the oil industry due to seasonal stream flow variations. Sufficient stream flows generally occur only in the spring after snowmelt (EERC, 2011). Groundwater from glacial and bedrock aquifer systems has traditionally supplied much of the water needed for Bakken development, but concerns over limited groundwater supplies have led to limits on the number of new groundwater withdrawal permits issued (Ceres, 2014; Plummer et al., 2013; EERC, 2011, 2010; North Dakota State Water Commission, 2010).

The water used for Bakken development is mostly fresh. The EPA FracFocus report shows that “fresh” was the only source of water listed in almost all disclosures reporting a source of water in North Dakota (U.S. EPA, 2015b).[1] Reuse of Bakken wastewater is limited due to its high TDS, which

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[1] Twenty-five percent of North Dakota disclosures included information related to water sources (U.S. EPA, 2015b).

presents challenges for treatment and reuse (Gadhamshetty et al., 2015). Industry is currently researching treatment technologies for reuse of this wastewater (Ceres, 2014; EERC, 2013, 2011).

Water for hydraulic fracturing is commonly purchased from municipalities or other public water systems in the region. The water is often delivered to trucks at water depots or transported directly to well pads via pipelines (EERC, 2011).

Water use per well: Water use per well is intermediate compared with other areas, with a median of 2.0 and 1.6 million gal (7.6 and 6.1 million L) per well in the Williston Basin in North Dakota and Montana, respectively, according to the EPA's FracFocus 1.0 project database (Appendix Table B-5). The North Dakota State Water Commission reports similar volumes (2.2 million gal (8.3 million L) per well on average for North Dakota) in a summary fact sheet (North Dakota State Water Commission, 2014).[1] Scanlon et al. (2016) show that average water use per well in the Bakken play has increased over time, from 580,000 gal (2.2 million L) in 2005 to 3.7 million gal (14.1 million L) in 2014, due in part to the increasing lengths of laterals in horizontal drilling.

In addition to water for hydraulic fracturing, Bakken wells may require "maintenance water" (Scanlon et al., 2016; Scanlon et al., 2014a). This extra water is reportedly needed because of the relatively high salt content of Bakken brine, potentially leading to salt buildup, pumping problems, and restriction of oil flow. Based on estimates from the North Dakota Department of Mineral Resources, Scanlon et al. (2016) report that approximately 400 – 600 gal (1,500 – 2,300 L) per day per each well may be required for well maintenance. Assuming a 15-year lifetime for wells, this could add up to 3.3 million gal (12.5 million L) per well of additional water (Scanlon et al., 2016).

Water use/consumption at the county scale: Water use for fracturing in this region is greatest in the northwestern corner of North Dakota (Gadhamshetty et al., 2015). Hydraulic fracturing water use in 2011 and 2012 averaged approximately 123 million gal (466 million L) per county in the two-state area, with use in McKenzie and Williams Counties in North Dakota exceeding 500 million gal (1.9 billion L) (Appendix Table B-2). There were four counties where 2011 and 2012 average hydraulic fracturing water use was 10% or more of 2010 total water use. Mountrail and Dunn Counties showed the highest percentages (36% and 29%, respectively). Outside of North Dakota's northwest corner, hydraulic fracturing used much less water in the rest of the state and Montana (Table 4-3; Appendix Table B-2).

Potential for impacts: In this region, there are concerns about over-pumping groundwater resources, but the potential for impacts appears to be low provided the Missouri River is determined to be a sustainable and usable source. This finding of a low potential for impacts is also supported by the comparison of hydraulic fracturing water use to water availability at the county scale (Text Box 4-2; Figure 4-6a,b). This area is primarily rural, interspersed with small towns. Residents rely on a mixture of surface water and groundwater for domestic use depending on the county, with most water supplied by local municipalities (Appendix Table B-6).

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[1] The fact sheet is a stand-alone piece, and it is not accompanied by an underlying report.

The state of North Dakota and the U.S. Army Corps of Engineers concluded that groundwater resources in western North Dakota are not sufficient to meet the needs of the oil and gas industry (U.S. Army Corps of Engineers, 2011; North Dakota State Water Commission, 2010). All users combined currently withdraw approximately 6.2 billion gal (23.5 billion L) of water annually in an 11-county region in western North Dakota, already stressing groundwater supplies (U.S. Army Corps of Engineers, 2011). By comparison, the total needs of the oil and gas industry are projected to range from approximately 2.2 and 8.8 billion gal (8.3 and 33.3 billion L) annually by the year 2020 (U.S. Army Corps of Engineers, 2011).

Due to concerns for already stressed groundwater supplies, the state of North Dakota limits industrial groundwater withdrawals, particularly from the Fox Hills-Hell Creek aquifer (Ceres, 2014; Plummer et al., 2013; EERC, 2011, 2010; North Dakota State Water Commission, 2010). Currently, the oil industry is the largest industrial user of water from the Fox Hills-Hell Creek aquifer (North Dakota State Water Commission, 2010). Many farms, ranches, and some communities in western North Dakota rely on flowing wells from this artesian aquifer, particularly in remote areas that lack electricity for pumping; however, low recharge rates and withdrawals throughout the last century have resulted in steady declines in the formation's hydraulic pressure (North Dakota State Water Commission, 2010). Declines in hydraulic pressure do not appear to be associated with impacts to groundwater quality; rather, the state is concerned with maintaining flows for users (North Dakota State Water Commission, 2010).

To reduce demand for groundwater, the state is encouraging the industry to seek surface water withdrawals from the Missouri River system. The North Dakota State Water Commission concluded the Missouri River and its dammed reservoir, Lake Sakakawea, are the only plentiful and dependable water supplies for the oil industry in western North Dakota (North Dakota State Water Commission, 2010). In 2011, North Dakota authorized the Western Area Supply Project, by which Missouri River water (via the water treatment plant in Williston, North Dakota) will be supplied to help meet water demands, including for oil and gas development, of the state's northwest counties (WAWSA, 2011). In July 2012, the U.S. Army Corps of Engineers made available approximately 32.6 billion gal (123 billion L) of water per year from Lake Sakakawea for municipal and industrial water demands over the next ten years (U.S. Army Corps of Engineers, 2011). The Army Corps estimated that the oil and gas industry could use up to 8.8 billion gal (33.3 billion L) annually during this time period in the 11-county surrounding area, and included this as part of the 32.6 billion gal total (123 billion L) to be made available (U.S. Army Corps of Engineers, 2011). For context, annual water use for hydraulic fracturing in all North Dakota counties combined was approximately 2.2 billion gal (8.3 billion L) per year in 2011 and 2012 according to EPA's FracFocus 1.0 project database (Appendix Table B-2). As such, Lake Sakakawea appears to be an adequate resource to meet the water demands of hydraulic fracturing in the region at least in the near term.

4.5.5 Arkansas and Louisiana

Arkansas and Louisiana were ranked seventh and tenth in the number of disclosures in the EPA FracFocus 1.0 project database, respectively (Appendix Table B-5). Hydraulic fracturing activity in Louisiana occurs primarily in the TX-LA-MS Salt Basin, which contains the Haynesville play; activity in Arkansas is dominated by the Arkoma Basin, which contains the Fayetteville play (Figure 4-12).

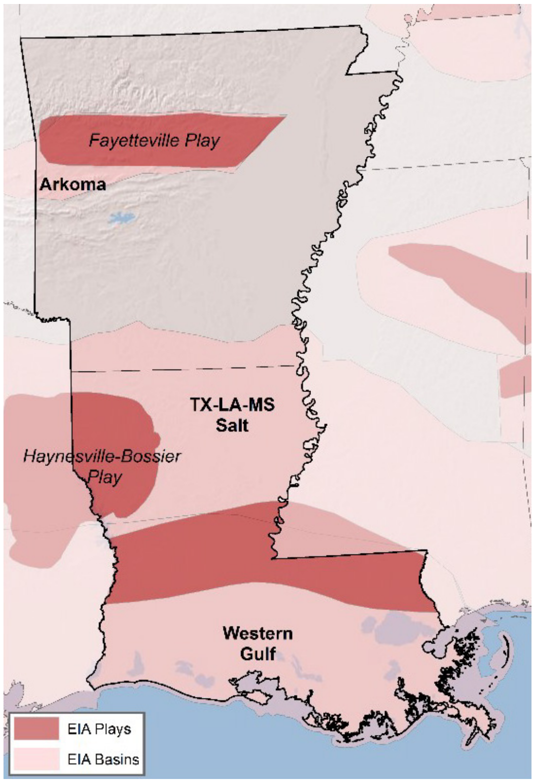

Figure 4-12. Major U.S. EIA shale plays and basins for Arkansas and Louisiana.
Source: EIA (2015).

Types of water used: Surface water is reported as the primary source of water for hydraulic fracturing operations in both Arkansas and Louisiana (ANRC, 2014; LA Ground Water Resources Commission, 2012; STRONGER, 2012). Quantitative information is lacking for Arkansas on the proportion of water sourced from surface versus groundwater. However, data are available for Louisiana, where an estimated 87% of water for hydraulic fracturing in the Haynesville Shale is from surface water (LA Ground Water Resources Commission, 2012) (Table 4-1). In 2008, during the early stages of development, hydraulic fracturing in Louisiana relied heavily on groundwater from the Carrizo-Wilcox aquifer, and concerns for the sustainability of groundwater resources prompted the state to encourage surface water withdrawals (LA Ground Water Resources Commission, 2012).

The EPA FracFocus report suggests that significant reuse of wastewater may occur in Arkansas to offset total fresh water used for hydraulic fracturing; 70% of all disclosures reporting a water source indicated a blend of “recycled/surface,” whereas 3% of disclosures reporting a water source noted “fresh” as the exclusive water source (U.S. EPA, 2015b).[1] According to Veil (2011), Arkansas’

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[1] Ninety-three percent of Arkansas disclosures included information related to water sources (U.S. EPA, 2015b).

Fayetteville Shale wastewater is of relatively good quality (i.e., low TDS), facilitating reuse.[1] Data are generally lacking on the extent to which hydraulic fracturing wastewater is reused in Louisiana.

Water use per well: Arkansas and Louisiana have the highest median water use per well of the states we considered from the EPA FracFocus 1.0 project database, at 5.3 million and 5.1 million gal (20.1 million and 19.3 million L), respectively (Appendix Table B-5).[2]

Water use/consumption at the county scale: On average, hydraulic fracturing uses 408 million gal (1.54 billion L) of water each year in Arkansas counties reporting activity, or 9.3% of 2010 total county water use (26.9% of total county consumption) (Appendix Table B-2). In 2011 and 2012, five counties dominated fracturing water use in Arkansas: Cleburne, Conway, Faulkner, Van Buren, and White Counties (Appendix Table B-2). Van Buren, which is sparsely populated and thus has relatively low total water use and consumption, is by far the Arkansas county highest in hydraulic fracturing water use and consumption relative to 2010 total water use and consumption (56% and 168%, respectively) (Table 4-3).

In Louisiana, hydraulic fracturing water use is concentrated in six parishes in the far northwestern corner of the state, associated with the Haynesville play.[3] On average in 2011 and 2012, hydraulic fracturing used 117 million gal (443 million L) of water annually per parish, representing approximately 3.6% and 10.8% of 2010 total water use and consumption, respectively (Appendix Table B-2). Operators in DeSoto Parish used the most water (over 1 billion gal (3.8 billion L) annually). Hydraulic fracturing water use and consumption was highest relative to 2010 total water use and consumption (35.5% and 83.2%, respectively) in Red River Parish (Table 4-3). These numbers may be low estimates, since Louisiana required disclosures to the state or FracFocus, and Arkansas required disclosures to the state but not FracFocus, during the time period analyzed (U.S. EPA, 2015b) (Appendix Table B-5).

Potential for impacts: Water availability is generally higher in Arkansas and Louisiana than in states farther west, reducing the potential for impacts to drinking water quantity and quality (Figure 4-6a, Figure 4-7a; Text Box 4-2). However, generally high water availability in this region does not preclude the potential for impacts at the local scale, particularly if surface water withdrawals occur during seasonal low flow periods. For instance, precipitation is highest in Arkansas in the late autumn and winter, with little rainfall occurring in the late spring and summer; thus, most small streams do not flow year round (Entrekin et al., 2015). Hydraulic fracturing surface water withdrawals from small streams during seasonal low flows have the potential to impact the quantity and quality of drinking water resources.

Additionally, in northwestern Louisiana, there are concerns about over-pumping of groundwater resources. Prior to 2008, most operators in the Louisiana portion of the Haynesville Shale used groundwater, withdrawing from the Carrizo-Wilcox, Upland Terrace, and Red River Alluvial aquifer

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[1] Veil (2011) reports a range of 20,000-25,000 ppm TDS for Fayetteville Shale wastewater.

[2] According to STRONGER (2012) and STRONGER (2011a), both states require disclosure of information on water use per well, but this has not been synthesized into state level reports to date.

[3] Louisiana is divided into parishes, which are similar to counties in other states.

systems (LA Ground Water Resources Commission, 2012). To mitigate stress on groundwater, the state issued a water use advisory to the oil and gas industry that recommended Haynesville Shale operators seek alternative water sources to the Carrizo-Wilcox aquifer, which is predominantly used for public supply (LDEQ, 2008). Operators then transitioned to mostly surface water, with a smaller groundwater component (approximately 13% of all fracturing water used) (LA Ground Water Resources Commission, 2012). Of this groundwater component, the majority (approximately 74%) still came from the Carrizo-Wilcox aquifer (LA Ground Water Resources Commission, 2012).

Although the potential for hydraulic fracturing withdrawals to affect water supplies and water quality in the aquifer was reduced, it was not entirely eliminated. Despite Louisiana's water use advisory, a combination of drought conditions and higher than normal withdrawals (for all uses, not solely hydraulic fracturing) from the Carrizo-Wilcox and Upland Terrace aquifers caused several water wells to go dry in July 2011 (LA Ground Water Resources Commission, 2012). In August 2011, a groundwater emergency was declared for southern Caddo Parrish (LA Ground Water Resources Commission, 2012). Hydraulic fracturing withdrawals contributed to these conditions, alongside other users of water and the lack of precipitation.

4.6 Chapter Synthesis

In this chapter, we examined the potential for water acquisition for hydraulic fracturing to impact the quantity and quality of drinking water resources, and identified factors affecting the frequency or severity of impacts. Whether impacts occur from water acquisition for hydraulic fracturing depends on the local balance between water withdrawals and availability, and this balance can be modified by a combination of site or regional-specific factors. For this reason, information is needed at the local scale to determine whether impacts actually occur, yet this information is not available in many locations where hydraulic fracturing takes place; see Section 4.6.3 on Uncertainties below. Despite these limitations, our chapter used the scientific literature, county level assessments, and, where available, local case studies to point to areas with a higher potential for impacts; understand local dynamics, including example cases of impacts; and identify common factors that increase or decrease the frequency or severity of impacts. In this section, we summarize our major findings regarding hydraulic fracturing water acquisition activities, potential impacts, and these common factors (4.6.1 and 4.6.2). We then discuss uncertainities (4.6.3), and provide final conclusions (4.6.4).

4.6.1 Major Findings

The first half of this chapter focused on water acquisition activities, providing an overview of the types of water used (including sources, quality, and provisioning), water use per well, and water use and consumption at the national, state, and county scale. The three major types of water used for hydraulic fracturing are surface water, groundwater, and reused hydraulic fracturing wastewater. Because trucking can be a major expense, operators tend to use water sources as close to the well pad as possible. Operators usually self-supply surface water or groundwater directly, but may also obtain water from public water systems or other suppliers. Hydraulic fracturing operations in the eastern United States rely predominantly on surface water, whereas operations in more semi-arid to arid western states use either surface water or groundwater. There are areas of the country that rely entirely on groundwater supplies (e.g., western Texas).

Reuse of wastewater reduces the demand on fresh water sources, which currently supply the vast majority of water used for hydraulic fracturing. The proportion of the water used in hydraulic fracturing that comes from reused hydraulic fracturing wastewater is generally low; in a survey of literature values from 10 states, basins, or plays, we found a median value of 5%, with this percentage varying by location (Table 4-2).[1] Available data on reuse trends indicate increasing reuse of wastewater over time in both Pennsylvania and West Virginia, likely due to the lack of nearby disposal options in Class II wells. Reuse as a percentage of water injected is typically lower in other areas of the United States, likely in part because of the availability of disposal wells; see Chapter 8 for more information.

The median amount of water used nationally per hydraulically fractured well was approximately 1.5 million gal (5.7 million L) in 2011 through early 2013 based on the EPA analysis of FracFocus disclosures (U.S. EPA, 2015b, c). This increased to approximately 2.7 million gal (10.2 million L) in 2014, driven by a proportional increase in horizontal wells (estimated from data in Gallegos et al., 2015). These national estimates represent a variety of fractured well types, including types requiring much less water per well than horizontal shale gas wells. Thus, published estimates for horizontal shale gas wells are typically higher (e.g., approximately 4 million gal (15 million L) per well (Vengosh et al., 2014), and should not be applied to all fractured wells to derive national estimates. There was also wide variation within and among states and basins in the median per well water volumes reported in 2011 and 2012, from more than 5 million gal (19 million L) in Arkansas and Louisiana to less than 1 million gal (3.8 million L) in Colorado, Wyoming, Utah, New Mexico, and California (U.S. EPA, 2015c). This variation can result from several factors, including geologic formation, well length, and fracturing fluid formulation.

Hydraulic fracturing uses billions of gallons of water every year at the national and state scales, and even in some counties. When expressed relative to total water use or consumption at these scales, however, hydraulic fracturing generally accounts for only a small percentage, usually less than 1%. These percentages are higher though in specific counties. Annual hydraulic fracturing water use was 10% or more compared to 2010 total water use in 6.5% of counties with FracFocus disclosures in 2011 and 2012 in the EPA FracFocus 1.0 project database, 30% or more in 2.2% of counties, and 50% or more in 1.0% of counties (Appendix Table B-2). Consumption estimates follow the same pattern, with higher percentages in each category: hydraulic fracturing water consumption was 10%, 30%, and 50% or more of 2010 total water consumption in 13.5%, 6.2%, and 4.0% of counties with FracFocus disclosures in the EPA FracFocus 1.0 project database (Appendix Table B-2). Thus, hydraulic fracturing represents a relatively large user and consumer of water in these counties.

Whether water quantity or quality impacts occur from water acquisition for hydraulic fracturing depends on the local balance between water withdrawals and availability. From our survey of the literature and our county level assessments, southern and western Texas appear to have the

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[1] Note that reused water as a percentage of total water injected differs from the percentage of wastewater that is reused. See Section 4.2 and Chapter 8 for more information.

highest potential for impacts of the areas assessed in this chapter, given the combination of high hydraulic fracturing water use, relatively low water availability, intense periods of drought, and reliance on declining groundwater resources; see Section 4.6.2 on Factors below. Importantly, our results do not preclude the possibility of local water impacts in areas with comparatively lower potential, nor do they necessarily mean impacts have occurred in the high potential areas. Our survey, however, provides an indicator of areas with higher *potential* for impacts, and could be used to target resources or future studies.

In two example cases, local impacts to drinking water resources occurred in areas with increased hydraulic fracturing activity. In a detailed case study, Scanlon et al. (2014b) observed generally adequate water supplies for hydraulic fracturing in the Eagle Ford play in southern Texas, except in specific locations. They found excessive drawdown of groundwater locally, with estimated declines of ~100-200 ft (30-60 m) in a small proportion of the play (~6% of the area) after hydraulic fracturing activity increased in 2009. In 2011, drinking water wells in an area overlapping with the Haynesville Shale ran out of water due to higher than normal groundwater withdrawals and drought (LA Ground Water Resources Commission, 2012). Hydraulic fracturing water withdrawals contributed to these conditions, along with other water users and the lack of precipitation. By contrast, two EPA case studies in the Upper Colorado and the Susquehanna River Basins found minimal impacts from hydraulic fracturing withdrawals currently (U.S. EPA, 2015e) (Sections 4.5.2, 4.5.3).

These site-specific findings emphasize the need to focus on regional and local dynamics when considering the impacts from hydraulic fracturing water withdrawals. The case studies and the scientific literature as a whole suggest some common factors that increase or decrease the frequency or severity of impacts. These are summarized in the section below.

4.6.2 Factors Affecting Frequency or Severity of Impacts

The potential for impacts depends on the combination of water withdrawals and water availability at a given withdrawal location. Where water withdrawals are relatively low compared to water availability, impacts are unlikely to occur. Where water withdrawals are relatively high compared to water availability, impacts are more likely.

Areas reliant on declining groundwater are particularly vulnerable to more frequent and severe impacts from cumulative water withdrawals, including withdrawals for hydraulic fracturing. Groundwater recharge rates can be extremely low, and groundwater pumping is exceeding recharge rates in many areas of the country (Konikow, 2013). When pumping exceeds recharge, the cumulative effects of withdrawals are manifested in declining water levels. For this reason, water levels in many aquifers in the United States have declined substantially over the last century (Konikow, 2013). Cumulative drawdowns can affect surface water bodies since groundwater can be the source of base flow in streams (Winter et al., 1998), and alter groundwater quality by mobilizing chemicals from geologic sources, among other means (DeSimone et al., 2014; Alley et al., 1999). Although in many of these areas (e.g., the Ogallala aquifer), irrigated agriculture is the dominant user of groundwater, hydraulic fracturing withdrawals now also contribute to declining groundwater levels. Hydraulic fracturing groundwater consumption, for example, exceeds estimated recharge rates in the seven most active hydraulic fracturing counties in the Eagle Ford Shale in southern Texas (Steadman et al., 2015). When necessary, state and local governments have encouraged or mandated industry to use surface water over groundwater, as evidenced in both Louisiana and North Dakota.

Among surface water sources, smaller streams, even in humid areas, are more vulnerable to frequent and severe impacts from withdrawals. A detailed EPA case study found that streams with the smallest contributing areas in northeastern Pennsylvania were particularly vulnerable to withdrawals (U.S. EPA, 2015e). Protecting smaller streams from excessive withdrawals is probably most important for aquatic life, but may also protect drinking water quantity and quality in certain instances.

Seasonal or long-term drought can also make impacts more frequent and severe for surface water and groundwater sources. Hot, dry weather depletes surface water bodies and reduces or prevents groundwater recharge, while water demand often increases simultaneously (e.g., for irrigation). The EPA case study in Pennsylvania found that even large streams could be vulnerable to withdrawals during times of low flows (U.S. EPA, 2015e). Much of the western United States has experienced prolonged periods of drought over the last decade (Figure 4-8). This dynamic will likely be magnified by future climate change in certain locations (Meixner et al., 2016).

By contrast to the above factors, consumption of water for hydraulic fracturing does not appear to substantially influence the frequency or severity of impacts. There are concerns that hydraulic fracturing permanently removes water from the hydrologic cycle, posing a threat to long-term water supplies. Since impacts occur locally and depend on the local water balance, impacts can occur regardless of whether the water is withdrawn and returned to the larger hydrologic cycle elsewhere or whether it is permanently sequestered underground. We acknowledge that whether the water is returned to the larger hydrologic cycle may make a difference for the water budget of a larger area, such as on the state, regional, or national scale. For example, water converted to steam during thermoelectric cooling in one location may condense and fall as precipitation in an adjacent state or region. At these larger scales, however, hydraulic fracturing water consumption is a very small fraction of total water availability.[1] Plus, at these scales, there are other larger factors that can affect regional water budgets, but which are out of scope for this assessment.[2] For these reasons, focusing on consumption distracts from the more salient issue that impacts depend upon the spatial and temporal balance between local water withdrawals and availability.

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[1] For example, hydraulic fracturing used approximately 3.3 billion gal (12.5 billion L) of water on average annually in all Colorado counties with hydraulic fracturing activities combined according to FracFocus disclosures in 2011 and 2012 (Appendix B-1). Using the consumption rate of 82.5% yields a consumption estimate of approximately 2.7 billion gal (10.2 billion L). This would be approximately 0.1% of the fresh water and total water availability metrics used in Textbox 4-2 for all of those same counties combined (approximately 2.6 trillion gal (9.8 trillion L) of fresh water and total water available).

[2] The combustion of methane produced by hydraulic fracturing, for example, adds water molecules to the environment, and at large scales, this may affect regional water budgets. However, quantifying this is outside the scope of this assessment. Similarly, there are other larger factors (e.g., water used for cooling thermoelectric power plants) that can affect regional water budgets, but these are also outside the scope of this assessment.

There are also factors that can decrease the frequency and severity of any impacts from water withdrawals. The literature suggests that water management, particularly wastewater reuse, the use of brackish groundwater, the use of passby flows, and transitioning from limited groundwater sources to more abundant surface water sources can reduce impacts. Reuse is not a universal solution, since in many areas of the country wastewater volumes from one well are often a small percentage of the water needed to fracture the next well. In the Marcellus Shale, for instance, 100% reuse of the wastewater produced from one well means reducing fresh water demand by 10 or 30% for the next (Section 4.2.1; Chapter 7). Nevertheless, reuse can be an important local factor reducing fresh water demand.

Switching to brackish water is another means by which fresh water demand can be—and is in some locations—reduced. This is a source of alternative water in western and southern Texas, for example. In these areas, use of brackish water is currently reducing impacts to fresh water sources, and could with continued use reduce future impacts (Scanlon et al., 2014b; Nicot et al., 2012). Our county level estimates suggest that brackish water could readily meet the volume demanded by hydraulic fracturing in Texas.

Water management also includes passby flows, a low stream flow threshold below which withdrawals are not allowed. Evidence suggests passby flows can be effective in protecting streams from hydraulic fracturing water withdrawals (U.S. EPA, 2015e). Finally, as evidenced by examples in both North Dakota and Louisiana, water management may include transitioning from declining groundwater sources to surface water, if available.

4.6.3 Uncertainties

There are several uncertainties inherent in our assessment of the potential impacts of water acquisition for hydraulic fracturing. The largest uncertainties stem from the lack of literature and data on this subject at local scales. Because impacts occur at a given withdrawal point, our assessment could assess the potential for impacts, but often could not determine if potential impacts were realized in the absence of local data. The exceptions were local case studies from the Eagle Ford play in Texas, the Upper Colorado River Basin in Colorado, and the Susquehanna River Basin in Pennsylvania. Moreover, it is also not clear if local impacts, for example a drinking water well going dry, are likely to be documented in the scientific literature.

Other uncertainties arise from data limitations on the volume and types of water used or consumed for hydraulic fracturing, future water use projections, and water availability estimates. There are no nationally consistent data sources, and therefore, water use estimates must be based on multiple, individual pieces of information. For example, in their National Water Census, the USGS includes hydraulic fracturing in the broader category of "mining" water use, but hydraulic fracturing water use is not reported separately (Maupin et al., 2014). There are locations where average annual hydraulic fracturing water use in 2011 and 2012 in the EPA FracFocus 1.0 project database exceeded total mining water use in 2010, and one county where it exceeded all water use (U.S. EPA, 2015c; Maupin et al., 2014). This could be due to a rapid increase in hydraulic fracturing water use, differences in methodology between the two databases (i.e., the USGS 2010 National Water Census and the EPA FracFocus 1.0 project database), or both.

We used the EPA FracFocus 1.0 project database for water use estimates, which itself has limitations. Many states in the project database did not require disclosure to FracFocus during the time period analyzed (U.S. EPA, 2015b). We conclude that this likely does not change the overall hydraulic fracturing water use patterns observed across the United States (Text Box 4-1), but could affect particular county level estimates. Also, the database covered the time period of 2011 through early 2013. Thus, changes in the industry since then are not reflected in these data.

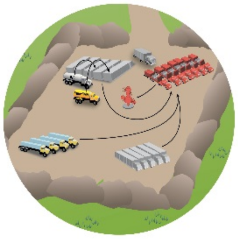
Hydraulic fracturing water use data that are often provided as water use associated with a particular well. While this is valuable information, the potential impacts of water acquisition for hydraulic fracturing could be better assessed if data were also available at the withdrawal point. If the total volume, date, location, and type (i.e., surface water or groundwater; and fresh, brackish, or reused wastewater) of each water withdrawal were documented, effects on availability could be better estimated. For example, surface withdrawal points could be aggregated by watershed or aquifer to estimate effects on downstream flow, groundwater levels, and water quality. Some of this information is available in disparate forms, but the lack of nationally consistent data on water withdrawal locations, timing, and amounts—data that are publicly available, easy to access and analyze—limits our assessment of potential impacts. The Susquehanna River Basin Commission collects this type of detailed data on hydraulic fracturing water withdrawals, but this type of information is not widely available across the nation.

Future hydraulic fracturing water use is also a source of uncertainty. Because water withdrawals and potential impacts are concentrated in certain localized areas, water use projections need to match this scale. Projections are available for Texas at the county scale, but more information at the county or sub-county scale is needed in other states with hydraulic fracturing activity and water availability concerns (e.g., northwest North Dakota, eastern Colorado). Due to a lack of data, we generally could not assess future water use and the potential for impacts in most areas of the country, nor could we examine these in combination with other relevant factors (e.g., climate change or population growth).

4.6.4 Conclusions

With notable exceptions, hydraulic fracturing uses and consumes a relatively small percentage of water when compared to total use, consumption, and availability at the national, state, and county scale. Despite this, impacts on drinking water resource quantity and quality from hydraulic fracturing water acquisition can occur at the local scale, because hydraulic fracturing water withdrawals are often concentrated in space and time, and impacts depend upon the local balance between withdrawals and availability. In two example cases, local impacts to drinking water resource quantity occurred in areas with increased hydraulic fracturing activity (e.g., in Texas's Eagle Ford play, and in Louisiana's Haynesville Shale). Declining groundwater resources, especially in the western United States, are particularly vulnerable to withdrawals, as are smaller streams, even in the more humid East. Finally, there are factors that increase or decrease the frequency and severity of impacts—included in this are times of low water availability, such as during drought, which can increase the frequency and severity of impacts, or conversely water management practices (e.g., shifting to brackish water, or passby flows), which can help protect drinking water resources.

Chapter 5. Chemical Mixing



Abstract

This chapter provides an analysis of the potential impacts on drinking water resources during the chemical mixing stage of the hydraulic fracturing water cycle and the factors governing the frequency and severity of these impacts. The chemical mixing stage includes the mixing of base fluid (90% to 97% by volume, typically water), proppant (2% to 10% by volume, typically sand), and additives (up to 2% by volume) on the well pad to make hydraulic fracturing fluid. This fluid is engineered to create and extend fractures in the targeted formation and to carry proppant into the fractures. Concentrated additives are delivered to the well pad and stored on site, often in multiple, closed containers, and moved around the well pad in hoses and tubing.

Changes in drinking water quality can occur if spilled fluids reach groundwater or surface water resources. In this assessment, a spill is considered to be any release of fluids. The EPA's analysis found that spills and releases of chemicals and fluids have occurred during the chemical mixing stage and have reached soil and surface water receptors. Spills of hydraulic fracturing fluids or additives included in the analysis had a median spill volume of 420 gal (1,590 L), with a range of 5 to 19,320 gal (9 to 72,130 L). Spills were caused most often by equipment failure or human error. The potential for spilled fluids to reach, and therefore impact, groundwater or surface water resources depends on the composition of the spilled fluid, spill characteristics, spill response activities, and the fate and transport of the spilled fluid.

The movement of spilled hydraulic fracturing fluids and chemicals through the environment is difficult to predict, because spills are site- and chemical-specific, and because hydraulic fracturing-related spills are typically complex mixtures of chemicals. Physicochemical properties, which depend on the molecular structure of a chemical, govern whether spilled chemicals volatilize, sorb, transform, and travel. Spill prevention practices and spill response activities can prevent spilled fluids from reaching ground or surface drinking water resources.

The severity of potential impacts on water quality from spills of additives or hydraulic fracturing fluids depends on the identity and amount of chemicals that reach ground or surface water resources, the hazards associated with the chemicals, and the characteristics of the receiving water body. The lack of monitoring following spills, along with the lack of publicly available information on the composition of additives and fracturing fluids, containment and mitigation measures in use, the proximity of chemical mixing to drinking water resources, and the fate and transport of spilled fluids limits the EPA's ability to fully assess potential impacts on drinking water resources and their frequency and severity. This chapter shows that spills of additives and hydraulic fracturing fluids during the chemical mixing stage of the hydraulic fracturing water cycle have occurred and have reached and impacted drinking water resources.

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5. Chemical Mixing

5.1 Introduction

This chapter provides an analysis of the potential impacts on drinking water resources during the chemical mixing stage of the hydraulic fracturing water cycle and the factors governing the frequency and severity of these impacts. Chemical mixing is a complex process that requires the use of specialized equipment and a range of different additives to produce the fluid that is injected into a well to fracture the formation. This fluid, the hydraulic fracturing fluid, generally consists of a base fluid (typically water), a proppant (typically sand), and additives (chemicals), although there is no standard or single composition of hydraulic fracturing fluid used. The number, type, and amount of chemicals used to create the hydraulic fracturing fluid vary from well to well based on site- and operator-specific factors. Spills may occur at any point in the chemical mixing process.[1] The potential for spilled fluids to reach, and therefore impact, ground or surface water resources depends on the composition of the spilled fluid, spill characteristics, spill response activities, and the fate and transport of the spilled fluid. This chapter is structured around these concepts.

The chapter starts by discussing the characteristics of hydraulic fracturing fluids (Sections 5.2 to 5.4). This includes an introductory overview of the chemical mixing process (Section 5.2), a description of the different components of the hydraulic fracturing fluid (Section 5.3), the range of different chemicals used and their classes, the most frequently used chemicals nationwide, and volumes used (Section 5.4).[2] (Appendix H provides a list of chemicals that the EPA identified as being used in hydraulic fracturing fluids.)

The chapter continues with a discussion on how chemicals are managed on the well pad, the characteristics of spills when they occur, and spill response activities (Sections 5.5 to 5.7). This includes a description on how potential impacts of a spill on drinking water resources depends upon chemical management practices, such as storage, on-site transfer, and equipment maintenance (Section 5.5). A summary analysis of reported spills and their common causes at hydraulic fracturing sites is then presented (Section 5.6). Then, there is a discussion on the different efforts of spill prevention, containment, and mitigation (Section 5.7).

Next, the fate and transport of spilled chemicals is discussed (Section 5.8). This section includes how a chemical can move through the environment and transform, and what governs exposure concentrations of chemicals in the environment. Due to the complexities of the processes and the site-specific and chemical-specific nature of spills, it is difficult to develop a full assessment of their fate and transport. This section provides a general overview and discusses how the fate and transport of a chemical depends on site conditions, environmental conditions, physicochemical

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[1] In this assessment, a spill is considered to be any release of fluids. Spills can result from accidents, fluid management practices, or illegal dumping.

[2] Chemical classes are groupings of different chemicals based on similar features, such as chemical structure, use, or physical properties. Examples of chemical classes include hydrocarbons, alcohols, acids, and bases.

properties of the released chemicals, fluid composition, volume of the release, the proximity to a drinking water resource, and the characteristics of the drinking water resource that is the receptor.

Next is an overview of on-going changes in chemical use in hydraulic fracturing, with an emphasis on industry efforts to reduce potential impacts from surface spills by using fewer and safer chemicals (Section 5.9). The chapter concludes by providing a synthesis, including a summary of findings, factors that affect frequency and severity of potential impacts, and a discussion of uncertainties and data gaps (Section 5.10).

Due to the limitations of available data and the scope of this assessment, it is not possible to provide a detailed analysis of all of the factors listed above. Data limitations preclude a quantitative analysis of the likelihood or severity of chemical spills or impacts. Spills that occur off-site, such as those during transportation of chemicals to the site or storage of chemicals in staging areas, are out of the scope of this assessment. This chapter qualitatively characterizes the potential for impacts on drinking water resources given the current understanding of overall operations and specific components of the chemical mixing process.

5.2 Chemical Mixing Process

Understanding the chemical mixing process is necessary to understand how, why, and when spills might occur. This section provides a general overview of the chemical mixing stage of the hydraulic fracturing water cycle (Carter et al., 2013; Knappe and Fireline, 2012; Spellman, 2012; Arthur et al., 2008). Figure 5-1 shows a hydraulic fracturing site during the chemical mixing process. In our discussion, we focus on the types of additives used at each phase of the process. While similar processes are used to fracture horizontal and vertical wells, a horizontal well treatment is described here. Horizontal well treatments are likely to be more complex and therefore illustrative of the variety of practices that have become more prevalent over time with advances in technology (Chapter 3). A water-based system is described, because water is the most commonly used base fluid, appearing in more than 93% of FracFocus 1.0 disclosures between January 1, 2011 and February 28, 2013 (U.S. EPA, 2015a).[1] While the number and types of additives may vary widely, the basic chemical mixing process and the on-site layout of hydraulic fracturing equipment are similar across sites (BJ Services Company, 2009). Equipment used in the chemical mixing process typically consists of chemical storage trucks, water supply tanks, proppant supply, slurry blenders, a number of high-pressure pumps, a manifold, surface lines and hoses, and a central control unit. Detailed descriptions of specific additives and the equipment used in the process are provided in Sections 5.3 and 5.5, respectively.

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[1] FracFocus (www.fracfocus.org) is a registry of information of water and chemical use in wells in which hydraulic fracturing is conducted. More details are provided in Text Box 5-1.

Figure 5-1. Representative hydraulic fracturing site showing equipment used on-site during the chemical mixing process.
The frac well head is located in the center bottom (green), the manifold runs down the middle, and high pressure pumps lead into the manifold from either side. Source: Schlumberger.

At a newly-drilled production well, the chemical mixing process begins after the drilling, casing, and cementing processes are finished and hydraulic fracturing equipment has been set up and connected to the well. The process can generally be broken down into one or more sequential stages with specific chemicals added at different phases during each stage phase to achieve a specific purpose (Knappe and Fireline, 2012; Fink, 2003). The process for water-based hydraulic fracturing is described in Figure 5-2 below.

The first phase is the cleaning and preparation of the well. The fluid used in this phase is often referred to as the pre-pad fluid, pre-pad volume, or spearhead. Acid is typically the first chemical introduced. Acid, with a concentration of 3% to 28% (by volume, typically hydrochloric acid, HCl), is used to clean any cement left inside the well from cementing the casing and dissolve any pieces of rock that may remain in the well that could block the perforations.[1] Acid is typically pumped directly from acid storage tanks or tanker trucks, without being mixed with other additives. The first, or pre-pad, phase may also involve mixing and injection of additional chemicals to facilitate the flow of fracturing fluid introduced in the next phase of the process. These additives may include biocides, corrosion inhibitors, friction reducers, and scale inhibitors (Carter et al., 2013; King, 2012; Knappe and Fireline, 2012; Spellman, 2012; Arthur et al., 2008).

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[1] Prior to the injection of the pad fluid, for wells that are cased in the production zone, the well casing is typically perforated to provide openings through which the pad fluid can enter the formation. A perforating gun is typically used to create small holes in the section of the well being fractured. The perforating gun is lowered into position in the horizontal portion of the well. An electrical current is used to set off small explosive charges in the gun, which creates holes through the well casing and out a short distance into the formation (Gupta and Valkó, 2007).

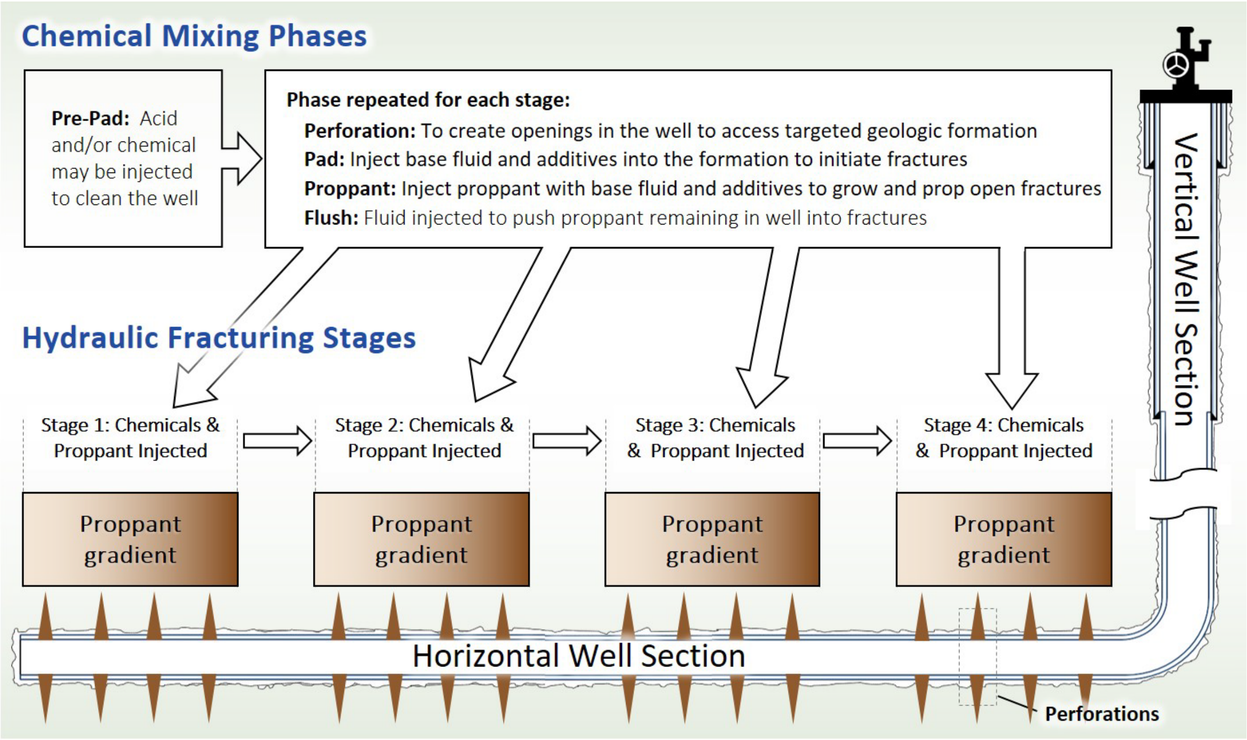

Figure 5-2. Overview of a chemical mixing process of the hydraulic fracturing water cycle.
This figure outlines the chemical mixing process for a generic water-based hydraulic fracture of a horizontal well. The chemical mixing phases outline the steps taken at the surface in the overall fracturing job, while the hydraulic fracturing stages outline how each section of the horizontal well would be fractured beginning with the toe of the well, shown on left-side. The proppant gradient represents how the proppant size may change within each stage of fracturing as the fractures are elongated. The chemical mixing process is repeated depending on the number of stages used for a particular well. The number of stages is determined in part by the length of the horizontal leg. In this figure, four stages are represented, but typically, a horizontal fracturing treatment would consist of 10 to 20 stages per well (Lowe et al., 2013). Fracturing has been reported to be done in as many as 59 stages (Pearson et al., 2013).

In the second phase, a hydraulic fracturing fluid, typically referred to as the pad or pad volume, is mixed, blended, and pumped down the well under high pressure to create fractures in the formation.[1] The pad is a mixture of base fluid, typically water, and additives and is designed to create, elongate, and enlarge fractures in the targeted geologic formation when injected under high pressure (Gupta and Valkó, 2007) (see Section 6.3 for additional information on fracture growth following injection). A typical pad consists of, at minimum, a mixture of water and friction reducer. A typical pad consists of, at minimum, a mixture of water and friction reducer. Other additives (see U.S. EPA (2015a) and Table 5-1) may be used to facilitate flow and kill bacteria (Carter et al., 2013; King, 2012; Knappe and Fireline, 2012; Spellman, 2012; Arthur et al., 2008). The pad is pumped into the formation through perforations or sliding sleeves in the well casing.

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[1] In terms of chemical mixing, "pad" is a term used to describe hydraulic fracturing fluid without solid at the start of the fracturing of the formation. In terms of the entire hydraulic fracturing process, the "well pad" or "pad" is the area of land where drilling occurs.

In the third phase, proppant, typically sand, is mixed into the hydraulic fracturing fluid. The proppant volume, as a proportion of the injected fluid, is increased gradually until the desired concentration in the fractures is achieved. Gelling agents, if used, are also mixed with the proppant and base fluid in this phase to increase the viscosity to help carry the proppant. Additional chemicals may be added to gelled fluids, initially to maintain viscosity and later to break down the gel and decrease viscosity, so the hydraulic fracturing fluid can more readily flow back out of the formation and through the well to facilitate production from the fractured formation (Carter et al., 2013; King, 2012; Knappe and Fireline, 2012; Spellman, 2012; Arthur et al., 2008).

A final flush or clean-up phase may be conducted after the stage is fractured, with the primary purpose of maximizing well productivity. The flush is a mixture of water and additives that work to aid the placement of the proppant, clean out the chemicals injected in previous phases, and prevent microbial growth in the fractures (Knappe and Fireline, 2012; Fink, 2003).

The second, third, and fourth phases are repeated multiple times in a well with multi-stage hydraulic fracturing. For each stage, the well is typically perforated and fractured beginning at the end, or toe, of the well and proceeding backwards toward the bend or heel of the well, near the vertical section. In vertical wells, stages typically begin in deeper portions of the well and proceed shallower. Each fractured stage is isolated before the next stage is fractured. The number of stages sets how many times the chemical mixing process is repeated at the site surface (Figure 5-2). The number of stages increases with longer intervals of the well subjected to hydraulic fracturing (Carter et al., 2013; King, 2012; Knappe and Fireline, 2012; Spellman, 2012; Arthur et al., 2008).

The number of stages per well can vary, with several sources suggesting between 10 and 20 stages is typical (GNB, 2015; Lowe et al., 2013).[1] The full range reported in the literature is much wider, with one source documenting between 1 and 59 stages per well (Pearson et al., 2013) and others reporting values within this range (NETL, 2013; STO, 2013; Allison et al., 2009). The number of stages per well seems to have increased over time. One study reports that the average number of stages per horizontal well rose from approximately 10 in 2008 to 30 in 2012 (Pearson et al., 2013). As more stages are used, the total volume of hydraulic fracturing fluid and chemicals increase. This increases the potential, frequency, and severity of surface spills associated with chemical mixing and thus potential impacts on drinking water resources.

In each of these phases, water is usually the primary component of the hydraulic fracturing fluid, though the exact composition of the fluid injected into the well changes over the duration of each stage. In water-based hydraulic fracturing, the composition, by volume, of a typical hydraulic fracturing fluid is 90% to 97% water, 2% to 10% proppant, and 2% or less additives (Carter et al., 2013; Knappe and Fireline, 2012; SWN, 2011).[2]

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[1] The number of stages has been reported to be 6 to 9 in the Huron in 2009 (Allison et al., 2009), 13 to 32 in the Marcellus (NETL, 2013), and up to 40 by STO (2013).

[2] This range is based on a compilation of sources. Sources present compositions as by mass, by volume, or without specificity. Because of non-additive volumes, the composition by volume can be different before and after mixing. By mass: 90% water, 8-9% proppant, 0.5 to 1.5% additives (Knappe and Fireline, 2012); 88% water, 11% proppant, <1%

5.3 Overview of Hydraulic Fracturing Fluids

Hydraulic fracturing fluids are formulated to perform specific functions: create and extend the fracture and transport and place the proppant in the fractures (Montgomery, 2013; Spellman, 2012; Gupta and Valkó, 2007).[1] The hydraulic fracturing fluid generally consists of three parts: (1) the base fluid, which is the largest constituent by volume, (2) the additives, and (3) the proppant. Additives, which can be a single chemical or a mixture of chemicals, are chosen to serve a specific purpose in the hydraulic fracturing fluid (e.g., friction reducer, gelling agent, crosslinker, biocide) (Spellman, 2012). Throughout this chapter, "chemical" is used to refer to an individual chemical substance (e.g., methanol, petroleum distillates).[2] Proppants are small particles, usually sand, mixed with fracturing fluid to hold fractures open so that the target hydrocarbons can flow from the formation through the fractures and up the wellbore. The combination of additives, and the mixing and injection process, varies based on a number of factors as discussed below. The additive combination determines the amount and type of equipment required for storage and, therefore, contributes to the determination of the potential for spills and impacts of those spills.

The particular composition of a hydraulic fracturing fluid is designed based on empirical experience, the geology and geochemistry of the production zone, economics, goals of the fracturing process, availability of the desired chemicals, and preference of the service company or operator (Montgomery, 2013; ALL Consulting, 2012; Klein et al., 2012; Ely, 1989).[3] No single set of specific chemicals is used at every site. Multiple types of fracturing fluids may be appropriate for a given site, and any given type of fluid may be appropriate at multiple sites. For the same type of fluid formulation, there can be differences in the additives, chemicals in those additives, and the concentrations selected. There are broad criteria for hydraulic fracturing fluid selection based on the targeted production zone temperature, pressure, water sensitivity, and permeability (Gupta and Valkó, 2007; Elbel and Britt, 2000). Figure 5-3 provides a general overview of the types of decisions to determine which fluid can be used for different situations. Similar fluids may be appropriate for different formations. For example, crosslinked fluids with 25% nitrogen foam (titanate or zirconate crosslink + 25% nitrogen) can be used in both gas and oil wells with high temperatures and

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additive (as median maximum concentration) (U.S. EPA, 2015a), 94% water, 6% proppant, <1% additive (Sjolander et al., 2011), 88% water, 11% proppant, <1% additive (OSHA, 2014a, b). By volume: 95% water, 5% proppant, <1% additive (before mixing), 97% water, 2% proppant, <1% additive (after mixing) (Sjolander et al., 2011), 90% water, 10% proppant, <1% additive (before mixing), 95% water, 5% proppant, <1% additive (after mixing) (OSHA, 2014a, b), 98-99.5%, water and sand 0.5 to 2% additives (Spellman, 2012). Not specified: 99.9% water and sand, 0.1% chemicals (SWN, 2011), 98-99% water and proppant, 1-2 % additives (Carter et al., 2013).

[1] We use "hydraulic fracturing fluid" to refer to the fluid that is injected into the well and used to create and hold open fractures the formation.

[2] In this chapter, because of the way many chemicals are reported, we use the word "chemical" to refer to any individual chemical or chemical substance that has been assigned a CASRN (Chemical Abstracts Service Registry Number). A CASRN is a unique identifier for a chemical substance, which can be a single chemical (e.g., hydrochloric acid, CASRN 7647-01-0) or a mixture of chemicals (e.g., hydrotreated light petroleum distillates (CASRN 64742-47-8), a complex mixtures of C9 to C16 hydrocarbons). For simplicity, we refer to both pure chemicals and chemical substances that are mixtures, which have a single CASRN, as "chemicals."

[3] Empirical experience tends to provide better result as operators gain experience at a new site or geology increases. When an operator moves to a new basin geology, there may be less than optimal results. With experience and understanding of the geology increases, the empirical evidence will inform what hydraulic fracturing fluid composition works better than others.

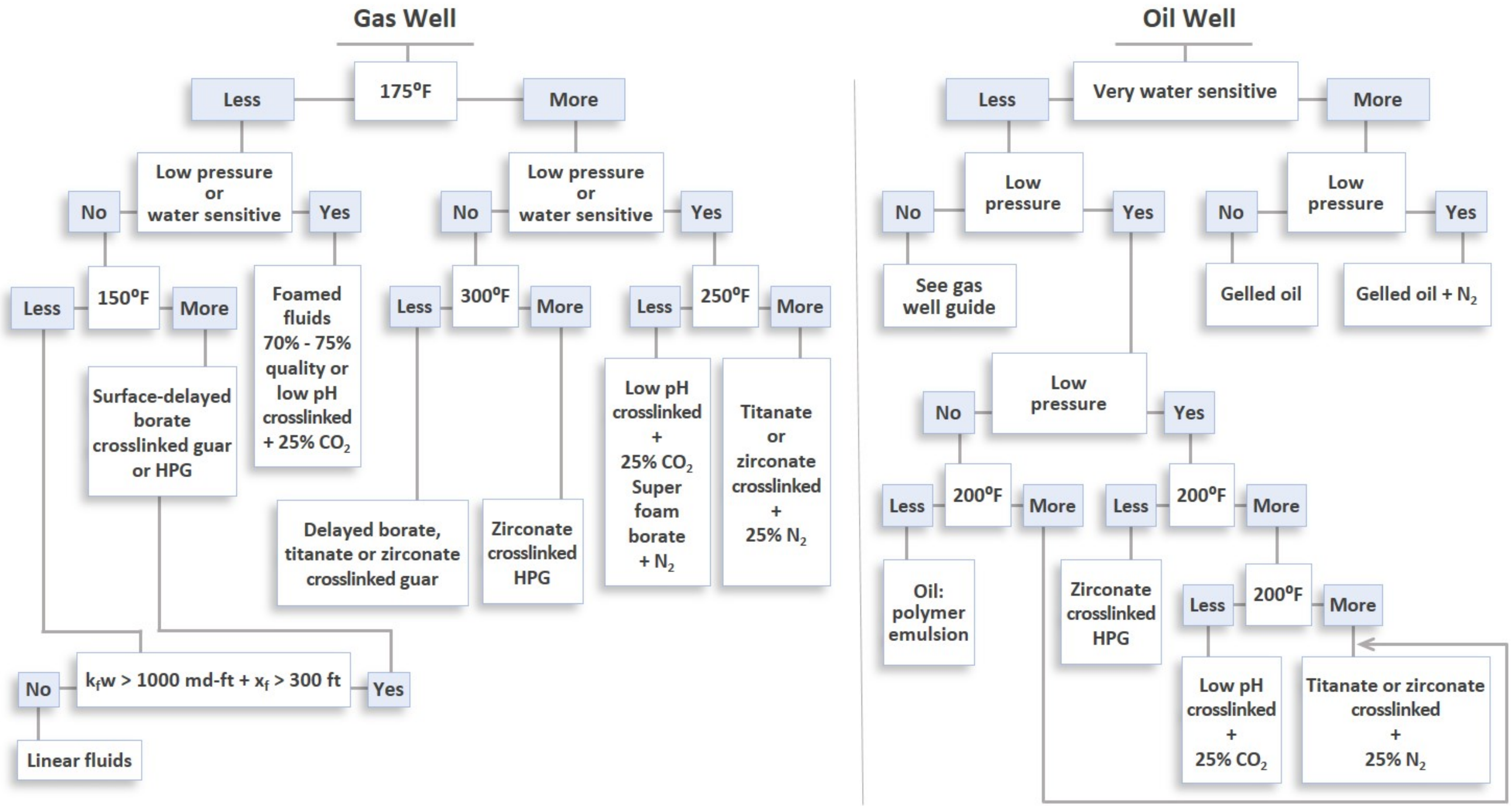

Figure 5-3. Example hydraulic fracturing fluid decision tree for gas and oil wells.

This decision tree figure serves as an example of the factors that determine the type of hydraulic fracturing fluid chosen to fracture a given formation, depending on whether the well will produce oil or gas. Factors include water sensitivity, formation temperature, and pressure. HPG is hydroxypropylguar, guar derivatized with propylene oxide. Parameters are: k_f, fracture permeability, w is the fracture width, and x_f is the fracture half-length. This figure was chosen to represent the differences between oil and gas wells and the types of decisions involved with choosing a fluid. This is adapted from Elbel and Britt (2000) and, as such, is dated to that time period. Since then, slickwater has become increasingly popular due to its simplicity and cheaper cost, and slickwater has often replaced linear and crosslinked gelled fluids, especially in shales. Other decision tree figures may exist. © 2000 Schlumberger. First published by John Wiley & Sons Ltd. All rights reserved.

variation in water sensitivity.[1,2] One of the most important properties in designing a hydraulic fracturing fluid is the viscosity (Montgomery, 2013).[3]

Table 5-1 provides a list of common types of additives, their functions, and the most frequently used chemicals for each purpose based on the EPA's analysis of disclosures to FracFocus 1.0 (U.S. EPA, 2015a, hereafter referred to as the EPA FracFocus 1.0 report), the EPA's project database of disclosures to FracFocus 1.0 (U.S. EPA, 2015c, hereafter referred to as the EPA FracFocus 1.0 project database), and other literature sources.[4] Additional information on more additives can be found in U.S. EPA (2015a).

A general description of typical hydraulic fracturing fluid formulations nationwide is difficult, because fracturing fluids vary from well to well. Based on the EPA FracFocus 1.0 report, the median number of chemicals reported for each disclosure was 14, with the 5th to 95th percentile ranging from four to 28 (see Appendix H for a list of hydraulic fracturing fluid chemicals). The median number of chemicals per disclosure was 16 for oil wells and 12 for gas wells (U.S. EPA, 2015a). Other sources have stated that between three and 12 additives and chemicals are used (Schlumberger, 2015; Carter et al., 2013; Spellman, 2012; GWPC and ALL Consulting, 2009).[5]

Water, the most commonly used base fluid for hydraulic fracturing, is inferred to be used as a base fluid in more than 93% of EPA FracFocus 1.0 disclosures (U.S. EPA, 2015c). Alternatives to water-based fluids, such as hydrocarbons and gases, including carbon dioxide and nitrogen-based foam, may also be used based on formation characteristics, cost, or preferences of the well operator or service company (ALL Consulting, 2012; GWPC and ALL Consulting, 2009). Non-aqueous base fluid ingredients were identified in 761 (2.2%) of EPA FracFocus 1.0 disclosures (U.S. EPA, 2015a). Gases and hydrocarbons may be used alone or blended with water; more than 96% of the disclosures identifying non-aqueous base fluids are blended (U.S. EPA, 2015a). There is no standard method to categorize the different fluid formulations (Patel et al., 2014; Montgomery, 2013; Spellman, 2012; Gupta and Valkó, 2007). Therefore, we broadly categorize the fluids as water-based or alternative fluids.

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[1] A crosslinked fluid is a fluid that has polymers that have been linked together through a chemical bond. A crosslink chemical is added to have the polymer chains linked together to form larger chemical structures with higher viscosity. The increased fracturing fluid viscosity allows the fluid to carry more proppant into the fractures. The fracturing fluid remains viscous until a breaking agent is introduced to break the cross-linked polymer.

[2] Water sensitivity refers to when a formation's physicochemical properties are affected in the presence of water. An example of a water sensitive formation would be one where the soil particles swell when water is added, reducing the permeability of the formation.

[3] Viscosity is a measure of the internal friction of fluid that provides resistance to shear within the fluid, informally referred to as how "thick" a fluid is. For example, custard is thick and has a high viscosity, while water is runny with a low viscosity. Sufficient viscosity is needed to create a fracture and transport proppant (Gupta and Valkó, 2007). In lower-viscosity fluids, proppant is transported by turbulent flow and requires more hydraulic fracturing fluid. Higher-viscosity fluids allows the fluid to carry more proppant, requiring less fluid but necessitating the reduction of viscosity after the proppant is placed (Rickman et al., 2008; Gupta and Valkó, 2007).

[4] A disclosure refers to all data submitted for a specific oil and gas production well for a specific fracture date.

[5] Sources may differ based on whether they are referring to additives or chemicals.

Table 5-1. Examples of common additives, their function, and the most frequently used chemicals reported to FracFocus for these additives.

The list of examples of common additives was developed from information provided in multiple sources (U.S. EPA, 2015a, c; Stringfellow et al., 2014; Montgomery, 2013; Vidic et al., 2013; Spellman, 2012; GWPC and ALL Consulting, 2009; Arthur et al., 2008; Gupta and Valkó, 2007; Gidley et al., 1989). The additive functions are based on information the EPA received from service companies (U.S. EPA, 2013a).

Additives	Function	Chemicals reported in 20% or more of disclosures in the EPA FracFocus 1.0 project database for given additive[a,b]
Acid	Dissolves cement, minerals, and clays to reduce clogging of the pore space	Hydrochloric acid
Biocide	Controls or eliminates bacterial growth, which can be present in the base fluid and may have detrimental effects on the long term well productivity	Glutaraldehyde; 2,2-dibromo-3-nitrilopropionamide
Breaker	Reduces the designed increase in viscosity of specialized treatment fluids such as gels and foams after the proppant has been placed and flowback commences to clean up the well	Peroxydisulfuric acid diammonium salt
Clay control	Prevents the swelling and migration of formation clays that otherwise react to water-based fluids	Choline chloride
Corrosion inhibitor	Protects the iron and steel components in the wellbore and treating equipment from corrosive fluids	Methanol; propargyl alcohol; isopropanol
Crosslinker	Increases the viscosity of base gel fluids by connecting polymer molecules	Ethylene glycol; potassium hydroxide; sodium hydroxide
Emulsifier	Facilitates the dispersion of one immiscible fluid into another by reducing the interfacial tension between the two liquids to achieve stability	2-Butoxyethanol; polyoxyethylene(10)nonylphenyl ether; methanol; nonyl phenol ethoxylate
Foaming agent	Generates and stabilizes foam fracturing fluids	2-Butoxyethanol; Nitrogen, liquid; isopropanol; methanol; ethanol
Friction reducer	Reduces the friction pressures experienced when pumping fluids through tools and tubulars in the wellbore	Hydrotreated light petroleum distillates
Gelling agent	Increases fracturing fluid viscosity allowing the fluid to carry more proppant into the fractures and to reduce fluid loss to the reservoir	Guar gum; hydrotreated light petroleum distillates
Iron control agent	Controls the precipitation of iron compounds (e.g., Fe_2O_3) from solution	Citric acid

Additives	**Function**	**Chemicals reported in 20% or more of disclosures in the EPA FracFocus 1.0 project database for given additive**[a,b]
Nonemulsifier	Separates problematic emulsions generated within the formation	Methanol; isopropanol; nonyl phenol ethoxylate
pH control	Affects the pH of a solution by either inducing a change (pH adjuster) or stabilizing and resisting change (buffer) to achieve desired qualities and optimize performance	Carbonic acid, dipotassium salt; potassium hydroxide; sodium hydroxide; acetic acid
Resin curing agents	Lowers the curable resin coated proppant activation temperature when bottom hole temperatures are too low to thermally activate bonding	Methanol; nonyl phenol ethoxylate; isopropanol; alcohols, C12-14-secondary, ethoxylated
Scale inhibitor	Controls or prevents scale deposition in the production conduit or completion system	Ethylene glycol; methanol
Solvent	Controls the wettability of contact surfaces or prevents or breaks emulsions[1]	Hydrochloric acid

[a] Chemicals (excluding water and quartz) listed in the EPA FracFocus 1.0 project database in more than 20% of disclosures for a given purpose when that purpose was listed as used on a disclosure (U.S. EPA, 2015c). These are not necessarily the active ingredients for the purpose, but rather are listed as being commonly present for the given purpose. Chemicals may be disclosed for more than a single purpose (e.g., 2-butoxyethanol is listed as being used as an emulsifier and a foaming agent).

[b] Analysis considered 32,885 disclosures and 615,436 ingredient records that met selected quality assurance criteria, including: completely parsed (parsing is the process of analyzing a string of symbols to identify and separate various components); unique combination of fracture date and API well number; fracture date between January 1, 2011, and February 28, 2013; valid CASRN; valid concentrations; and valid purpose. Disclosures that did not meet quality assurance criteria (5,645) or other, query-specific criteria were excluded from analysis.

5.3.1 Water-Based Fracturing Fluids

The advantages of water-based fracturing fluids are low cost, ease of mixing, and ability to recover and reuse the water. The disadvantages are that they have low viscosity, they create narrow fractures, and they may not provide optimal performance in water-sensitive formations (Montgomery, 2013; Gupta and Valkó, 2007) (Section 5.3.2). Water-based fluids can be as simple as water with a few additives to reduce friction, such as “slickwater,” or as complex as water with crosslinked polymers, clay control agents, biocides, and scale inhibitors (Spellman, 2012). (See Figure 5-4 for a slickwater example.)

Gels may be added to water-based fluids to increase viscosity, which assists with proppant transport and results in wider fractures. Gelling agents include natural polymers, such as guar, starches, and cellulose derivatives, which require the addition of biocide to minimize bacterial growth (Spellman, 2012; Gupta and Valkó, 2007). Gels may be linear or crosslinked. Crosslinking

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[1] Wettability is the ability of a liquid to maintain contact with a solid surface. When wettability is high, a liquid droplet will lie flat across a surface, maximizing the area of contact between the liquid and the solid. When wettability is low, a liquid droplet will approach a spherical shape, minimizing the area of contact between the liquid and solid.

increases viscosity without adding more gel. Gelled fluids require the addition of a breaker, which breaks down the gel after it carries in the proppant, to reduce fluid viscosity to facilitate fluid flowing back after treatment (Spellman, 2012; Gupta and Valkó, 2007). The presence of residual breakers may make it difficult to reuse recovered water (Montgomery, 2013).

5.3.2 Alternative Fracturing Fluids

Alternative hydraulic fracturing fluids can be used for water sensitive formations (i.e., formations where permeability is reduced when water is added) or as dictated by production goals (Halliburton, 1988). Examples of alternative fracturing fluids include acid-based fluids; non-aqueous-based fluids; energized fluids, foams, or emulsions; viscoelastic surfactant fluids; gels; methanol; and other unconventional fluids (Montgomery, 2013; Saba et al., 2012; Gupta and Hlidek, 2009; Gupta and Valkó, 2007; Halliburton, 1988).

Acid fracturing is generally used in carbonate formations without the use of a proppant. Fractures are initiated with a hydraulic fracturing fluid, and acid (gelled, foamed, or emulsified) is added to irregularly etch the wall of the fracture. The etching serves to prop open the formation, for a high-conductivity fracture (Spellman, 2012; Gupta and Valkó, 2007).

Non-aqueous fluids, like petroleum distillates and propane, are used in water-sensitive formations. Non-aqueous fluids may also contain additives, such as gelling agents, to improve performance (Gupta and Valkó, 2007). The use of non-aqueous fluids has decreased due to safety concerns, and because water-based and emulsion fluid technologies have improved (Montgomery, 2013; Gupta and Valkó, 2007). Methanol, for example, was previously used as a base fluid in water-sensitive reservoirs beginning in the early 1990s, but was discontinued in 2001 for safety concerns and cost (Saba et al., 2012; Gupta and Hlidek, 2009; Gupta and Valkó, 2007). Methanol is still widely used as an additive or in additive mixtures in hydraulic fracturing fluid formulations.

Energized fluids, foams, and emulsions minimize fluid leakoff in low pressure targeted geologic formations, have high proppant-carrying capacity, improve fluid recovery, and are sometimes used in water-sensitive formations (Barati and Liang, 2014; Gu and Mohanty, 2014; Spellman, 2012; Gupta and Valkó, 2007; Martin and Valko, 2007).[1] However, these treatments tend to be expensive, can require high pressure, and pose potential health and safety concerns (Montgomery, 2013; Spellman, 2012; Gupta and Valkó, 2007). Energized fluids (see Figure 5-4 for an example of an energized fluid composition) are mixtures of liquid and gas (Patel et al., 2014; Montgomery, 2013). Nitrogen (N_2) or carbon dioxide (CO_2), the gases used, make up less than 53% of the fracturing fluid volume, typically ranging from 20% to 30% by volume (Montgomery, 2013; Gupta and Valkó, 2007; Mitchell, 1970). Energized foams are liquid-gas mixtures, with nitrogen or carbon dioxide gas comprising more than 53% of the fracturing fluid volume, with a typical range of 65% to 80% by volume (Montgomery, 2013; Mitchell, 1970). Emulsions are liquid-liquid mixtures, typically a

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[1] Leakoff is the fraction of the injected fluid that infiltrates into the formation (e.g., through an existing natural fissure) and is not recovered during production (Economides et al., 2007). See Chapter 6, Section 6.3 for more discussion on leakoff.

hydrocarbon (e.g., condensate or diesel) with water.[1] Both water-based fluids, including gels, and non-aqueous fluids can be energized fluids or foams.

Foams and emulsions break easily using gravity separation and are stabilized by using additives such as foaming agents (Gupta and Valkó, 2007). Emulsions may be used to stabilize active chemical ingredients or to delay chemical reactions, such as the use of carbon dioxide-miscible, non-aqueous fracturing fluids to reduce fluid leakoff in water-sensitive formations (Taylor et al., 2006).

Other types of fluids not addressed above include viscoelastic surfactant fluids, viscoelastic surfactant foams, crosslinked foams, liquid carbon dioxide-based fluid, and liquid carbon dioxide-based foam fluid, and hybrids of other fluids (King, 2010; Brannon et al., 2009; Curtice et al., 2009; Tudor et al., 2009; Gupta and Valkó, 2007; Coulter et al., 2006; Boyer et al., 2005; Fredd et al., 2004; MacDonald et al., 2003).

5.3.3 Tracers

Some chemicals are added to the fluid to act as tracers. Tracers are added to hydraulic fracturing fluid to assess the efficiency of fracturing and proppant placement. As an example, the efficiency of oil production from multistage fracturing was assessed by using 17 oil soluble tracers. Each tracer was used to assess production from a specific interval of the well (Catlett et al., 2013), although the specific compounds used were not identified (Table 5-2). Chemical classes of tracers and individual examples show a range of compounds employed including both inorganic and organic, and including radioactive elements, although only a few specific chemicals have been revealed. Of these, examples are proppant tracers and fluorocarbons. Although radioactive fluids have also been used for proppant tracing, a commonly-used approach has the short-half-life elements Antimony^{124}, Iridium^{192}, and Scandium^{46} bound to the proppants and gamma emissions are subsequently measured by a neutron-logging device (Sonnenfield et al., 2016; Odegard et al., 2015; Lowe et al., 2013; Osborn and McIntosh, 2011; McDaniel et al., 2010).[2,3] Of the organic tracers, 14 fluorinated organics have been identified through an analysis of FracFocus 2.0 disclosures (Konschnik and Dayalu, 2016). Three fluorinated tracers and Antimony^{124} were identified in produced water (Maguire-Boyle and Barron, 2014) (Appendix Table H-4).

Table 5-2. Classes and specifically identified examples of tracers used in hydraulic fracturing fluids.

Class	Specific Chemical[a]	Reference
Thiocyanates (SCN^-)	ND	Dugstad (2007)
Fluorobenzoic acids	ND	Dugstad (2007)

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[1] Diesel is a mixture typically of C8 to C21 hydrocarbons. The shorthand "C8" is used to represent a hydrocarbon with 8 carbons. Thus "C21" represents a hydrocarbon with 21 carbons. Octane has 8 carbons and is thus a C8, and is a component of gasoline.

[2] Antimony^{124}: 60.2 days, Iridium^{192}: 74 days, Scandium^{46}: 83.8 days.

[3] Gadolinium^{155} and Gadolinium^{157} have been suggested as bound proppant tracers because of their high-gamma-capture cross-sections (Liu et al., 2015).

Class	Specific Chemical[a]	Reference
Radioactive tracers	Tritiated Water	Dugstad (2007)
	Tritiated Methanol	Dugstad (2007)
	Antimony^{124}	Silber et al. (2003)
	Iridium^{192}	Silber et al. (2003)
	Scandium^{46}	Silber et al. (2003)
Fluorocarbons	2,2,3,3,4,4,4-heptafluorobutyl undecylate	Maguire-Boyle and Barron (2014)
	2,3,4-Trifluorobenzoic acid	Konschnik and Dayalu (2016)
	2,4,5-Trifluorobenzoic acid	Konschnik and Dayalu (2016)
	2,4-Difluorobenzoic acid	Konschnik and Dayalu (2016)
	2,6-Difluorobenzoic acid	Konschnik and Dayalu (2016)
	2-Chloro-4-fluorobenzoic acid	Konschnik and Dayalu (2016)
	2-Fluorobenzoic acid	Konschnik and Dayalu (2016)
	2-Trifluoromethylbenzoic acid	Konschnik and Dayalu (2016)
	3-Trifluoromethylbenzoate	Konschnik and Dayalu (2016)
	4-(Trifluoromethyl)benzoic acid	Konschnik and Dayalu (2016)
	4-Chloro-2-fluorobenzoic acid	Konschnik and Dayalu (2016)
	4-fluoro-2-(trifluoromethyl)benzoic acid	Konschnik and Dayalu (2016)
	4-Fluoro-3-(trifluomethyl)benzoic acid	Konschnik and Dayalu (2016)
	Benzoic acid, 3,5-difluoro-	Konschnik and Dayalu (2016)
	cis-4-ethyl-5-octyl-2,2-*bis*(trifluoromethyl)-1,3 dioxolane	Maguire-Boyle and Barron (2014)
	p-Fluorobenzoic acid	Konschnik and Dayalu (2016)
	tri-fluoromethyl tetradeculate	Maguire-Boyle and Barron (2014)
Oil soluble alkyl esters	ND	Deans (2007)
Unstable emulsions	ND	Catlett et al. (2013)
Controlled-release polymers and solid tracers	ND	Salman et al. (2014)

[a] ND = none disclosed.

A different set of tracers have been proposed for identifying environmental impacts from hydraulic fracturing fluids (Kurose, 2014). These tracers are designed so that the fluids from individual wells are identifiable while having no environmental impact themselves. DNA and nanoparticles with magnetic properties made specifically for each well have been proposed for this purpose (Kurose, 2014).

5.3.4 Proppants

Proppants are small particles carried down the well and into fractures by hydraulic fracturing fluid. They hold the fractures open after the injection pressure has been released and the hydraulic fracturing fluid has been removed (Brannon and Pearson, 2007). The propped fractures provide a path for the hydrocarbon to flow from the reservoir. The EPA's analysis of FracFocus 1.0 data showed that 98% of disclosures reported sand as the proppant, making sand (i.e., quartz) the most commonly reported proppant (U.S. EPA, 2015a). Other proppants include man-made or specially engineered particles, such as high-strength ceramic materials or sintered bauxite (Schlumberger, 2014; Brannon and Pearson, 2007). Proppant types can be used individually or in combinations.

5.3.5 Example Hydraulic Fracturing Fluids

There is no standard composition of hydraulic fracturing fluid used across the United States, and the literature does not present any typical hydraulic fluid composition. In Figure 5-4, we present two examples of hydraulic fracturing fluid mixtures based on analyses conducted on the EPA FracFocus 1.0 project database (U.S. EPA, 2015c). These examples represent two different types of fluids used at two different wells. The first is a slickwater, and the second is an energized fluid.[1] Details of each fluid are presented in the figure along with pie charts of their composition, as given by maximum percent by mass of the total hydraulic fracturing fluid.

The first hydraulic fracturing fluid (Figure 5-4a), the slickwater, is composed of 87% water, 13% sand, and 0.05% chemicals, by mass. The fluid is 71% fresh water and 16% reused produced water, with a total water volume of 4,763,000 gal (18,030,000 L). The chemical composition consists of six different additive types (acid, friction reducer, biocide, scale inhibitor iron control, and corrosion inhibitor) and a total of 13 chemicals.

The second hydraulic fracturing fluid (Figure 5-4b), the energized fluid, is more complex and consists of 58% water, 28% nitrogen gas, 13% sand, and 1.5% additives, by mass, with a total water volume of 105,000 gal (397,000 L). The hydraulic fracturing fluid composition consists of 10 additives (acid, surfactant, foamer, corrosion inhibitor, biocide, friction reducer, breaker, scale inhibitor, iron control, and clay stabilizer) and a total of 28 chemicals.

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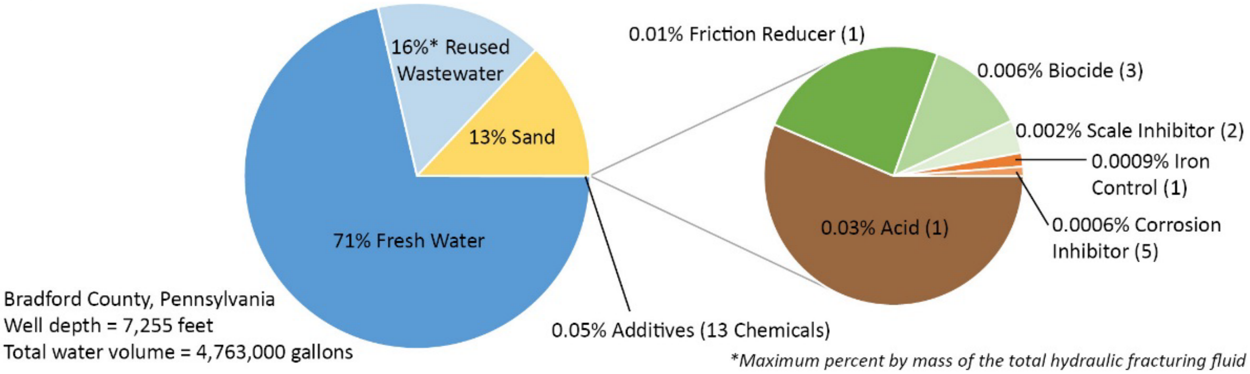
[1] A slickwater is a hydraulic fracturing fluid designed to have a low viscosity to allow pumping at high rates. The critical additive in a slickwater is the friction reducer, which makes the fluid "slick."

(a) Slickwater



(b) Energized Fluid

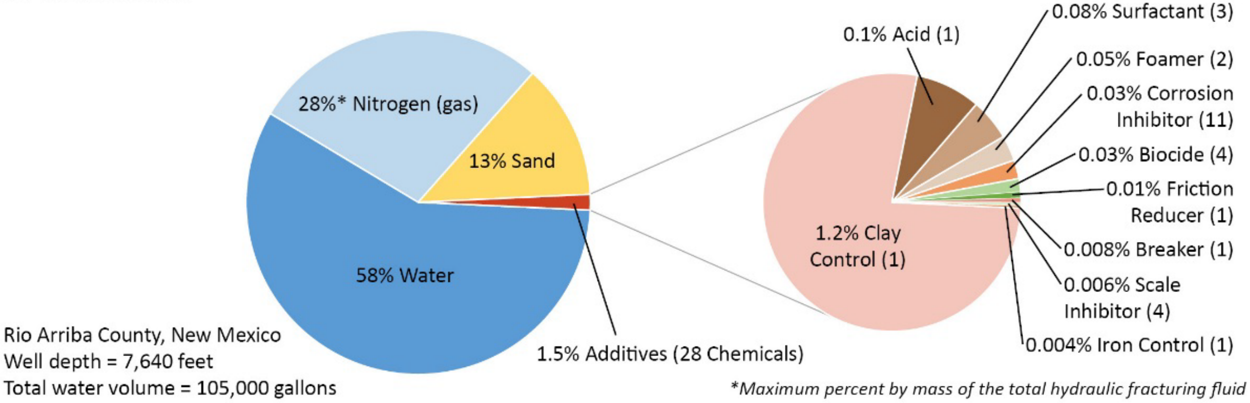


Figure 5-4. Example hydraulic fracturing fluids.

Example compositions of (a) slickwater and (b) energized fluid. The base fluid and proppants are on the left, and the additive breakdown is on the right. The number in parentheses represents the number of chemicals in that additive. See Table 5-1 for the function of different additives and the most common chemicals in those additives reported as based on the analysis of the EPA FracFocus 1.0 project database (U.S. EPA, 2015c).

These two examples give an idea of the difference in the compositions of two example hydraulic fracturing fluids. These compositions are the final mixture as if the entire fluid were mixed at once; they are generally not the actual composition at any given point in time. These compositions provide the potential composition of a spilled hydraulic fracturing fluid during the chemical mixing stage. Any of these ingredients (e.g., biocide) could be released by itself or mixed with the base fluid with other additives. The variability of hydraulic fracturing fluids from well to well and site to site makes it difficult to assess the potential of hydraulic fracturing additive or fluid release.

5.4 Frequency and Volume of Hydraulic Fracturing Chemical Use

This section highlights the different chemicals used in hydraulic fracturing fluids and discusses the frequency and volume of use. Using the EPA FracFocus 1.0 project database (Text Box 5-1), we focus our analysis on the individual chemicals that are used as ingredients in additive formulations, rather than on the complete mixture of chemicals that may be present in a hydraulic fracturing fluid. Operators can report information about well location, date of operations, and water and chemical use to the FracFocus registry. Chemicals are reported in FracFocus by using the chemical name and the Chemical Abstract Services Registration Number (CASRN), which is a unique number identifier for every chemical.[1] The information on specific chemicals, particularly those most commonly used, can be used to assess potential impacts on drinking water resources. The volume of chemicals stored on-site provides information on the potential volume of a chemical spill.

Text Box 5-1. The FracFocus Registry and EPA FracFocus Report.

The Ground Water Protection Council (GWPC) and the Interstate Oil and Gas Compact Commission (IOGCC) developed a national hydraulic fracturing chemical registry, FracFocus (www.fracfocus.org). Well operators can use the registry to disclose information about chemicals and water they use during hydraulic fracturing. As part of the EPA's Study of the Potential Impacts of Hydraulic Fracturing for Oil and Gas on Drinking Water Resources, the EPA published the report titled *Analysis of Hydraulic Fracturing Fluid Data from the FracFocus Chemical Disclosure Record Registry 1.0* (U.S. EPA, 2015a). For this report, the EPA accessed data from FracFocus 1.0 from January 1, 2011 to February 28, 2013, which included more than 39,000 disclosures (records of well data) in 20 states that had been submitted by operators prior to March 1, 2013. Accompanying the U.S. EPA (2015a) report is the published EPA FracFocus 1.0 project database, which. It supported analyses of FracFocus chemical and water use data (U.S. EPA, 2015c), and a report describing the details of data management for development of the project database (U.S. EPA, 2015b).

Submission to FracFocus was initially voluntary and varied from state to state. During the timeframe covered in the EPA FracFocus 1.0 report (January 2011 to February 2013), six of the 20 states with data submitted to FracFocus and included in the EPA FracFocus 1.0 project database began requiring operators to disclose chemicals used in hydraulic fracturing fluids to FracFocus (Colorado, North Dakota, Oklahoma, Pennsylvania, Texas, and Utah). Three other states started requiring disclosure to either FracFocus or the state (Louisiana, Montana, and Ohio), and five states required or began requiring disclosure to the state (Arkansas, Michigan, New Mexico, West Virginia, and Wyoming). Alabama, Alaska, California, Kansas, Mississippi, and Virginia did not have reporting requirements during the period of the EPA's study.

The EPA's analysis may or may not be nationally representative. Disclosures from the five states reporting the most disclosures to FracFocus (Texas, Colorado, Pennsylvania, North Dakota, and Oklahoma) comprise over 78% of the disclosures in the database; nearly half (47%) of the disclosures are from Texas. Thus, data from these states are most heavily represented in the EPA's analyses.

A disclosure reports the total water volume (in gallons) and the chemicals used in the fluid (as maximum ingredient concentration by mass both in the additive and in the hydraulic fracturing fluid). The actual mass of the chemicals used in the fluid are not reported. The fluid composition reported in the disclosure does not necessarily reflect the actual composition of the fluid at any time. Rather, the disclosure represents what the total composition of the fluid would be if all chemicals used were mixed together at their maximum reported concentration.

The EPA summarized information on the locations of the wells in the disclosures, water volumes used, and the frequency of use and maximum ingredient concentrations of the chemicals in the additives and the hydraulic fracturing fluid. Additional information can be found in the EPA FracFocus 1.0 report (U.S. EPA, 2015a) and in the EPA FracFocus 1.0 project database (U.S. EPA, 2015c).

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[1] A CASRN and chemical name combination identify a chemical substance, which can be a single chemical (e.g., hydrochloric acid, CASRN 7647-01-0) or a mixture of chemicals (e.g., hydrotreated light petroleum distillates (CASRN 64742-47-8), a complex mixtures of C9 to C16 hydrocarbons). For simplicity, we refer to both pure chemicals and chemical substances that are mixtures, which have a single CASRN, as "chemicals."

The EPA compiled a list of 1,084 chemicals with unique CASRNs reported as used in the hydraulic fracturing process between 2005 and 2013 (full list, methodology, and details on sources in Appendix H).[1] These chemicals fall into different chemical classes and include 455 organic chemicals, 258 inorganic chemicals, and 361 organic mixtures or polymers. The chemical classes of commonly used hydraulic fracturing chemicals include but are not limited to:

- Acids (e.g., hydrochloric acid, peroxydisulfuric acid, acetic acid, citric acid);
- Alcohols (e.g., methanol, isopropanol, ethylene glycol, propargyl alcohol, ethanol);
- Aromatic hydrocarbons (e.g., benzene, naphthalene, heavy aromatic petroleum solvent naphtha);
- Bases (e.g., sodium hydroxide, potassium hydroxide);
- Hydrocarbon mixtures (e.g., petroleum distillates);
- Polysaccharides (e.g., guar gum);
- Surfactants (e.g., poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy, 2-butoxyethanol); and
- Salts (e.g., sodium chlorite, dipotassium carbonate).

Further details on these chemicals and their associated hazards are presented in Chapter 9.

All of the sources of information used to compile the list of chemicals found in hydraulic fracturing fluids (Appendix H) relied on reported use of those chemicals. In some cases, analysis of produced water samples by advanced analytical methods could provide information on suspected hydraulic fracturing additives, but other sources for the chemicals need careful consideration (Hoelzer et al., 2016). These sources include chemicals originating from components of the well, lab contamination, or subsurface reaction. We limit our discussion of hydraulic fracturing fluid chemicals to those directly reported as used.

An additional complication in providing an assessment on the use of chemicals in hydraulic fracturing is that companies can withhold reporting chemicals to the FracFocus registry by claiming that a chemical is Confidential Business Information (CBI). The use of CBI is to protect proprietary information, such as trade secrets. Details on CBI are provided in Text Box 5-2.

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[1] The EPA used eight different sources to identify chemicals used in hydraulic fracturing fluids. This included the EPA FracFocus report (U.S. EPA, 2015a) and seven other sources (U.S. EPA, 2013a; Colborn et al., 2011; House of Representatives, 2011; NYSDEC, 2011; PA DEP, 2010a; U.S. EPA, 2004a; Material Safety Data Sheets).

Text Box 5-2. Confidential Business Information (CBI).

This assessment relies in large part upon information provided to the EPA or to other organizations. The submitters (e.g., businesses that operate wells or perform hydraulic fracturing services) may view some of the information as confidential business information (CBI) and accordingly asserted CBI claims to protect it. Information deemed to be CBI may include trade secrets or other proprietary business information entitled to confidential treatment under Exemption 4 of the Freedom of Information Act (FOIA) and other applicable laws. The FOIA and EPA's CBI regulations may allow for information claimed as CBI provided to the EPA to be withheld from the public, including in this document. In practical terms, when a well operator claims CBI for a specific chemical, they do not report the name or CASRN for that chemical in the disclosure submitted to the FracFocus registry (see Text Box 5-1 for information on FracFocus).

The EPA evaluated data from FracFocus, a national hydraulic fracturing chemical registry used and relied upon by some states, industry groups, and non-governmental organizations, as described in Text Box 5-1. A company submitting a disclosure to FracFocus may choose to not report the identity of a chemical it considers CBI. More than 70% of disclosures contained at least one chemical claimed as CBI and 11% of all chemicals were claimed as CBI. Of the disclosures containing CBI chemicals, there were an average of five CBI chemicals per disclosure (U.S. EPA, 2015a). Rates of withholding chemical information (designating a chemical as CBI) have increased from 11% in the 2011 to early 2013 time period of the EPA report, to 16.5% across the 2011 to early 2015 time period in another study using FracFocus data, with 92% of FracFocus 2.0 disclosures including at least one chemical claimed as CBI (Konschnik and Dayalu, 2016). When a chemical is claimed as CBI, there is no public means of accessing information on these chemicals (e.g., CASRN, name). Sometimes a CBI entry will provide the chemical family (Appendix H).

Consistent with the EPA's *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (U.S. EPA, 2011d), data were submitted by nine service companies to the EPA regarding chemicals used in hydraulic fracturing from 2005 to 2009. These data were separate from the EPA FracFocus 1.0 project database. The data were submitted directly to the EPA, with the actual names and CASRNs of any chemicals the company considered CBI. This included a total of 381 CBI chemicals, with a mean of 42 CBI chemicals per company and a range of 7 to 213 (U.S. EPA, 2013a). Of these 381 chemicals, some companies only provided a generic chemical name and no CASRN, some provided neither a chemical name or CASRN, while others provided a CASRN and a specific chemical name. This resulted in 80 CASRNs/chemical names on this CBI list. Table H-3 lists generic chemical names, which may have been designed to mask CBI chemical names given to the EPA. The EPA does not know if the 381 chemicals represent 381 unique chemicals or if there are duplicates on this list.

The prevalence of CBI claims in the EPA FracFocus 1.0 project database limits completeness of the data set and introduces uncertainty. Ideally, all data would be available on all chemicals to do a full assessment.

5.4.1 National Frequency of Use of Hydraulic Fracturing Chemicals

A total of 692 chemicals were identified in the EPA FracFocus 1.0 project database that were reported as used in hydraulic fracturing from January 1, 2011, to February 28, 2013. This information comes from a total of 35,957 disclosures with chemical data in the database (U.S. EPA, 2015a).[1]

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[1] Chemicals may be pure chemicals (e.g., methanol) or chemical mixtures (e.g., hydrotreated light petroleum distillates), and they each have a single CASRN. Of these 692 chemicals, 598 had valid fluid and additive concentrations (34,675 disclosures). Sixteen chemicals were removed, because they were minerals listed as being used as proppants. This left a total of 582 chemicals (34,344 disclosures).

Table 5-3 presents the 35 chemicals (5% of all chemicals identified in the EPA's study) that were reported as ingredients in additives in at least 10% of the EPA FracFocus 1.0 project database disclosures for all states reporting to FracFocus 1.0 during this time (U.S. EPA, 2015c). This table also includes the top four additives in which the given chemical was reported as an ingredient.

Table 5-3. Chemicals identified in the EPA FracFocus 1.0 project database in 10% or more disclosures, with the percent of disclosures for which each chemical is reported as an ingredient in an additive and the top four reported additives for which the chemical is used. If a chemical is reported to be used in less than four additives, the table presents all additives (U.S. EPA, 2015c).

No.	Chemical name[a]	CASRN	Percent of disclosures[b]	Additives in which chemical is used (four most common, EPA FracFocus 1.0 project database)[c]
1	Methanol	67-56-1	72%	Corrosion inhibitors, surfactants, non-emulsifiers, scale control
2	Hydrotreated light petroleum distillates[d]	64742-47-8	65%	Friction reducers, gelling agents and gel stabilizers, crosslinkers and related additives, viscosifiers
3	Hydrochloric acid	7647-01-0	65%	Acids, solvents, scale control, clean perforations
4	Water[e]	7732-18-5	48%	Acids, biocides, clay control, scale control
5	Isopropanol	67-63-0	47%	Corrosion inhibitors, non-emulsifiers, surfactants, biocides
6	Ethylene glycol	107-21-1	46%	Crosslinkers and related additives, scale control, corrosion inhibitors, friction reducers
7	Peroxydisulfuric acid, diammonium salt	7727-54-0	44%	Breakers and breaker catalysts, oxidizer, stabilizers, clean perforations
8	Sodium hydroxide	1310-73-2	39%	Crosslinkers and related additives, biocides, pH control, scale control
9	Guar gum	9000-30-0	37%	Gelling agents and gel stabilizers, viscosifiers, clean perforations, breakers and breaker catalysts
10	Quartz[e]	14808-60-7	36%	Breakers and breaker catalysts, gelling agents and gel stabilizers, scale control, crosslinkers and related additives
11	Glutaraldehyde	111-30-8	34%	Biocides, surfactants, crosslinkers and related additives, sealers
12	Propargyl alcohol	107-19-7	33%	Corrosion inhibitors, inhibitors, acid inhibitors, base fluid
13	Potassium hydroxide	1310-58-3	29%	Crosslinkers and related additives, pH control, friction reducers, gelling agents and gel stabilizers

No.	Chemical name[a]	CASRN	Percent of disclosures[b]	Additives in which chemical is used (four most common, EPA FracFocus 1.0 project database)[c]
14	Ethanol	64-17-5	29%	Surfactants, biocides, corrosion inhibitors, fluid foaming agents and energizers
15	Acetic acid	64-19-7	24%	pH control, iron control agents, acids, gelling agents and stabilizers
16	Citric acid	77-92-9	24%	Iron control agents, scale control, gelling agents and gel stabilizers, pH control
17	2-Butoxyethanol	111-76-2	21%	Surfactants, corrosion inhibitors, non-emulsifiers, fluid foaming agents and energizers
18	Sodium chloride	7647-14-5	21%	Breakers/breaker catalysts, friction reducers, scale control, clay control
19	Solvent naphtha, petroleum, heavy arom.[f]	64742-94-5	21%	Surfactants, non-emulsifiers, inhibitors, corrosion inhibitors
20	Naphthalene	91-20-3	19%	Surfactants, non-emulsifiers, corrosion inhibitors, inhibitors
21	2,2-Dibromo-3-nitrilopropionamide	10222-01-2	16%	Biocides, clean perforations, breakers and breaker catalysts, non-emulsifiers
22	Phenolic resin	9003-35-4	14%	Proppants, biocides, clean perforations, base fluid
23	Choline chloride	67-48-1	14%	Clay control, clean perforations, base fluid, biocides
24	Methenamine	100-97-0	14%	Proppants, crosslinkers and related additives, biocides, base fluid
25	Carbonic acid, dipotassium salt	584-08-7	13%	pH control, proppants, acids, surfactants
26	1,2,4-Trimethylbenzene	95-63-6	13%	Surfactants, non-emulsifiers, corrosion inhibitors, inhibitors
27	Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides[g]	68424-85-1	12%	Biocides, non-emulsifiers, corrosion inhibitors, scale control
28	Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture)[h]	127087-87-0	12%	Surfactants, friction reducers, non-emulsifiers, inhibitors
29	Formic acid	64-18-6	12%	Corrosion inhibitors, acids, inhibitors, pH control

No.	Chemical name[a]	CASRN	Percent of disclosures[b]	Additives in which chemical is used (four most common, EPA FracFocus 1.0 project database)[c]
30	Sodium chlorite	7758-19-2	11%	Breakers/breaker catalysts, biocides, oxidizer, proppants
31	Nonyl phenol ethoxylate	9016-45-9	11%	Non-emulsifiers, resin curing agents, activators, friction reducers
32	Tetrakis(hydroxymethyl) phosphonium sulfate	55566-30-8	11%	biocides, scale control, clay control
33	Polyethylene glycol	25322-68-3	11%	Biocides, non-emulsifiers, surfactants, clay control
34	Ammonium chloride	12125-02-9	10%	Friction reducers, crosslinkers and related additives, scale control, clay control
35	Sodium persulfate	7775-27-1	10%	Breakers and breaker catalysts, oxidizer, pH control

[a] Chemical refers to chemical substances with a single CASRN; these may be pure chemicals (e.g., methanol) or chemical mixtures (e.g., hydrotreated light petroleum distillates). Chemical names are sometimes different between FracFocus 1.0 and Appendix H, though they will have the same CASRN.

[b] Analysis considered 34,675 disclosures and 676,376 ingredient records that met selected quality assurance criteria, including: completely parsed; unique combination of fracture date and API well number; fracture date between January 1, 2011, and February 28, 2013; valid CASRN; and valid concentrations. Disclosures that did not meet quality assurance criteria (3,855) or other, query-specific criteria were excluded from analysis.

[C] Analysis considered 32,885 disclosures and 615,436 ingredient records that met selected quality assurance criteria, including: completely parsed; unique combination of fracture date and API well number; fracture date between January 1, 2011, and February 28, 2013; valid CASRN; valid concentrations; and valid purpose. Disclosures that did not meet quality assurance criteria (5,645) or other, query-specific criteria were excluded from analysis.

[d] Hydrotreated light petroleum distillates (CASRN 64742-47-8) is a mixture of hydrocarbons, in the C9 to C16 range.

[e] Quartz (CASRN 14808-60-7), the proppant most commonly reported, and water were also reported as an ingredient in other additives (U.S. EPA, 2015a).

[f] Heavy aromatic solvent naphtha (petroleum) (CASRN 64742-94-5) is mixture of aromatic hydrocarbons in the C9 to C16 range.

[g] Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides (CASRN 68424-85-1) is a mixture of benzalkonium chloride with carbon chains between 12 and 16.

[h] Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture) (CASRN 127087-87-0) is mixture with varying length ethoxy links.

There is no single chemical used in all hydraulic fracturing fluids across the United States. Methanol is the most commonly used chemical, reported at 72.1% of wells in the EPA FracFocus 1.0 project database and is associated with 33 types of additives, including corrosion inhibitors, surfactants, non-emulsifiers, and scale control (U.S. EPA, 2015c).[1] Table 5-3 also shows the variability in different chemicals included in the EPA FracFocus 1.0 project database. The percentage of disclosures reporting a given chemical suggests the likelihood of that chemical's use at a site. Only three chemicals (methanol, hydrotreated light petroleum distillates, and hydrochloric acid) were used at more than half of the sites nationwide, and only 12 were used at more than one-third.

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[1] The number of additives may be an overestimate due to parsing issues. The true number of additives may be smaller.

In addition to providing information on frequency of use, the EPA FracFocus 1.0 project database provides the maximum concentration by mass of a given chemical in an additive. For example, methanol is the most frequently reported chemical. The median value for the maximum mass concentration reported for an additive in FracFocus disclosures is 30%, with a range of 0.44% to 100% (5th to 95th percentile).[1] Thus, methanol is generally used as part of a mixture of chemicals in the hydraulic fracturing fluid (typically at a concentration around 30% by mass). Other times, methanol is used as an additive in its pure form (concentration 100%). Therefore, methanol will sometimes be stored on-site in a mixture of chemicals and other times as pure methanol. This wide range of possible concentrations of methanol further complicates assessing the potential impact of spills, as the properties of the fluid will depend on the different chemicals present and on their concentrations. For all chemicals, spills of a highly concentrated chemical can have different potential impacts than spills of dilute mixtures. For more discussion on fluid and additive chemical composition, see Section 5.4.5.

A more recent study of FracFocus 2.0 data evaluated disclosures dating from March 9, 2011 to April 13, 2015 (96,449 disclosures) and reported 981 unique chemicals used in hydraulic fracturing (Dayalu and Konschnik, 2016; Konschnik and Dayalu, 2016). The earlier, EPA study (covering the 2011 to early 2013 time period) found 692 chemicals (U.S. EPA, 2015a). Konschnik and Dayalu (2016) identified 263 new CASRNs in addition to the 1,084 identified by the EPA (Appendix H), increasing the number of chemicals by approximately 24%. Of the new CASRNs, the only chemical reported in more than 1% of all disclosures was Alcohols, C9-11-iso-,C10-rich, ethoxylated propoxylated (CASRN 154518-36-2).

The 20 most common chemicals reported in Konschnik and Dayalu (2016) are similar to those listed in Table 5-3. There are three chemicals reported on their 20 most common list that are not included in Table 5-3. These chemicals are: sorbitan, mono-(9Z)-9-octadecenoate (CASRN 1338-43-8, reported in 29.6% disclosures (Konschnik and Dayalu, 2016) vs. 4% (U.S. EPA, 2015c), ethoxylated C12-16 alcohols (CASRN 68551-12-2, 27.9% vs. 4%), and thiourea polymer (CASRN 68527-49-1, 24.8% vs. 8%). Ammonium chloride was on each list, but disclosures increased from 10% to 30.5%. Four chemicals in Table 5-3 were not on their 20 most frequently used list: solvent naphtha, petroleum, heavy arom. (CASRN 64742-94-5), naphthalene (CASRN 91-20-3), 2,2-Dibromo-3-nitrilopropionamide (CASRN 10222-01-2), and phenolic resin (CASRN 9003-35-4).

5.4.2 Nationwide Oil versus Gas

Analyses based on the EPA FracFocus 1.0 project database also can elucidate the differences between the chemicals used during hydraulic fracturing for oil production and those used for gas production, providing a better understanding of potential spill impacts from each. Appendix Tables C-1 and C-2 present the chemicals reported in at least 10% of all gas (34 chemicals) and oil (39 chemicals) disclosures nationwide.

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[1] For more information on how chemicals are reported to FracFocus see www.fracfocus.org and U.S. EPA (2015a).

Many of the same chemicals are used for oil and gas, but some chemicals are used more frequently in oil production and others more frequently in gas.[1] For example, hydrochloric acid is the most commonly reported chemical for gas wells (73% of disclosures); it is the fifth most frequently reported chemical for oil wells (58% of disclosures). However, both oil and gas operators each reports using methanol in 72% of disclosures. Methanol is the most common chemical used in hydraulic fracturing fluids at oil wells and the second most common chemical in hydraulic fracturing fluids at gas wells.

5.4.3 State-by-State Frequency of Use of Hydraulic Fracturing Chemicals

The composition of hydraulic fracturing fluids varies from site to site. Since the impacts of hydraulic fracturing occur locally, the potential impact depends on the chemicals used locally. We investigated geographic variation of chemical use based on the frequency of chemicals reported to FracFocus and included in the EPA FracFocus 1.0 project database by state (U.S. EPA, 2015c). Appendix Table C-3 presents and ranks chemicals reported most frequently for each state (U.S. EPA, 2015c). The list of the 20 most frequently reported chemicals used in each state together include 94 unique chemicals. A total of 94 chemicals indicates some level of similarity in chemical usage among states.[2]

Methanol is reported in 19 of the 20 states (95%). Alaska is the only state in which methanol is not reported (based on the state's 20 disclosures). The percentage of disclosures reporting use of methanol ranges from 38% (Wyoming) to 100% (Alabama, Arkansas).

Ten chemicals (excluding water) are among the 20 most frequently reported in 14 of the 20 states. These chemicals are: methanol; hydrotreated light petroleum distillates; ethylene glycol; isopropanol; quartz; sodium hydroxide; ethanol; guar gum; hydrochloric acid; and peroxydisulfuric acid, diammonium salt.[3] These 10 chemicals are also the most frequently reported chemicals nationwide.

This state analysis showed that methanol is used across the contiguous U.S. (not Alaska). There are 9 other chemicals that are frequently used across the United States. Beyond those, however, there are a number of different chemicals that are used in one state more commonly than others, and many chemicals may not be used at all in other states.

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[1] This separation was done solely based on whether it was an oil or gas disclosure. The analysis did not separate out reservoir factors, such as temperature, pressure, or permeability, which may be important factors for which chemicals are used. There is no nationwide criterion to distinguish oil wells from gas wells. Production wells often produce some of both. A well identified as gas-producing in one place might be identified as oil-producing in another. This could affect the distribution of chemical use among these wells.

[2] The range of possible number of chemicals is from 20 to 400. If every state used the same 20 chemicals, there would be 20 different chemicals. If all 20 states each used 20 different chemicals, then there would be a total of 400 chemicals used.

[3] Quartz was the most commonly reported proppant and also reported as an ingredient in other additives (U.S. EPA, 2015a).

5.4.4 Volume of Chemical Use

Understanding the volume of chemicals used at each site is important for understanding potential impacts of chemicals as well as potential severity of impacts on drinking water resources. The chemical volume governs how much will be stored on-site, the types of containers required, the total amount that could spill, and how much could end up in a drinking water resource. While the on-site hydraulic fracturing service company has precise knowledge of the composition and volume of chemicals stored on-site, this information is not generally publicly available. We conducted a comprehensive review of publicly available sources and found two sources (OSHA, 2014a, b; Sjolander et al., 2011) that identify specific chemicals used at a hydraulic fracturing site and provide information on volumes. These are presented in Table 5-4. The volume of chemicals totaled 7,500 gal (28,000 L) and 14,700 gal (55,600 L) for the two sources, with a mean volume for an individual chemical of 1,900 gal (7,200 L) and 1,225 gal (4,637 L), respectively. The range of volumes for each chemical used is 30 to 3,690 gal (114 to 14,000 L).

Table 5-4. Example list of chemicals and chemical volumes used in hydraulic fracturing.
Volumes are for wells with an unknown number of stages and at least one perforation zone. Every well and fluid formulation is unique. Blank cells are data not reported.

		Sjolander et al. (2011)[a]		OSHA (2014a, 2014b)[b]	
Ingredient	**Examples**	**Volume (gal) or mass (lb)**	**Percent overall[c]**	**Volume (gal)**	**Percent by volume**
Water		4,000,000 gal	94.62	2,700,000 gal	90
Proppant	Sand	~ 1,500,000 lb[d]	5.26	285,300 gal	9.51
Acid	Hydrochloric acid or muriatic acid	1,338 gal	0.03	3,690 gal	0.123
Friction reducer	Polyacrylamide, mineral oil	2,040 gal	0.05	2,640 gal	0.088
Surfactant	Isopropanol			2,550 gal	0.085
Potassium chloride				1,800	0.06
Gelling agent	Guar gum or hydroxymethyl cellulose	-[e]	-[e]	1,680	0.056
Scale inhibitor	Ethylene glycol, alcohol, and sodium hydroxide	2,040 gal	0.05	1,290	0.043
pH buffer	Carbonate			330	0.011
Preservative	Ammonium persulfate			300	0.01

		Sjolander et al. (2011)[a]		OSHA (2014a, 2014b)[b]	
Ingredient	**Examples**	**Volume (gal) or mass (lb)**	**Percent overall[c]**	**Volume (gal)**	**Percent by volume**
Crosslinker	Borate salts	-[e]	-[e]	210	0.007
Iron control	Citric acid	-[e]	-[e]	120	0.004
Corrosion inhibitor	n,n-Dimethyl formamide	-[e]	-[e]	60	0.002
Biocide / antimicrobial agent	Glutaraldehyde, ethanol, methanol	2,040 gal	0.05	30	0.001
Gel-breaker	Ammonium persulfate	-[e]	-[e]		
Total volume of all chemicals		7,458 gal	0.18	14,700	0.49
Individual chemical volume: mean (full range)		1,864.5 gal (1,338 – 2,040 gal)		1,225 (30 – 3,690)	

[a] Adapted from Penn State "Water Facts" publication entitled *Introduction to Hydrofracturing* (Sjolander et al., 2011). Composite from two companies: Range Resources, LLC, and Chesapeake Energy, which released in July 2010 the chemistry and volume of materials typically used in their well completions and stimulations.

[b] Adapted from a table generated by the Occupational Safety and Health Administration (OSHA) for use in a training module (OSHA, 2014a, b).

[c] As presented in Sjolander et al. (2011); does not explicitly state percent by mass or by volume.

[d] Sjolander et al. (2011) presents proppant in pounds instead of gallons.

[e] Listed as an ingredient, but no information on volume or percentage.

Because of the limited information on chemical volumes publicly available, we estimated chemical volumes used across the nation based on the information provided in the EPA FracFocus 1.0 project database. Figure 5-5 plots median estimated chemical volumes, ranked from high to low, with the range of 5th to 95th percentiles. Estimated volumes used are presented for the 74 chemicals that were reported in at least 100 disclosures in the EPA FracFocus 1.0 project database and for which density data were available. The estimated median volumes vary widely among the different chemicals, covering a range of near zero to 27,000 gal (98,000 L). The mean of the estimated median volumes was 650 gal (2,500 L), and the mean of the estimated median mass was 3,200 lb (1,500 kg) (U.S. EPA, 2015c). Mass, volume, and density data are presented in Appendix C along with the estimation methodology and assumptions used.

With the median chemical volume, we can estimate total chemical volume for all chemicals used. Based on the above mean of median chemical volumes of 650 gal (2,500 L) per chemical, and given that the median number of chemicals used at a site is 14 (U.S. EPA, 2015a), an estimated 9,100 gal (34,000 L) of chemicals may be used per well. Given that the number of chemicals per well ranges from 4 to 28 (U.S. EPA, 2015a), the total volume of chemicals per well may range from 2,600 to 18,000 gal (9,800 to 69,000 L).

Another way to estimate total volume of chemicals per well is to use the estimated median volume of 1.5 million gal (5.7 million L) of fluid used to fracture a well (U.S. EPA, 2015a) (Chapter 4) and assume that up to 2% of that volume consists of chemicals added to base fluid (Carter et al., 2013; Knappe and Fireline, 2012), resulting in up to 30,000 gal (114,000 L) of chemicals used per well.

Using the estimated volume per chemical of 650 gal (2,500 L), we can also estimate volume per additive and extrapolate to estimate on-site chemical storage. If we assume three to five chemicals per additive, then total volume per additive stored on-site would be approximately 1,900 to 3,200 gal (7,400 to 12,000 L). On-site containers generally store 20% to 100% more additive volume than ultimately used (Houston et al., 2009; Malone and Ely, 2007). This would suggest that 2,300 to 6,500 gal (8,800 to 25,000 L) per additive are stored on site.

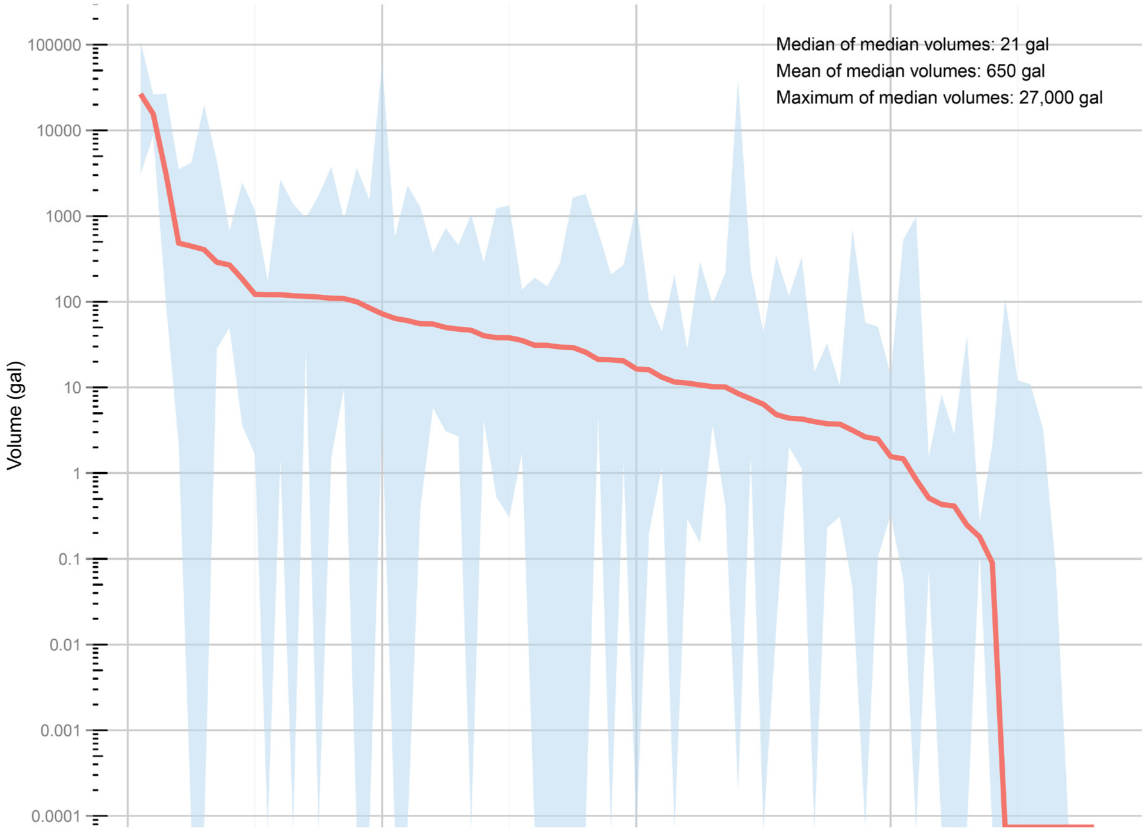

Figure 5-5. Estimated median volumes for 74 chemicals reported in at least 100 disclosures in the FracFocus 1.0 project database for use in hydraulic fracturing from January 1, 2011 to February 28, 2013.

Chemicals are plotted in order of largest to smallest median volume. Shaded area represents the zone of 5% and 95% confidence limits. Derived from U.S. EPA (2015c).

5.4.5 Chemical Composition of Hydraulic Fracturing Fluids and Additives

As the hydraulic fracturing process proceeds, the composition of the fluid injected changes over time. The overall composition of additives and hydraulic fracturing fluid may be reported by well operators to the FracFocus national registry, depending on the local disclosure requirements and operator preference. For each chemical that is injected into a well (excluding CBI chemicals), the maximum concentration in the resulting overall fluid and in each additive is given as maximum percent by mass. Based on this information, we calculated the median chemical composition reported in at least 10% of the disclosures in the EPA FracFocus 1.0 project database (Table 5-3) and a range based on the 5th and 95th percentile. Table 5-5 shows that some chemicals may be used in their pure form (100% of mass in a given additive). These chemicals include: methanol, hydrochloric acid, water, isopropanol, guar gum, citric acid, 2,2-Dibromo-3-nitrilopropionamide, tetrakis(hydroxymethyl) phosphonium sulfate, and sodium persulfate.

Chemicals may be stored in their concentrated, pure form, resulting in the potential for spills of concentrated volumes of these chemicals, which may increase the severity of impacts if they reach a drinking water resource. Once chemicals are mixed with the base fluid to form the hydraulic fracturing fluid, the chemical is diluted to much lower concentrations, which has the potential for a less severe impact. However, a larger volume of spill could occur with smaller concentrations. The larger volume may increase the potential for a spill reaching a drinking water resource, albeit at a lower concentration. There is the further complication of the hazard of the associated chemicals, since a smaller mass of a more hazardous chemical may be of more concern than a larger mass of a less hazardous chemical (as discussed in Chapter 9). It is therefore impossible to make a general statement without more detail on the spill characteristics, including the hazard, concentration, and volume.

Appendix Table C-6 provides mean, median, 5th and 95th percentile mass (kg) estimates for all reported chemicals in 100 or more disclosures in the EPA FracFocus 1.0 project database where density information was available.

Table 5-5. Fluid and additive composition by maximum mass percent.

Median, 5th and 95th percentile maximum concentration in hydraulic fracturing fluid and in additive (percent by mass) for the chemicals identified in the EPA FracFocus 1.0 project database in 10% or more disclosures. See Table 5-3 for percentage of disclosures and the common additives for which these chemicals are used. Analysis considered 34,675 disclosures and 676,376 ingredient records that met selected quality assurance criteria, including: completely parsed; unique combination of fracture date and API well number; fracture date between January 1, 2011, and February 28, 2013; valid CASRN; and valid concentrations. Disclosures that did not meet quality assurance criteria (3,855) or other, query-specific criteria were excluded from analysis.

EPA-standardized chemical name	CASRN	Maximum concentration in hydraulic fracturing fluid (percent by mass)			Maximum concentration in additive (percent by mass)		
		Median	5th Percentile	95th Percentile	Median	5th Percentile	95th Percentile
Methanol	67-56-1	0.0092	0.00011	0.12	30	0.44	100
Distillates, petroleum, hydrotreated light	64742-47-8	0.025	0.0013	0.35	30	0.70	70
Hydrochloric acid	7647-01-0	0.15	0.0083	1.3	15	2.8	60

EPA-standardized chemical name	CASRN	Maximum concentration in hydraulic fracturing fluid (percent by mass)			Maximum concentration in additive (percent by mass)		
		Median	5th Percentile	95th Percentile	Median	5th Percentile	95th Percentile
Water	7732-18-5	0.53	0.00065	82	65	5.0	100
Isopropanol	67-63-0	0.0038	0.000020	0.15	20	0.30	100
Ethylene glycol	107-21-1	0.016	0.00027	0.11	30	0.59	60
Peroxydisulfuric acid, diammonium salt	7727-54-0	0.0069	0.00010	0.064	100	0.11	100
Sodium hydroxide	1310-73-2	0.0092	0.000040	0.077	10	0.085	52
Guar gum	9000-30-0	0.16	0.0019	0.42	50	1.6	100
Quartz	14808-60-7	0.0033	0.000030	12	2.0	0.10	97
Glutaraldehyde	111-30-8	0.0072	0.00039	0.023	27	0.040	60
Propargyl alcohol	107-19-7	0.00015	0.000010	0.0028	8.0	0.0032	30
Potassium hydroxide	1310-58-3	0.0070	0	0.053	15	0.14	50
Ethanol	64-17-5	0.0034	0.000060	0.098	30	1.0	60
Acetic acid	64-19-7	0.0033	0	0.037	50	1.0	90
Citric acid	77-92-9	0.0027	0.000060	0.017	60	7.0	100
2-Butoxyethanol	111-76-2	0.0047	0	0.14	10	0.29	60
Sodium chloride	7647-14-5	0.0083	0	0.14	30	0.020	50
Solvent naphtha, petroleum, heavy arom.	64742-94-5	0.0051	0.000020	0.035	10	0.00052	30
Naphthalene	91-20-3	0.0014	0	0.0055	5.0	0.0023	5.0
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	0.0018	0.000010	0.022	98	10	100
Phenolic resin	9003-35-4	0.12	0.0046	1.1	5.0	0.80	20
Choline chloride	67-48-1	0.062	0.00068	0.14	75	0.75	80
Methenamine	100-97-0	0.010	0	0.21	1.0	0	2.0
Carbonic acid, dipotassium salt	584-08-7	0.039	0	0.15	60	30	60
1,2,4-Trimethylbenzene	95-63-6	0.00067	0	0.0068	1.0	0.010	20

EPA-standardized chemical name	CASRN	Maximum concentration in hydraulic fracturing fluid (percent by mass)			Maximum concentration in additive (percent by mass)		
		Median	5th Percentile	95th Percentile	Median	5th Percentile	95th Percentile
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides	68424-85-1	0.0019	0	0.0041	7.0	3.0	10
Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture)	127087-87-0	0.0025	0.000010	0.0089	5.0	5.0	10
Formic acid	64-18-6	0.0021	0	0.030	60	0.11	98
Sodium chlorite	7758-19-2	0.0040	0.00018	0.037	10	5.0	30
Nonyl phenol ethoxylate	9016-45-9	0.0088	0.000030	0.085	10	5.0	54
Tetrakis(hydroxymethyl) phosphonium sulfate	55566-30-8	0.011	0.00025	0.065	60	0.029	100
Polyethylene glycol	25322-68-3	0.0035	0.000010	0.038	20	0.0071	70
Ammonium chloride	12125-02-9	0.0025	0.00029	0.022	10	1.5	30
Sodium persulfate	7775-27-1	0.0017	0.000020	0.022	100	100	100

5.5 Chemical Management and Spill Potential

This section provides a description of the primary equipment used in the chemical mixing and well injection processes, along with a discussion of the spill vulnerabilities specific to each piece of equipment. Equipment breakdown or failure can trigger a spill itself, and it can also lead to a suspension of activity and the disconnection and reconnection of various pipes, hoses, and containers. Each manipulation of equipment poses additional potential for a spill. The EPA found that 31% of chemical spills on or near the well pad related to hydraulic fracturing resulted from equipment failure (U.S. EPA, 2015m). When possible, we describe documented spills, associated with or attributed to specific pieces of equipment, in text boxes in the relevant subsections.

Equipment used in hydraulic fracturing operations typically consists of chemical storage trucks, oil storage tanks/tanker trucks; a slurry blender; one or more high-pressure, high-volume fracturing pumps; the main manifold; surface lines and hoses; and a central control unit (Table 5-6). There are many potential sources for leaks and spills in this interconnected system. Furthermore, hydraulic fracturing operations are mobile and must be assembled at each well site, and each assembly and disassembly presents a potential for spills.

Equipment varies in age and technological advancement depending upon service company standards and costs associated with purchase and maintenance. Older equipment may have experienced wear and tear, which may be a factor in spills caused by equipment failure. New equipment may be more automated, potentially reducing opportunities for human error. Information detailing the extent of technological and age differences in fracturing equipment across sites and operators is limited.

Table 5-6. Examples of typical hydraulic fracturing equipment and its function.

Equipment	**Function**
Acid transport truck	Transports acids to job sites; the truck has separate compartments for multiple acids or additives.
Chemical storage truck	Transports chemicals to the site in separate containment units or totes. Chemicals are typically stored on and pumped from the chemical storage truck.
Base fluid tanks	Stores the required volume of base fluid to be used in the hydraulic fracturing process.
Proppant storage units	Holds proppant and feeds it to the blender via a large conveyor belt.
Blender	Takes fluid (e.g., water) from the fracturing tanks and proppant (e.g., sand) from the proppant storage unit and combines them with additives before transferring the mixture to the fracturing pumps
High-pressure fracturing pumps	Pressurizes mixed fluids received from the blender and injected into the well.
Manifold trailer with hoses and pipes	Serves as a transfer station for all fluids. Includes a trailer with a system of hoses and pipes connecting the blender, the high-pressure pumps, and the fracturing wellhead.
Fracturing wellhead or frac head	Allows fracture equipment to be attached to the well; located at the wellhead.
Central control unit or frac van	Monitors the hydraulic fracturing job using pressure and rate data supplied from around the job site.

While the primary equipment and layout are generally the same across well sites, the type, size, and number of pieces of equipment may vary depending on a number of factors (Malone and Ely, 2007):

- Size and type of the fracture treatment;
    - Length of well and number of stages;
    - Number of wells drilled per well pad;
    - Geographic location;
    - Depth below surface;
    - Length of the fractures;

- Volumes and types of additives, proppants, and fluids used; and
- Operating procedures of the well operator and service company (e.g., some companies require backup systems in case of mechanical failure, while others do not).

Figure 5-6 provides a schematic diagram of a typical layout of hydraulic fracturing equipment.

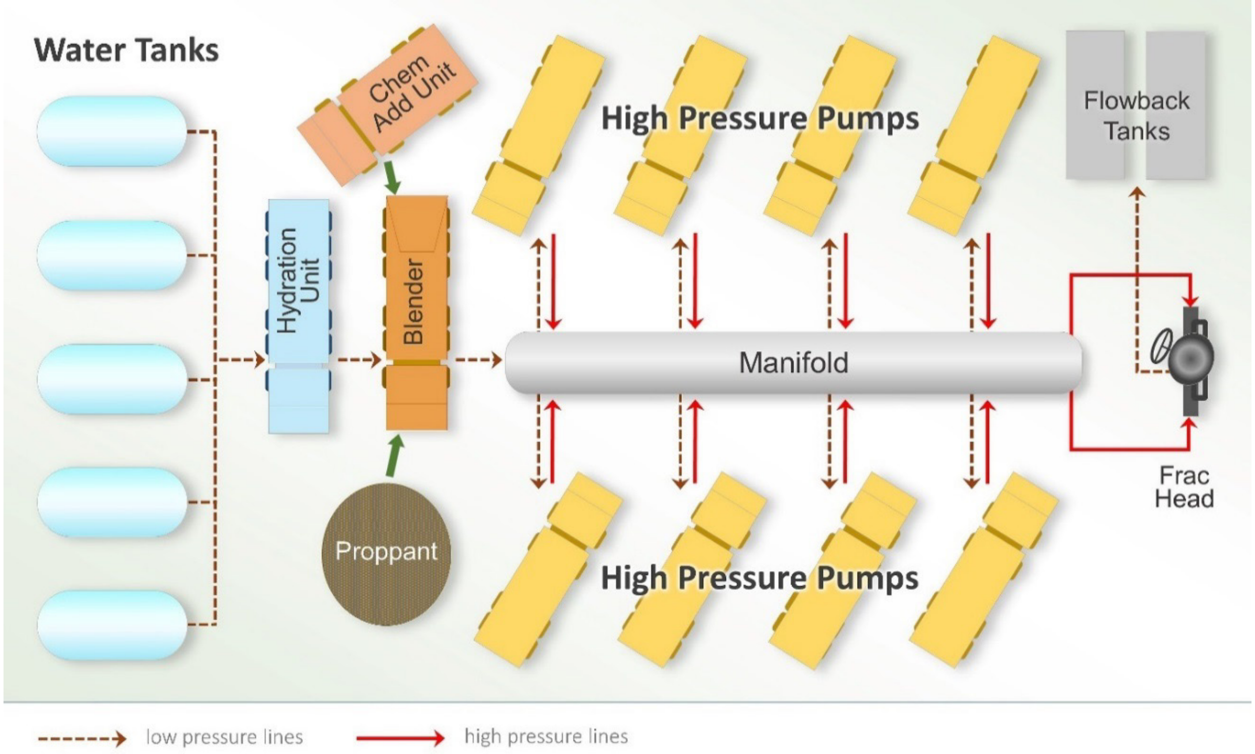

Figure 5-6. Typical hydraulic fracturing equipment layout.
This illustration shows how the various components of a typical hydraulic fracturing site fit together. The numbers of pumps and tanks vary from site to site. Some sites do not use a hydration unit as the gel is batch mixed prior to the treatment (Olson, 2011; BJ Services Company, 2009).

5.5.1 Storage

This section provides an overview of publicly available information on storage and containment of chemicals used in the hydraulic fracturing process. Most public sources provide general information on the types and sizes of containment units. While operators maintain a precise inventory of volumes of chemicals stored and used for each site, this information is typically not made public.

The volumes of each chemical used are based on the size and site-specific characteristics of each fracture treatment. Sites often store an excess of the design volume of chemicals for contingency purposes, typically 20% to 100% beyond what is necessary (Houston et al., 2009; Malone and Ely, 2007). See Text Box 5-3 for documented spills from storage units.

Text Box 5-3. Spills from Storage Units.

Of the 151 spills of chemicals, additives, or fracturing fluid discussed and evaluated in (U.S. EPA, 2015m) (see Text Box 5-10 for more information), 54 spills were from storage units. Storage units include totes or tanks used for storing individual chemicals or additives and larger tanks containing hydraulic fracturing fluid. These spills resulted from equipment failure, failure of storage integrity, or human error. Sixteen of these spills were due to failure of container integrity, which includes holes and cracks in containers, demonstrating the importance of properly constructed and maintained storage units. The remaining spills from storage containers resulted from human error or equipment malfunctions or had an unknown cause.

5.5.1.1 Hydraulic Fracturing Base Fluid Storage

Base fluids used in hydraulic fracturing are typically stored on-site in large volume tanks. Non-water-based fluids may be stored in specialized containment units designed to prevent or minimize releases. For example, nitrogen and carbon dioxide must be stored in compressed gas or cryogenic liquid cylinders, as required by U.S. Department of Transportation (DOT) and OSHA regulations. Due to the large volume of base fluid storage tanks (about 21,000 gal or 80,000 L) (Halliburton, 1988), uncontrolled spills could damage other storage units and equipment, which could result in additional spills. Fresh water used as a base fluid is generally not a source of concern for spills. Reused wastewater, brine, and non-aqueous base fluids have the potential to adversely impact drinking water resources in the event of a spill. Chapter 7 discusses reusing hydraulic fracturing wastewater as a base fluid and the spill/release potential on-site from pits and impoundments.

5.5.1.2 Additive Storage

Additives are typically stored on-site in the containers in which they were transported and delivered. The additive trailer typically consists of a flatbed truck or van enclosure that holds a number of chemical totes, described below, and is equipped with metering pumps that feed chemicals to the blender. Depending on the size and type of the fracturing operation, there may be one or more additive trailers per site (NYSDEC, 2015; ALL Consulting, 2012). While additives constitute a relatively small portion of fluids used in a hydraulic fracturing fluid, additive volumes can range from the tens to tens of thousands of gallons.

The storage totes generally remain on the transportation trailers, but they also may be unloaded from the trailers and transferred to alternative storage areas before use. Our investigation did not find much information on how often, when, or why these transfers occur. Additional transfers and movement can increase the likelihood of a spill. See Text Box 5-4 for a documented spill from an additive storage unit.

Text Box 5-4. Spill from Additive (Crosslinker) Storage Tote.

On Sept 19, 2009, during a tote transfer in Pennsylvania, a tote of crosslinker fell off a forklift spilling approximately 15 – 20 gal (60 – 80 L) onto the well pad. The area was scraped clean with a backhoe, and the waste was placed in a lined containment area (PA DEP, 2012, ID# 1845178).

The most commonly used chemical totes are 200 – 375 gal (760 – 1,420 L) capacity polyethylene containers that may be reinforced with steel or aluminum mesh (NYSDEC, 2015). Metal containers may also be used. The totes are typically equipped with bottom release ports, which enable direct feed of the additives to the blending equipment (NYSDEC, 2015). Spills may occur if lines are improperly connected to these ports or if the connection equipment is faulty.

Figure 5-7. Metal and high-density polyethylene (HDPE) additive units.
The image on the left depicts metal totes (industry source). The image on the right depicts plastic totes. Source: NYSDEC (2011).

Certain additives require specialized containment units with added spill prevention measures. For example, additives containing methanol may be subject to federal safety standards, and industry has developed guidance on methanol's safe storage and handling (Methanol Institute, 2013).

Dry additives are typically transported and stored on flatbed trucks in 50 or 55 lb (23 or 25 kg) bags, which are set on pallets containing 40 bags each (NYSDEC, 2015; UWS, 2008; Halliburton, 1988). Proppants are stored on-site in large tanks or bins with typical capacities of 350,000 to 450,000 lb (150,000 to 200,000 kg) (ALL Consulting, 2012; BJ Services Company, 2009; Halliburton, 1988).

5.5.1.3 Acid Storage

Acids are generally stored on-site in the containment units in which they are transported and delivered. A typical acid transport truck holds up to 5,000 gal (19,000 L) of acid and can have multiple compartments to hold different kinds of acid (Arthur et al., 2009b). Acids such as hydrochloric acid and formic acid are corrosive and can be extremely hazardous in concentrated form. Therefore, acid transport trailers and fracture tanks must be lined with chemical-resistant coating designed to prevent leakage and must meet applicable DOT regulatory standards (pursuant to 40 Code of Federal Regulations (CFR) 173) designed to prevent or minimize spills.

Acid fracture treatments may use thousands of gallons of acid per treatment (Spellman, 2012). Given the large volumes used, failure of containment vessels during storage or failure of connections and hoses during pumping could result in high-volume acid spills. Details of a documented acid spill are presented in Text Box 5-5.

Text Box 5-5. Spill of Acid from Storage Container.

In July 2014, in Oklahoma, 20,000 gal (76,000 L) of hydrochloric acid spilled from a storage container when a flange malfunctioned. The acid spilled into a nearby alfalfa field, where it was contained with an emergency berm (Phillips, 2014; Wertz, 2014). There is no information on how much leached into soils or if the spill reached drinking water resources.

5.5.1.4 Gel Storage

Gels can be added to hydraulic fracturing fluid using either batch or continuous (also called "on-the-fly") mixing systems. Gelling agents and gel slurries are stored differently on-site and can pose different potential spill scenarios depending on whether the site is using batch or continuous mixing processes (BJ Services Company, 2009).

In a typical batch mixing process, powdered gelling agents and related additives (e.g., buffers, surfactants, biocides) are mixed on-site with base fluid water and proppant in large tanks, typically 20,000 gal (80,000 L)(BJ Services Company, 2009; Halliburton, 1988). The number of gel slurry tanks used varies based on site-specific conditions and the size of the fracture job. These tanks can be subject to leaks or overflow during the batch mixing process and during storage prior to injection. One of the disadvantages of batch mixing is the need for multiple suction hoses to draw pre-gelled fluids from storage tanks into the blender, if used, which can increase the potential for spills. Yeager and Bailey (2013) state that a drawback of batch mixing is the "fluid spillage and location mess encountered when pre-mixing tanks," suggesting that small spills are not uncommon during batch mixing. Details of a documented gel slurry spill are presented in Text Box 5-6. Details of a documented gel slurry spill are presented in Text Box 5-6.

Text Box 5-6. Spill of Gel Slurry during Mixing.

On April 9, 2010, in Louisiana, a company was mixing a gel slurry for an upcoming fracture job. The tank had developed a crack, which allowed approximately 10,000 gal (38,000 L) of water mixed with 60 gal (230 L) of gel to leak out. The mixture did not reach a water receptor, and absorbents were used to clean up the gel (LDEQ, 2013).

In continuous mixing operations, powdered gels are typically replaced with liquid gel concentrates (Allen, 2013; BJ Services Company, 2009). Operators prepare dilute gelling agents as needed using specialized hydration units (BJ Services Company, 2009). Liquid gel concentrates may be stored on-site in single-purpose tanker trucks (Harms and Yeager, 1987) but are more often stored in specialized mixing and hydration units (Ayala et al., 2006). Continuous mixing requires less preparation than batch mixing but typically requires more equipment (BJ Services Company, 2009; Browne and Lukocs, 1999). This can increase the possibility for spills resulting from equipment malfunctions or human error.

5.5.2 Hoses and Lines

High- and low-pressure hoses and lines are used to transfer hydraulic fracturing fluids from storage units to specialized mixing and pumping equipment and ultimately to the wellhead. A discussion of the different types of hoses and lines and possible points of failure is provided below. Figure 5-8 shows an example of hoses and lines at a hydraulic fracturing site.

Figure 5-8. Hoses and lines at a site in Arkansas.
Photo credit: Christopher Knightes (U.S. EPA).

Suction pumps and hoses move large volumes of base fluid to the blender. Incomplete or damaged seals in inlet or outlet connections can cause fluid leaks at the connection points. Improperly fitted seals also severely limit or eliminate suction lift, which can impair the suction pump and increase spill potential. Suction hoses themselves are susceptible to leaks due to wear and tear. Equipment providers recommend hoses be closely inspected to ensure they are in good operating condition prior to use (Upstream Pumping, 2015; BJ Services Company, 2009; Malone and Ely, 2007).

Discharge hoses transfer additives from containment vessels or totes to the blender. Given the potential for concentrated chemicals to spill during transfer from storage totes to the blender, it is particularly important that these hoses are in good condition and that connector seals or washers fit properly and are undamaged. Discharge hoses are also used to carry fracturing fluid pumped from the blender via the low-pressure manifold to the high-pressure pumps. Proppant-heavy fluids are pumped through discharge hoses at relatively low rates. If a sufficient flow rate is not maintained, proppant may settle out, damaging pumps and creating a potential for spills and leaks (Upstream Pumping, 2015; BJ Services Company, 2009; Malone and Ely, 2007).

High-pressure flow lines convey pressurized fluids from the high-pressure pumps into the high-pressure manifold and from the manifold into the wellbore. High-pressure flow lines are subject to erosion caused by the high-velocity movement of abrasive, proppant-laden fluid. Curved sections of flow lines (e.g., swivel joints) where abrasive fluids are forced to turn corners are particularly subject to erosion and are more likely to develop stress cracks or other defects that can result in a leak or spill. Safety restraints are typically used to prevent movement of flow lines such as in the event of failure and to help control spills. High-pressure flow lines are pressure-tested to detect fatigue or stress cracks prior to the fracturing treatment (OSHA, 2015; BJ Services Company, 2009; Arthur et al., 2008; Malone and Ely, 2007; Halliburton, 1988).

Nineteen spills of chemicals or fracturing fluids associated with leaks from hoses or lines had a total spill volume of 12,756 gal (48,287 L), with a median volume of 420 gal (1,600 L) (U.S. EPA, 2015m).

5.5.3 Blender

The blender is the central piece of equipment used to create the fracturing fluid for injection. It moves, meters, and mixes precise amounts of the base fluid, additives, and proppant and pumps the mixed slurry to high-pressure pumping equipment (BJ Services Company, 2009; Malone and Ely, 2007; Halliburton, 1988) (Figure 5-6). A typical blender consists of a centrifugal suction pump for pulling base fluid, one or more chemical metering pumps to apportion the additives, one or more proportioners to measure and feed proppant, and a central agitator tank where fluid components are mixed together.

The blending process is monitored to ensure that a uniform mixture is maintained regardless of injection rates and volumes. Excessive or reduced rates of flow during treatment can cause the blender to malfunction or to shut down, which can result in spills (Malone and Ely, 2007; Halliburton, 1988). For aqueous hydraulic fracturing fluid blends, spills that occur downstream of the blender will be a dilute mixture (less than or equal to 2%) of chemicals. Details of a spill from a blender are presented in Text Box 5-7.

Text Box 5-7. Spill of Hydraulic Fracturing Fluid from Blender.

In May 2006, a blender malfunctioned during a fracture job in Oklahoma. Approximately 294 gal (1,110 L) of fluid spilled into a nearby wheat field. The fluid consisted of hydrochloric acid, clay stabilizer, diesel, and friction reducer. Contaminated soil was removed by the operator (OCC, 2013, ID#137000).

5.5.4 Manifold

A trailer-mounted manifold and pump system functions as a central transfer station for all fluids used in the hydraulic fracturing operation. The manifold is a collection of low- and high-pressure pipes equipped with multiple fittings for connector hoses. Fluids are pumped from the blender through the low-pressure manifold hoses, which distribute fluids to high-pressure pump trucks. Pressurized slurry is sent from the pump trucks through high-pressure manifold lines and into additional high pressure lines that lead to the wellhead (Malone and Ely, 2007).

Manifold and pump system components require varying amounts of manual assembly and undergo varying amounts of pre-testing (Malone and Ely, 2007). Improperly tested parts may be more likely to break or lose functionality, leading to a spill. In manifolds requiring more manual assembly, there may be more opportunities for human error.

5.5.5 High-Pressure Fracturing Pumps

High-pressure fracturing pumps take the fracturing fluid mixture from the blender, pressurize it, and propel it down the well. Typically, multiple high-pressure, high-volume fracturing pumps are needed for hydraulic fracturing (Upstream Pumping, 2015). Such pumps come in a variety of sizes. Bigger pumps move greater volumes of fluid at higher pressures; therefore, spills from these pumps can be larger. Smaller pumps can require more operators and more maintenance (BJ Services Company, 2009), and therefore have the potential for an increased frequency of spills.

The “fluid ends” of hydraulic fracturing pumps are the pump components through which fluids are moved and pressurized. Pump fluid ends must withstand high pressure and move a large volume of abrasive fluid high in solids content. These pumps have multiple parts (e.g., seals, valves, seats and springs, plungers, stay rods, studs) that can wear out under the stress of high-pressure pumping (Upstream Pumping, 2015). Given the sustained pressures involved, careful maintenance of fluid ends is necessary to prevent equipment failure (Upstream Pumping, 2015; API, 2011). Details of a documented spill from a fracture pump are presented in Text Box 5-8.

Text Box 5-8. Spill of Fluid from Fracture Pump.

On December 19, 2011, in Arkansas, a fluid end on a fracture pump developed a leak, spilling approximately 840 gal (3,200 L) of fracturing fluid. A vacuum truck was used to recover the spilled fluid, and all affected soils were neutralized and taken to a landfill at the end of the job, after removal of the equipment (Arkansas DEQ, 2012, ID#063012).

5.5.6 Surface Wellhead for Fracture Stimulation

A wellhead assembly, often referred to as a frac head or frac stack, is temporarily installed on the wellhead during the fracture treatment. The frac head assembly allows high volumes of high-pressure proppant-laden fluid to be injected into the formation (OSHA, 2015; Halliburton, 2014; Stinger Wellhead Protection, 2010). The temporary frac head is equipped with specialized isolation tools so that the wellhead is protected from the effects of pressure and abrasion.

Figure 5-9. Multiple fracture heads.
Source: DOE/NETL.

As with all components of hydraulic fracturing operations, repeated and prolonged stress from highly pressurized, abrasive fluids may lead to equipment damage. The presence of minute holes or cracks in the frac head may result in leaks when pressurized fluids are pumped. In addition, surface blowouts or uncontrolled fluid releases may occur at the frac head because of valve failure or failure of other components of the assembly.[1] Details of a documented frac head failure are presented in Text Box 5-9.

Text Box 5-9. Spill from Frac Head Failure.

On March 2, 2011, in Colorado, a frac head failed during fracturing operations. Approximately 8,400 gal (32,000 L) of slickwater fracturing fluid leaked. The majority of the spill was contained on-site, though a small amount ran off into a nearby cornrow. There were 5,460 gal (20,700 L) of the fluid recovered, and saturated soils were scraped and stockpiled on the well pad. There was a net loss of 2,940 gal (11,100 L) (COGCC, 2012, ID#2524586).

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[1] A well blowout is when there is uncontrolled flow of fluids out of a well.

5.6 Overview of Chemical Spills Data

Spills of hydraulic fracturing fluids have occurred across the country and have affected the quality of drinking water resources (U.S. EPA, 2015m; Brantley et al., 2014; COGCC, 2014; Gradient, 2013).[1] Spills may infiltrate drinking water resources by reaching surface water or by leaching into the groundwater. Potential impacts depend upon a variety of factors including the chemical spilled, environmental conditions, and actions taken in response to the spill.

5.6.1 EPA Analysis of Spills Associated with Hydraulic Fracturing

The EPA used data gathered from state and industry sources to characterize hydraulic fracturing-related spills between January 2006 and April 2012 (2015m) (see Text Box 5-10 for additional information). In this study, the sources had data on over 36,000 spills. Of these spills, the EPA identified 457 spills that occurred on or near the well pad and definitively related to hydraulic fracturing. Of these 457 spills, 151 were related to the chemical mixing process – spills that consisted of chemicals, additives, or fracturing fluids. Information in the spill reports included: spill causes (e.g., human error, equipment failure), sources (e.g., storage tank, hose or line), volumes, and environmental receptors. Spill reports contain little information on chemical-specific spill composition. Spilled fluids were often described by their additive type (e.g., acids, biocides, friction reducers, cross-linkers, gels,) or as a blended hydraulic fracturing fluid. Specific chemicals mentioned in spill reports included hydrochloric acid and potassium chloride.

Text Box 5-10. EPA Review of State and Industry Spill Data: Characterization of Hydraulic Fracturing-Related Spills.

As part of the EPA's Study of the Potential Impacts of Hydraulic Fracturing for Oil and Gas on Drinking Water Resources, the EPA published the report titled *Review of State and Industry Spill Data: Characterization of Hydraulic Fracturing-Related Spills* (U.S. EPA, 2015m). In this document, hereafter referred to as the EPA spills report, the EPA used data gathered from state and industry sources to characterize hydraulic fracturing-related spills with respect to volumes spilled, materials spilled, sources, causes, environmental receptors, containment, and responses. For the purposes of the study, hydraulic fracturing-related spills were defined as those occurring on or near the well pad before or during the injection of hydraulic fracturing fluids or during the post-injection recovery of fluids. Because the main focus of this study is to identify hydraulic fracturing-related spills on the well pad that may reach surface or groundwater resources, the following topics were not included in the scope of this project: transportation-related spills, drilling mud spills, and spills associated with disposal through underground injection control wells.

Data on spills that occurred between January 2006 and April 2012 were obtained from nine state agencies with online spill databases or other data sources, nine hydraulic fracturing service companies, and nine oil and gas production well operators. The data sources used in this study contained over 36,000 spills. The EPA searched each spill report for keywords related to hydraulic fracturing (e.g., frac, glycol, flowback). Spill records from approximately 12,000 spills (33 percent of the total number of spills reviewed) contained insufficient information to determine whether the event was related to hydraulic fracturing.

(Text Box 5-10 is continued on the following page.)

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[1] In this assessment, a spill is considered to be any release of fluids. Spills can result from accidents, fluid management practices, or illegal dumping.

Text Box 5-10 (continued). EPA Review of State and Industry Spill Data: Characterization of Hydraulic Fracturing-Related Spills.

Of the spills with sufficient information, the EPA identified approximately 24,000 spills (66%) as not related to hydraulic fracturing on or near the well pad. The remaining 457 spills (approximately 1%) occurred on or near the well pad and were definitively related to hydraulic fracturing. These 457 spills occurred in 11 different states over six years (January 2006 to April 2012). Of these 457 spills, 151 spills were chemical mixing-related and included spills of chemicals, additives, and hydraulic fracturing fluid, and 225 releases were of produced water (Chapter 7).

The EPA categorized spills according to the following causes: equipment failure, human error, failure of container integrity, other (e.g., well communication, weather, vandalism), and unknown.[1] Figure 5-10 presents the percent distribution of causes of hydraulic fracturing-related spills and for spills associated specifically with chemicals or fracturing fluid. The distributions for causes of hydraulic fracturing- and chemical mixing-related spills are similar.[2]

Spills in the EPA spills report were also categorized by the following sources: storage, equipment, well or wellhead, hose or line, and unknown. Figure 5-11 presents the percent distribution for all hydraulic fracturing- and chemical mixing-related spills associated with each source.

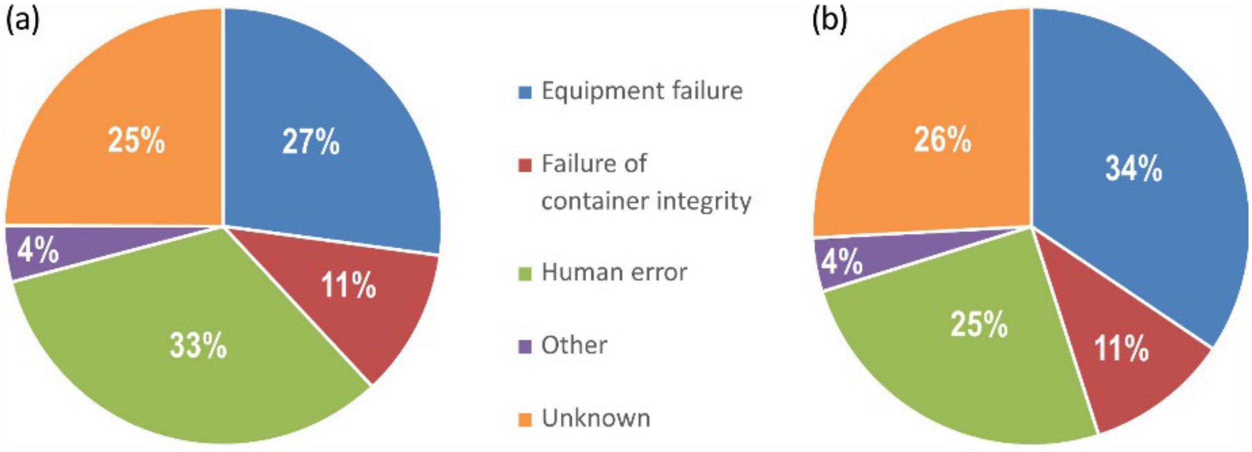

Figure 5-10. Percent distribution of the causes of spills.
Percent distribution by spill type for (a) 457 hydraulic fracturing-related spills (all spills) and (b) 151 chemical mixing-related spills. Data from U.S. EPA (2015m). Legend shows categories in clockwise order, from the top left of each pie chart.

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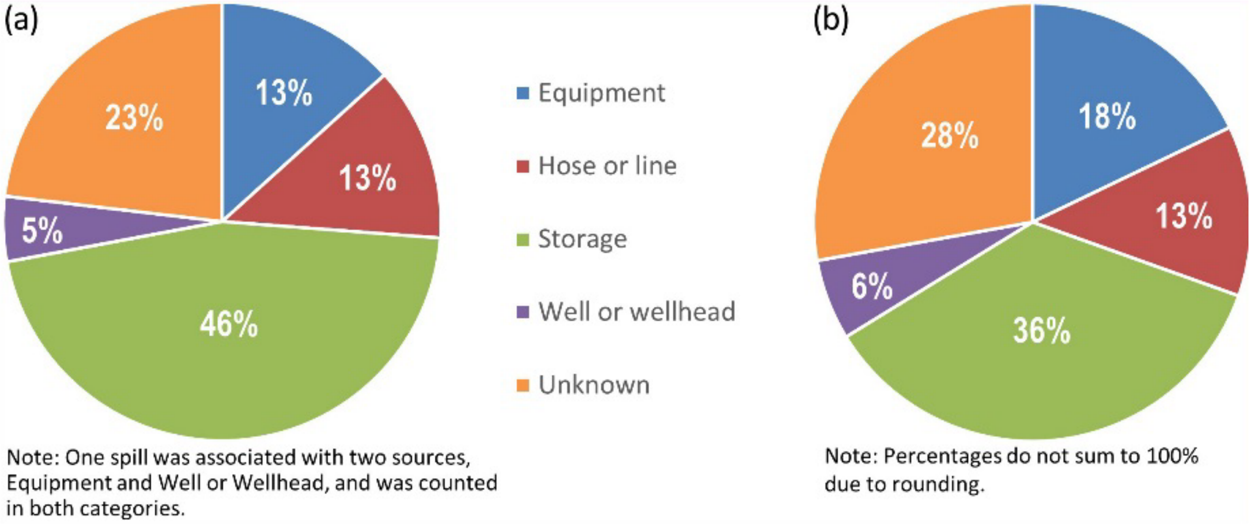
[1] Well communication is when hydraulic fracturing fluids or displaced subsurface fluids move through newly created fractures into an offset well or its fracture network (See Section 6.3.2.3 for more details),

[2] Hydraulic fracturing-related spills are spills that occur at any phase within the hydraulic fracturing water cycle. These include chemicals, additives, hydraulic fracturing fluids (chemical mixing phase); produced water; and wastewater.



Note: One spill was associated with two sources, Equipment and Well or Wellhead, and was counted in both categories.

Note: Percentages do not sum to 100% due to rounding.

Figure 5-11. Percent distribution of the sources of spills.

Percent distribution of spill source of (a) 457 hydraulic fracturing-related spills (all spills) and (b) 151 chemical mixing-related spills. Data from U.S. EPA (2015m). Legend shows categories in clockwise order, from the top left of each pie chart.

Figure 5-12 presents the distribution of the number of spills for different volumes for hydraulic fracturing- and chemical mixing-related spills. The spills associated with chemical mixing ranged in volume from 5 to 19,320 gal (19 to 73,130 L), with a median volume of 420 gal (1,600 L). The source of largest spills was storage containers, which released approximately 83,000 gal (314,000 L) of spilled fluid (Figure 5-13b). Spills from wells or wellheads are often associated with high spill volumes. There were no reported chemical mixing-related spills greater than 100,000 gal (380,000 L) (Figure 5-15b).

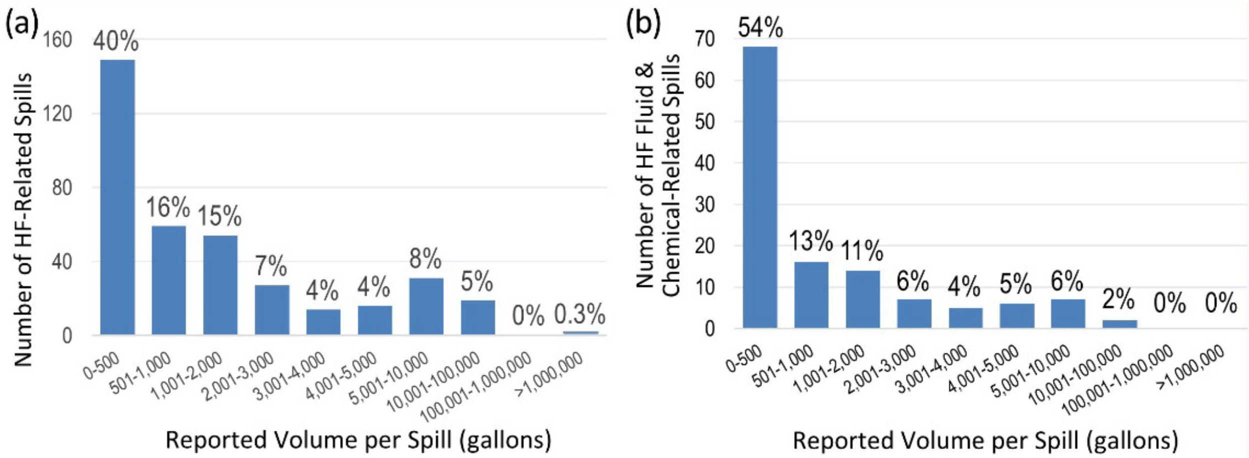


Figure 5-12. Distribution of the number of spills for different ranges of spill volumes.

Number of spills due to Hydraulic Fracturing related activities and distribution of spill volumes for (a) 457 hydraulic fracturing-related spills (all spills) and (b) 151 chemical mixing-related spills. A value of 0% means that there were no spills in that category. Data from U.S. EPA (2015m).

Figure 5-13 presents the total volume of spills for different sources for all hydraulic fracturing-related activity and those associated with chemicals and fracturing fluid. The reported total volume of 125 of 151 chemical or hydraulic fracturing fluid spills was approximately 184,000 gal (697,000 L). The volume was unknown for 26 of these spills.

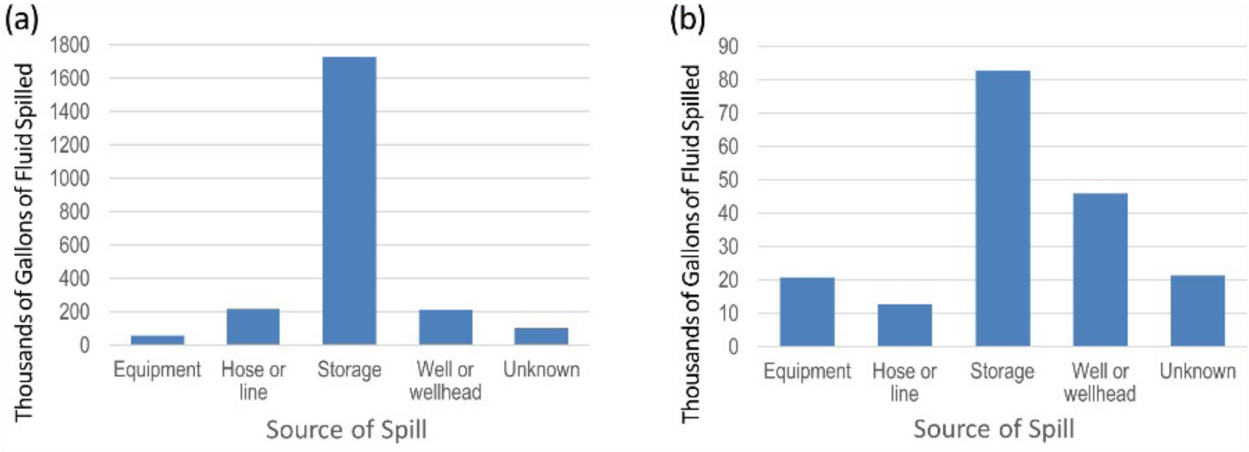


Figure 5-13. Total volume of fluids spilled from different sources.

Total volume of fluids spilled for (a) 457 hydraulic fracturing-related spills (all spills) and (b) 151 chemical mixing-related spills. Data from U.S. EPA (2015m).

Figure 5-14 presents the number of spills that reached environmental receptors, by receptor type, for all hydraulic fracturing-related activity (Figure 5-14a) and those associated with chemicals and fracturing fluid (Figure 5-14b). Environmental receptors (i.e., surface water, groundwater, soil) were identified in 101 of the 151 chemical mixing-related spills, or 67% of all chemical and fracturing fluid spills in the EPA's analysis (U.S. EPA, 2015m). Soil was by far the dominant environmental receptor, with 97 spills reaching soil; reported spill volumes ranged from 5 gal to 8,300 gal (19 L to 31,000 L). Thirteen spill reports indicated that the spilled fluid had reached surface water; reported spill volumes ranged from 28 gal to 7,350 gal (105 L to 27,800 L). Nine spill reports identified both soil and surface water as a receptor; spill volumes ranged from 28 gal to 2,856 gal (106 L to 10,800 L). Groundwater was not identified as a receptor from spills of chemicals or hydraulic fracturing fluid in any of the spill reports. Due to the lack of observations, it is often unclear if there was impact on groundwater. Movement through the subsurface is generally slow.[1] It may take years for a spilled fluid to reach groundwater or to reach a drinking water well. Thus, even if there is a pre-drilling characterization of groundwater chemistry in private/public wells, the time period of transport to actually detect a release at these private/public wells for contaminants that are transported at the rates of groundwater flow (see Section 5.8 for discussion on fate and transport of spilled chemicals).

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[1] For example, a groundwater flow rate of 1 foot per day (not uncommon) would mean it could take approximately 1,000 days (~3 years) to travel 1,000 ft (305 m) from the well pad. Likewise, for a groundwater travel rate of 0.1 ft (0.03m) per day, impact would not be observed for at least 10,000 days (~27 years). For a travel rate of 10 ft (3 m) per day, the time for impact would be at least 100 days (~0.3 years).

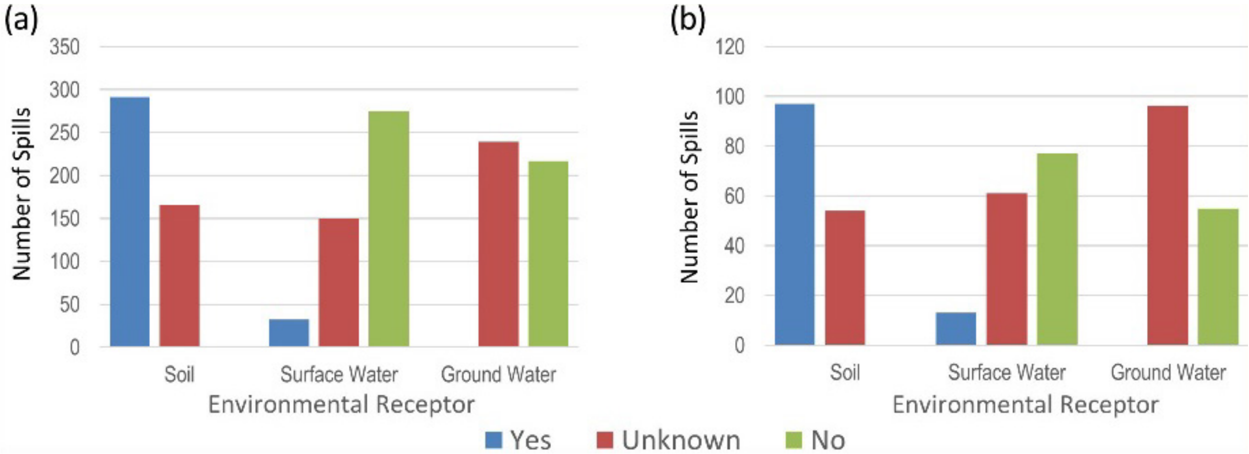

Figure 5-14. Number of spills by environmental receptor.

Number of hydraulic fracturing-related spills and chemical mixing-related spills that reported whether an environmental receptor was reached for (a) 457 hydraulic fracturing-related spills (all spills) and (b) 151 chemical mixing related spills. "Yes" means that the spill was reported to reach this receptor. "Unknown" refers to hydraulic fracturing related spill events for which environmental receptors were specified as unknown or not identified (positively or negatively). "No" means the spill was reported to not meet this receptor. Data from U.S. EPA (2015m).

Storage units were the predominant sources of spills that reached an environmental receptor. Six spills from storage containers reached a surface water receptor. Thirty-eight of the spills from storage units reached a soil receptor. If a spill was confined to a lined well pad, for example, it might not have reached the soil, but most incident reports did not include whether the well pad was lined or unlined. Regarding spills of hydraulic fluids and chemicals from storage containers, 16 spills were due to failure of container integrity, which includes holes and cracks in containers, and overflowing containers as a result of human error or equipment malfunctions.

5.6.2 Estimated Spill Rate and Other Spill Reports and Data

The rate of reported spills during the hydraulic fracturing water cycle is estimated to range from 0.4 to 12.2 reported spills for every 100 wells, based on spills data from Brantley et al. (2014), Gradient (2013), Rahm et al. (2015), U.S. EPA (2013a), and North Dakota Department of Health (2015) (Appendix E) with a median rate of 2.6 reported spills for every 100 wells. (See Appendix Section C.4 and Appendix Table C-8 for details.) The estimated rates provide an approximate estimate of the potential frequency of the number of spills at a site. It is uncertain how representative these rates are of national spill rates or rates in other states. These numbers are not specific to the chemical mixing stage.

There are an estimated 2.6 reported spills of injected fluids and chemicals per 100 wells hydraulically fractured in North Dakota, based on an analysis of the North Dakota spills database for 2015, separate from the EPA spills report. The median spill volume of injection fluid was 1750 gal (6620 L), with a range of 2.9 to 17,600 gal (11 to 66,600 L). The median spill volume of injection chemical was 44 gal (167 L), with a range of 2.1 to 126 gal (7.9 to 477 L) (see Appendix E for more information).

A study of spills reported to the Colorado Oil and Gas Conservation Commission identified 125 spills during well stimulation (i.e., a part of the life of an oil and gas well that often, but not always, includes hydraulic fracturing) between January 2010 and August 2013. Of these spills, 51% were caused by human error and 46% were due to equipment failure (COGCC, 2014).

Considine et al. (2012) identified spills related to oil and gas development in the Marcellus Shale that occurred between January 2008 and August 2011 from Notices of Violations issued by the Pennsylvania Department of Environmental Protection. The authors identified spills greater than 400 gal (1,500 L) and spills less than 400 gal (1,500 L). Among these spills, spilled fluids included hydrochloric acid, gel friction reducer, and blended hydraulic fracturing fluid. Brantley et al. (2014) identified fewer than 10 instances of spills of additives and/or hydraulic fracturing fluids greater than 400 gal (1,500 L) that reached surface waters in Pennsylvania between January 2008 and September 2013. Reported spill volumes, among these spills, ranged from 3,400 gal to 227,000 gal (13,000 L to 859,000 L).

Surface spills related to hydraulic fracturing activities are not well documented in the scientific literature. There is some evidence of spills and impacts on environmental media (e.g., U.S. EPA, 2015i; Brantley et al., 2014; Gross et al., 2013; Papoulias and Velasco, 2013). Papoulias and Velasco (2013) stated that fluid overflowed a retention pit into surface water and likely contributed to the distress and deaths of threatened blackside dace fish in Kentucky. A variety of chemicals entered the creek and significantly reduced the stream's pH and increased stream conductivity. Using data from post-spill sampling reports in Colorado, Gross et al. (2013) identified concentrations of benzene, toluene, ethylbenzene, and xylene (BTEX) in groundwater samples. They attributed this to numerous hydraulic fracturing-related spills, although not necessarily specifically related to the chemical mixing process. This work, however, demonstrate that surface spills impacted groundwater, with a frequency of < 0.5% of active wells. Drollette et al. (2015) reported that organic compounds detected in shallow aquifers were consistent with surface spills, and that diesel range compounds had elevated concentrations compared to gasoline range compounds, further suggesting evidence of feasible groundwater impact.

5.7 Spill Prevention, Containment, and Mitigation

Spill prevention, containment, and mitigation affect the frequency and severity of the impacts of spills. Several factors influence spill prevention, containment, and mitigation, including federal, state, and local regulations and company practices. State regulations governing spill prevention, containment, and mitigation at hydraulic fracturing facilities vary in scope and stringency (Powell, 2013; GWPC, 2009). Employee training and equipment maintenance are also factors in effective spill prevention, containment, and mitigation. Analysis of these factors was outside the scope of this assessment.

The province of New Brunswick, Canada released rules for industry on responsible environmental management of oil and natural gas activities (GNB, 2013). Hydraulic fracturing service companies themselves may develop and implement spill prevention and containment procedures. It was beyond the scope of this assessment to evaluate the efficacy of these practices or the extent to which they are implemented.

Spill containment systems include primary, secondary, and emergency containment systems. Primary containment systems are the storage units, such as tanks or totes, in which fluids are intentionally kept. Secondary containment systems, such as liners and berms installed during site set-up, are intended to contain spilled fluids until they can be cleaned up. Emergency containment systems, such as berms, dikes, and booms, can be implemented temporarily in response to a spill.

The EPA investigated spill containment and mitigation measures in an analysis of spills related to hydraulic fracturing activities (U.S. EPA, 2015m). Of the approximately 25% of reports that included information on containment, the most common types of containment systems referenced in the hydraulic fracturing-related spill records included berms, booms, dikes, liners, and pits, though many of the spill reports did not indicate specific containment measures. Some spills were reported to breach the secondary containment systems. Breaches of berms and dikes were most commonly reported.

In cases where secondary containment systems were not present or were inadequate, operators sometimes built emergency containment systems. The most common were berms, dikes, and booms, but there were also instances where ditches, pits, or absorbent materials were used to contain the spilled fluid. Absorbent materials were generally used when small volumes (10 – 200 gal or 40 – 800 L) of additives or chemicals were spilled (U.S. EPA, 2015m). There was not enough information to detail the use of emergency containment systems or their effectiveness.

Remediation is the action taken to clean up a spill and its affected environmental media. The most commonly reported remediation activity, mentioned in approximately half of the hydraulic fracturing-related spill records evaluated by the EPA, was removal of spilled fluid and/or affected media, typically soil. Other remediation methods reported in U.S. EPA (2015m) included the use of absorbent material, vacuum trucks, flushing the affected area with water, and neutralizing the spilled material. Removal activities were found to occur in various combinations. For example, a spill of approximately 4,200 gal (16,000 L) of acid was cleaned up by first spreading soda ash to neutralize the acid and then removing the affected soil (U.S. EPA, 2015m).

5.8 Fate and Transport of Spilled Chemicals

The fate and transport of chemicals in the environment is complex. Due to the complexities of the processes and the site-specific and chemical-specific nature of spills, it is difficult to develop a full assessment of their fate and transport. The potential for hydraulic fracturing chemicals and fluids to reach drinking water resources is further complicated by the fact that these chemicals are typically present as mixtures, and unlike many organic contaminant mixtures (e.g., gasoline, diesels, PCBs, PAHs), hydraulic fracturing fluid chemicals are present as complex mixtures of chemicals covering a range of chemical classes with varying properties, often in aqueous solutions.

In this section, we provide a general overview of fate and transport of hydraulic fracturing-related chemicals spilled in the environment to give the reader a general understanding of the potential pathways and processes with which these chemicals can impact drinking water resources (Figure 5-15). We also include a discussion of the physicochemical properties of the organic chemicals used in hydraulic fracturing fluids, because these properties directly affect the transport of chemicals in the environment. This presentation is not meant to be exhaustive.

A chemical spill has the potential to migrate to and have an impact on drinking water resources. Once spilled, there are different paths that chemicals can travel and different processes they can undergo. Chemicals can react and transform into other chemicals, volatilize, travel to surface water, leach into and partition to soils, and/or reach groundwater. The potential path and the severity of the impact of a spill depend on different factors, including site conditions; the length of the path to a drinking water resource; the type and characteristics of the drinking water resource (stream, lake, aquifer); environmental conditions; climate; weather; chemical properties, constituents, and concentrations; and the volume of the release. The point in the chemical mixing stage where the spill occurs affects potential impact. If the spill occurs before chemicals are mixed into the base fluid, the chemicals will be in a more concentrated form. If the hydraulic fracturing fluid spills, then the chemicals will be diluted by the base fluid and can feasibly be present in lower concentrations. There can also be effects on persistence and mobility due to interactions among the chemicals present. The total mass of spilled chemical can therefore be dependent on what stage in the process a spill occurs.

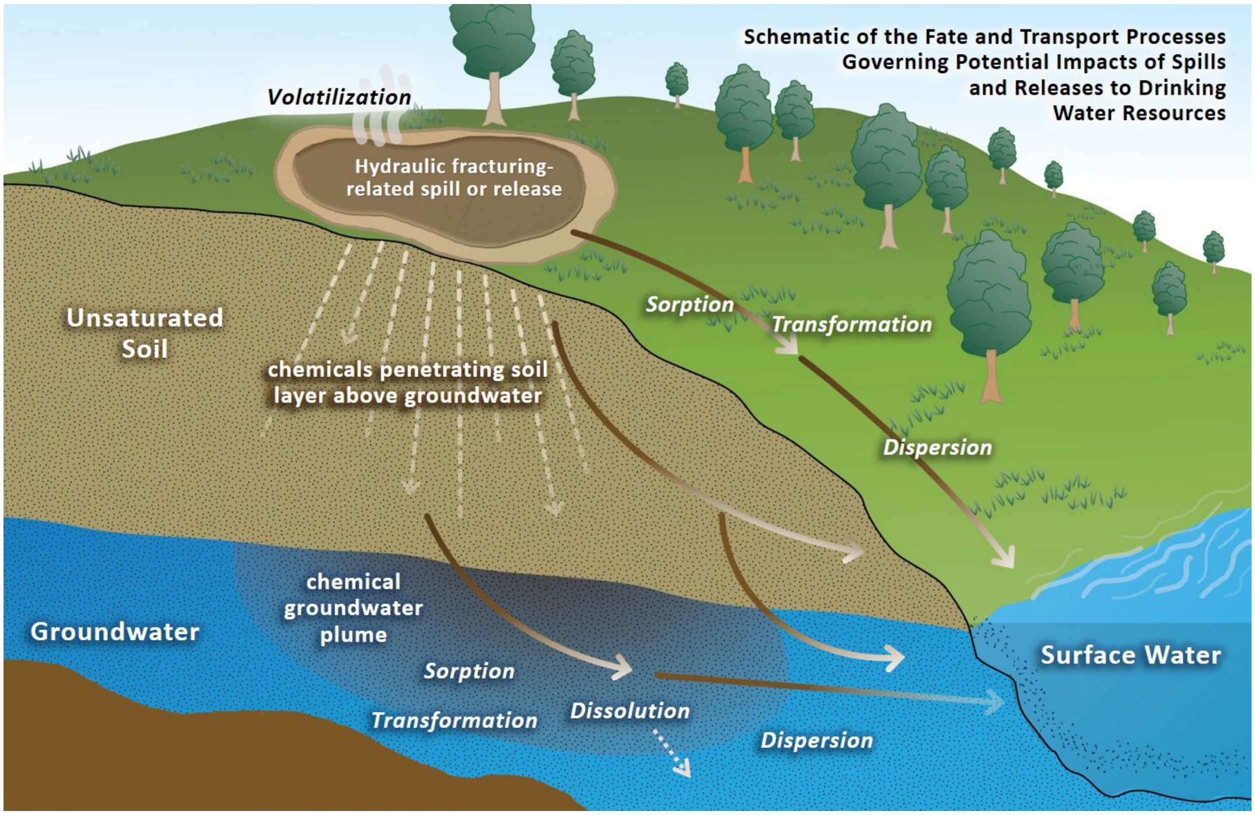

Figure 5-15. Fate and transport schematic for a spilled hydraulic fracturing fluid.

Schematic shows the potential paths and governing processes by which spilled chemicals can lead to potential impacts on drinking water resources.

For inorganic chemicals, the properties and processes governing fate and transport depend on pH, oxidation state, presence of iron oxides, soil organic matter, cation exchange capacity, and major ion chemistry (U.S. EPA, 1996).[1] Transport of these chemicals into groundwater depends on the nature of groundwater flow and flow through the unsaturated zone above the water table.[2] Potential transformations of inorganic chemicals differ from those of organic chemicals. Some inorganic anions (i.e., nitrate, chloride, and bromide) move with their carrier liquid and are affected mostly by physical transport mechanisms. For many inorganic chemicals, transport is driven by the physical flow processes (advection and dispersion), sorption, and precipitation. The relative role of each of these depends on both chemical and environmental characteristics.[3,4]

Determining the fate and transport of organic chemicals and mixtures is a complex problem, because of the many processes and different environmental media (air, soil, water). Unlike inorganic chemicals, organic chemicals degrade, which can affect their movement and potential impact. Schwarzenbach et al. (2002) formalized a general framework for organic chemical transport, where transport and transformation depend on both the nature of the chemical and the properties of the environment. The fate and transport of organic chemicals in soils has been presented in the literature (e.g., Bouchard et al., 2011; Rivett et al., 2011; Abriola and Pinder, 1985a, b) and in textbooks (e.g., Domenico and Schwartz, 1997; Schnoor, 1996; Freeze and Cherry, 1979b).

5.8.1 Potential Paths

Chemicals and hydraulic fracturing fluids that are released into the environment may travel along different potential paths, as detailed in Figure 5-15. Liquids can flow overland to nearby surface water or infiltrate the subsurface, where they may eventually reach the underlying groundwater or travel laterally to reach surface water. Movement can occur quickly or be delayed and have a later or longer-term impact. Surface and groundwater gain or lose flow to each other (Chapter 2), and can transport chemicals in the process. A dry chemical (e.g., gelling agents, biocides, friction reducers) released to the environment can remain where it is spilled. Any spill that is not removed could act as a long-term source of contamination. Wind could cause the chemical to disperse and rain could mobilize soluble chemicals. Dissolved chemicals can infiltrate into soil or flow overland. Insoluble chemicals and those sorbed to soil particles could be mobilized by rain events via runoff and erosion.

5.8.1.1 Movement across the Land Surface

In low permeability soils, there may be little infiltration and greater overland flow. Higher permeability soils will allow fluid to penetrate into the soil layer. In either case, some of the

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[1] Cation exchange capacity is the total amount of cations (positively charged ions) that a soil can hold. For example, when metal ions like Ca^{2+} and Na^{+} pass through the soil, they adhere and remain attached to the soil.

[2] The unsaturated zone is also referred to as the vadose zone. Meaning “dry,” the vadose zone is the soil zone above the water table that is only partially filled by water.

[3] Advection is a mechanism for moving chemicals in flowing water, where a chemical moves along with the flow of the water itself.

[4] Sorption is the general term used to describe the partitioning of a chemical between soil and water and depends on the nature of the solids and the properties of the chemical.

chemicals in the fluid can sorb to the soil particles and the vegetation, and then these chemicals can be mobilized during precipitation, runoff, or erosion. As precipitation percolates through the soil, it can dissolve stored chemicals, which can then migrate toward groundwater. The type of release is also important. If the spill is a slow leak, then the liquid may pond and the affected area will expand slowly with greater potential for infiltration. If a more rapid release occurs, like a blowout or tank failure, then momentum can result in greater overland movement and less soil infiltration during the event, with greater potential to reach a nearby surface water.

5.8.1.2 Movement through the Subsurface

The unsaturated and saturated zones are the two zones of soils below the ground surface. Movement through the unsaturated zone is driven by the depth of ponding of the spilled fluid, gravity, and capillary properties of the subsurface.[1] In fractured rock or highly permeable soils, fluids can move quickly through the subsurface. In low permeability soil, the movement of the fluid may be slower. However, the presence of preferential pathways (e.g., fractures, heterogeneities, root holes, and burrows) can result in faster movement than the overall permeability would suggest.

As chemicals pass through the subsurface, some can sorb to soil or remain in the open spaces between soil particles, effectively slowing their movement. Chemicals can be mobilized during future precipitation events, resulting in infiltration towards groundwater or movement through the unsaturated zone towards surface water.

Fluids that move through the subsurface into the saturated zone will move in the direction of the flowing groundwater. Generally, fluids travel farther in systems with high groundwater flow rates and high recharge (e.g., sandy aquifers in humid climates) than in systems with low flow and low recharge. Chemicals can sorb to suspended soil particles, complex with naturally occurring chemicals (e.g., dissolved organic carbon), or associate with colloids and be transported with the flowing water.[2] These mechanisms can mobilize sparingly soluble chemicals that would otherwise be immobile.

5.8.2 Physicochemical Properties of Organic Hydraulic Fracturing Chemicals

Three physicochemical properties are useful to describe the movement of organic chemicals in the environment: (1) K_{ow}, the octanol-water partition coefficient, (2) the aqueous solubility, and (3) the Henry's law constant.[3] These properties describe whether a chemical will sorb to soil and organic

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[1] Capillarity occurs because of the forces of attraction of water molecules to themselves (cohesion) and to other solid substances such as soils (adhesion).

[2] Complexation is a reaction between two chemicals that form a new complex, either through covalent bonding or ionic forces. This often results in one chemical solubilizing the other.

[3] The octanol-water partition coefficient (K_{ow}) represents the ratio of the solubility of a compound in octanol (a nonpolar solvent) to its solubility in water (a polar solvent) in a mixture of the two. The higher the K_{ow}, the more nonpolar the compound.

matter or stay in water (K_{ow}), how much of a chemical may dissolve in water (aqueous solubility), and whether a chemical will tend to remain in the water or volatilize (Henry's law constant).[1]

The K_{ow} measures the relative hydrophobicity (chemicals that prefer to be in oil, log $K_{ow} > 0$) and hydrophilicity (chemicals that prefer to be in water, log $K_{ow} < 0$) of a chemical. Aqueous solubility is the maximum amount of a chemical that will dissolve in water in the presence of a pure chemical; solubility generally serves as an upper bound on possible concentrations. The Henry's law constant is the ratio of the concentration of a chemical in air (or vapor pressure) to the concentration of that chemical in water.

Estimates and measured values for physicochemical properties were obtained by using the Estimation Program Interface (EPI) Suite 4.1, as described in Appendix C.[2] Of the 1,084 chemicals the EPA listed as used in hydraulic fracturing (Appendix H), EPI Suite™ has estimated properties for 455 organic chemicals (42% of all chemicals) with structures that are considered suitably representative of the substance to compute properties within the constraints of EPI Suite™ software. Only uniquely defined organic desalted structures were submitted for property calculation. Figure 5-16 presents histograms of all 455 of the organic chemicals, sorted by four physicochemical parameters: measured log K_{ow} (n = 195), estimated log K_{ow} (n=455), estimated log of the aqueous solubility (n = 455), and estimated log of Henry's law constant (at 77°F or 25°C, n = 449). Property estimation methods are limited in their ability to predict physicochemical properties. Chemicals that are different than the chemicals used to develop the estimation techniques may have more error associated with their predictions. These figures enable comparison of physicochemical properties across the organic chemicals for which we have values. These figures show how the physicochemical properties are distributed and which chemicals have higher values compared to others with lower values. Limitations in knowing what chemicals are present (e.g., CBI) further hinders our ability to know the physicochemical properties of these chemicals and their potential to move through the environment and impact drinking water resources. These estimates are solely for the organic chemicals for which EPI Suite™ could be used. This does not provide information on the 258 inorganic chemicals or the 361 organic mixtures or polymers. This limits our ability to make a full assessment on the physicochemical properties of all chemicals, yet provides insight into the properties of the organic chemicals used.

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[1] We present the physicochemical parameter values using $\log_{10}$ because of the wide range of values that these parameters cover.

[2] EPI Suite™, version 4.1, http://www.epa.gov/opptintr/exposure/pubs/episuite.htm (U.S. EPA, 2012c). The EPI (Estimation Programs Interface) Suite™ is a Windows®-based suite of physicochemical property and environmental fate estimation programs developed by the EPA Office of Pollution Prevention and Toxics and Syracuse Research Corporation. EPI Suite™ provides estimates of physicochemical properties for organic chemicals and has a database of measured values for physicochemical properties when available. EPI Suite™ cannot estimate parameters for inorganic chemicals.

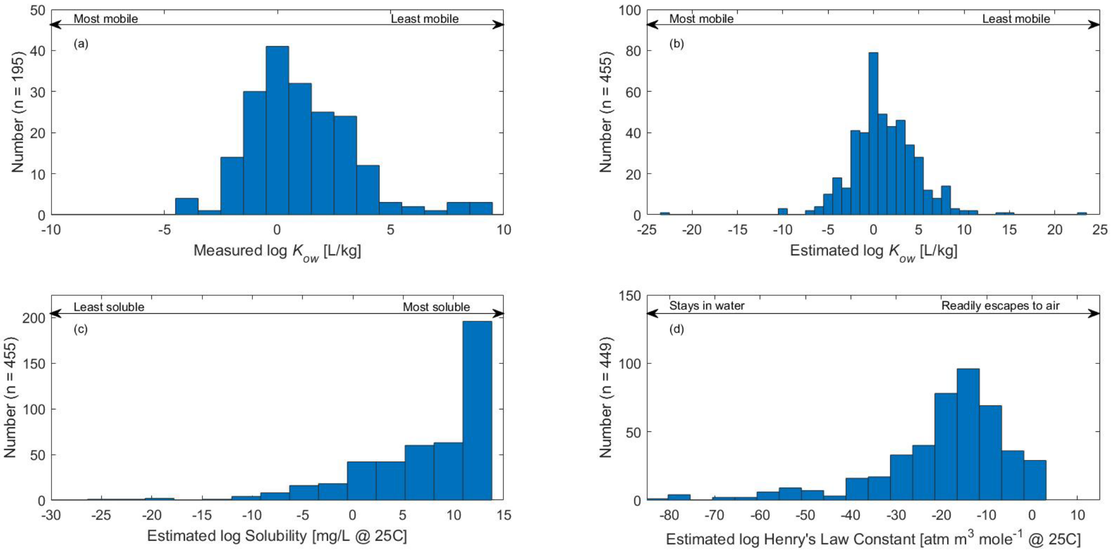

Figure 5-16. Histograms of physicochemical properties of organic chemicals used in the hydraulic fracturing process.

Physicochemical properties as given by EPI Suite™ (a) measured values of log K_{ow}, (b) estimated log K_{ow}, (c) estimated log Solubility, and (d) estimated log Henry's law constant.

We used EPI Suite™ to determine the physicochemical properties for 19 CBI chemicals used in hydraulic fracturing fluids. These chemicals were submitted to the EPA by nine service companies from 2005 to 2009 (see Text Box 5-3 for discussion on CBI).[1] The CBI chemical physicochemical properties are plotted as histograms in Appendix Figure C-1. The values of the physicochemical properties of known and CBI chemicals are similar, covering similar ranges and centered on similar values, suggesting that even though these chemicals are not publicly known, their physicochemical properties are not appreciably different from the known chemicals. This suggests that their fate and transport would not be appreciably different than the chemicals that are publicly known.

5.8.3 Mobility of Organic Hydraulic Fracturing Chemicals

Figure 5-16 shows the distribution of log K_{ow}, solubility, and Henry's Law constant for organic chemicals used in hydraulic fracturing fluids. These figures suggest that the organic chemicals used in hydraulic fracturing cover a wide range of physicochemical properties. For example, many chemicals are centered around log $K_{ow} = 0$, which indicates that these chemicals are likely to associate roughly equally with organic or aqueous phases. Many chemicals have log $K_{ow} > 0$, indicating less mobility, which may cause these chemicals to serve as later-term or long-term sources of impact on drinking water. Solubilities range from fully miscible to sparingly soluble. Many chemicals have log Henry's law constants less than 0, indicating that most are not highly volatile. Volatilization may not serve as a dominant loss process for hydraulic fracturing chemicals.

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[1] Well operators may specify certain ingredients as confidential business information (CBI) and not disclose the chemicals used to FracFocus. The CASRNs of a range of CBI chemicals were provided to the EPA by nine service companies.

The 20 chemicals with the smallest K_{ow} (most mobile) may have greater potential to cause immediate impacts on drinking water resources (Appendix Table C-10). Most of these chemicals were infrequently reported in disclosures (≤2% of wells) in the EPA FracFocus 1.0 project database (U.S. EPA, 2015a). Choline chloride (14% of wells), used for clay control, and tetrakis(hydroxymethyl)-phosphonium sulfate (11% of wells), a biocide, were more commonly reported. The 20 chemicals with the largest K_{ow} (least mobile) may have a greater potential to serve as long-term sources of contamination (Appendix Table C-11). The estimated aqueous solubilities for some of these chemicals are extremely low, with highest solubilities of less than 10 µg/L. Seven low mobility chemicals were reported in disclosures in the EPA FracFocus 1.0 project database (U.S. EPA, 2015c). Five were reported infrequently (<1% of wells). Tri-n-butyltetradecylphosphonium chloride (6% of wells), used as a biocide, and C>10-alpha-alkenes (8% of wells), a mixture of alpha-olefins with carbon numbers greater than 10 used as a corrosion inhibitor, were more commonly reported. Sorbitan, tri-(9Z)-9-octadecenoate, a mineral oil co-emulsifier (0.05% of wells) had the highest estimated log K_{ow} of 22.56.[1]

Table 5-7 shows the EPI Suite™ estimated physicochemical property values of the 20 chemicals most frequently reported nationwide in disclosures along with estimated mean and median volumes based on disclosures in the EPA FracFocus 1.0 project database (U.S. EPA, 2015c). Most have log $K_{ow} < 1$, meaning that they are generally hydrophilic and will associate with water. These chemicals also have very high solubilities, so they will be mobile in the environment, transport with water, and can occur at high concentrations. These chemicals have the potential for faster impacts on drinking water resources.

Naphthalene (CASRN 91-20-3) has a measured log $K_{ow} = 3.3$ with an estimated solubility of 142.1 mg/L, which means it will be less mobile in the environment. Naphthalene will sorb to particles and move slowly through the environment and has the potential to act as a long-term source of contamination.[2] All of these chemicals have low Henry's law constants, so they tend not to volatilize. We also include ranges of similar physicochemical properties for two chemicals that are organic mixtures: distillates, petroleum, hydrotreated light (CASRN 64742-47-8) and solvent naphtha, petroleum, heavy arom. (CASRN 64742-94-5). Both of these are complex organic mixtures, and thus EPI Suite™ cannot estimate their properties. However, the Total Petroleum Hydrocarbon Work Group has provided regressions to relate physicochemical properties to the number of carbons for aliphatic and aromatic hydrocarbons (Gustafson et al., 1997), which shows that they have low solubilities and large log K_{ow}.

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[1] Sorbitan, tri-(9Z)-9-octadecenoate, CASRN 26266-58-0, is soluble in hydrocarbons and insoluble in water, listed as an effective coupling agent and co-emulsifier for mineral oil (Santa Cruz Biotechnology, 2015; ChemicalBook, 2010).

[2] Chemicals can have the potential to be long-term sources of contamination when they move slowly through the environment. In this discussion, we are not accounting for biodegradation or other transformation processes, which may reduce the persistence of certain chemicals in the environment. Under certain conditions, for example, naphthalene is biodegradable, which can reduce or remove it from the environment, and thus may not be a long-term source of contamination.

Table 5-7. The 20 chemicals reported most frequently nationwide for hydraulic fracturing based on the EPA FracFocus 1.0 project database, with EPI Suite™ physicochemical parameters where available, and estimated mean and median volumes of those chemicals where density was available.

Excludes water, sodium chloride, and quartz. NA means that the physicochemical parameter is not provided by EPI Suite™ or the volume could not be estimated due to missing data. For organic salts, parameters are estimated using the desalted form. Analysis considered 34,675 disclosures and 676,376 ingredient records that met selected quality assurance criteria, including: completely parsed; unique combination of fracture date and API well number; fracture date between January 1, 2011, and February 28, 2013; valid CASRN; and valid concentrations. Disclosures that did not meet quality assurance criteria (3,855) or other, query-specific criteria were excluded from analysis.

Rank	**Chemical name**	**CASRN**	**Number of wells using chemical (% of wells)**	Log K_{ow} (unitless)		Water solubility estimate from log K_{ow} (mg/L @ 25°C)	Henry's Law Constant (atm m^3/mole @ 25°C)			Estimated volume, per disclosure (gal)	
				Estimated	**Measured**		Estimated, bond method	Estimated, group method 25	Measured	Mean	Median
1	Methanol	67-56-1	24,753 (72%)	-0.63	-0.77	1.00×10^{6}	4.27×10^{-6}	3.62×10^{-6}	4.55×10^{-6}	1,218	110
2	Distillates, petroleum, hydrotreated light[a,b]	64742-47-8	22,463 (65%)	log K_{oc} = 4.5 to 6.7	NA	0.00035 to 0.12	55 to 69 cm^3/cm^3	NA	NA	NA	NA
3	Hydrochloric acid	7647-01-0	22,380 (65%)	NA	NA	NA	NA	NA	NA	28,320	3,110
4	Isopropanol	67-63-0	16,039 (47%)	0.28	0.05	4.024×10^{5}	7.52×10^{-6}	1.14×10^{-5}	8.10×10^{-6}	2,095	55
5	Ethylene glycol	107-21-1	15,800 (46%)	-1.2	-1.36	1.00×10^{6}	1.31×10^{-7}	5.60×10^{-11}	6.00×10^{-8}	614	184
6	Peroxydisulfuric acid, diammonium salt	7727-54-0	14,968 (44%)	NA	NA	NA	NA	NA	NA	NA	NA
7	Sodium hydroxide	1310-73-2	13,265 (39%)	NA	NA	NA	NA	NA	NA	551	38
8	Guar gum	9000-30-0	12,696 (37%)	NA	NA	NA	NA	NA	NA	NA	NA
9	Glutaraldehyde	111-30-8	11,562 (34%)	-0.18	NA	1.672×10^{5}	1.10×10^{-7}	2.39×10^{-8}	NA	1,313	122
10	Propargyl alcohol	107-19-7	11,410 (33%)	-0.42	-0.38	9.355×10^{5}	5.88×10^{-7}	NA	1.15×10^{-6}	183	2
11	Potassium hydroxide	1310-58-3	10,049 (29%)	NA	NA	NA	NA	NA	NA	NA	NA
12	Ethanol	64-17-5	9,861 (29%)	-0.14	-0.31	7.921×10^{5}	5.67×10^{-6}	4.88×10^{-6}	5.00E-06	831	121
13	Acetic acid	64-19-7	8,186 (24%)	0.09	-0.17	4.759×10^{5}	5.48×10^{-7}	2.94×10^{-7}	1.00×10^{-7}	646	47
14	Citric acid	77-92-9	8,142 (24%)	-1.67	-1.64	1.00×10^{6}	8.33×10^{-18}	NA	4.33×10^{-14}	163	20

Rank	**Chemical name**	**CASRN**	**Number of wells using chemical (% of wells)**	Log K_{ow} (unitless)		Water solubility estimate from log K_{ow} (mg/L @ 25°C)	Henry's Law Constant (atm m^3/mole @ 25°C)			Estimated volume, per disclosure (gal)	
				Estimated	**Measured**		Estimated, bond method	Estimated, group method 25	Measured	Mean	Median
15	2-Butoxyethanol	111-76-2	7,347 (21%)	0.57	0.83	6.447×10^4	9.79×10^{-8}	2.08×10^{-8}	1.60×10^{-6}	385	26
16	Solvent naphtha, petroleum, heavy arom.[b,c]	64742-94-5	7,108 (21%)	log K_{oc} = 3.2 to 2.7	NA	5.8 to 65	0.028 to 0.39 cm^3/cm^3	NA	NA	NA	NA
17	Naphthalene	91-20-3	6,354 (19%)	3.17	3.3	1.421×10^2	5.26×10^{-4}	3.7×10^{-4}	4.4×10^{-4}	72	12
18	2,2-Dibromo-3-nitrilopropionamide	10222-01-2	5,656 (16%)	1.01	0.82	2.841×10^3	6.16×10^{-14}	NA	1.91×10^{-8}	183	5
19	Phenolic resin	9003-35-4	4,961 (14%)	NA	NA	NA	NA	NA	NA	NA	NA
20	Choline chloride	67-48-1	4,741 (14%)	-5.16	NA	1.00×10^6	2.03×10^{-16}	NA	NA	2,131	290

[a] Hydrotreated light petroleum distillates (CASRN 64742-47-8) is a mixture of hydrocarbons in the C9 to C16 range.

[b] Physicochemical parameters are estimated using Gustafson et al. (1997). Parameters are presented as log K_{oc} (soil organic carbon-water partition coefficient), solubility (mg/L), and Henry's Law Constant (cm^3/cm^3).

[c] Heavy aromatic solvent naphtha (petroleum) (CASRN 64742-94-5) is mixture of aromatic hydrocarbons in the C9 to C16 range.

For the top 20 chemicals, many chemicals have high solubilities and negative or almost zero log K_{ow} (e.g., methanol, isopropanol, ethylene glycol). These chemicals are likely to travel quickly through the environment and could result in an immediate impact. Three chemicals, with larger log K_{ow} and smaller solubilities (distillates, petroleum, hydrotreated light; solvent naphtha, petroleum, heavy arom.; and naphthalene) may result in more severe impacts. These chemicals could associate with the soil particles, releasing into the groundwater at low concentrations slowly over time, and thus serve as long-term sources of contamination.

Mobility of a chemical is complex, and these numbers solely represent how a chemical behaves in an infinitely dilute aqueous solution, a simplifying approximation of the real world. Many factors can affect the fate and transport of a chemical, such as the transformation process (e.g., biodegradation), the presence of other chemicals, and site and environmental conditions. We discuss these factors in the next sections.

5.8.4 Transformation Processes

Once a chemical is released into the environment, it can transform or degrade. Understanding the processes governing these reactions in the environment is important to assessing potential impacts. The transformation of a chemical may reduce its concentration over time. Chemicals may completely degrade before reaching a drinking water resource. Transformation processes can be biotic or abiotic and may transform a chemical into a less or more harmful chemical.

One important transformation process is biodegradation. Biodegradation is a biotic process where microorganisms transform a chemical from its original form into another chemical. For example, the general biodegradation pathway of methanol is $CH_3OH \rightarrow CH_2O \rightarrow CHOOH \rightarrow CO_2$ or methanol → formaldehyde → formic acid → carbon dioxide (Methanol Institute, 2013).[1] This pathway shows how the original chemical transforms through a series of steps until it becomes the final product, carbon dioxide. Some chemicals are readily biodegraded, while others break down slowly over time. Biodegradation is a highly site-specific process, requiring nutrients, a carbon source, water, and an energy source. A highly biodegradable chemical could be persistent if the conditions for biodegradability are not met. Conversely, a chemical could biodegrade quickly under the right conditions, affecting its potential to impact a drinking water resource. The relationship between mobility and biodegradability is complex, and a variety of factors can influence a particular chemical's movement through the environment.

Abiotic processes, such as oxidation, reduction, photochemical reactions, and hydrolysis, can transform or break apart chemicals. The typical results are products that are more polar than the

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[1] In methanol biodegradation, PQQ (pyrroloquinoline quinone) is a redox cofactor that goes from PQQ to $PQQH_2$ removing two hydrogen from methanol in the first step to form formaldehyde. Water is added to formaldehyde to provide the second oxygen to form formic acid. Nicotinamide adenine dinucleotide (NAD) is a coenzyme that takes up a hydrogen, going from NAD to $NADH^+$. This removes the hydrogen in the second and third steps, to result in carbon dioxide.

original compounds, and thus have different physicochemical properties (Schwarzenbach et al., 2002).[1]

5.8.5 Fate and Transport of Chemical Mixtures

Spills during the chemical mixing stage are often present as mixtures of chemicals. Additives are often mixtures of a few to several chemicals, possibly highly concentrated, and hydraulic fracturing fluids are often dilute mixtures of several additives. Chemical mixtures can act differently in the environment than individual chemicals. Individual chemicals can affect the fate and transport of other chemicals in a mixture primarily by changing their physicochemical properties and transformation rates.

Chemical mixtures can be more mobile than individual chemicals due to cosolvency, which increases solubility in the aqueous phase. Methanol and ethanol are examples of cosolvent alcohols used frequently in hydraulic fracturing fluids (U.S. EPA, 2015a). The presence of either greatly increases BTEX solubility (Rasa et al., 2013; Corseuil et al., 2011; Heermann and Powers, 1998).[2] By increasing solubility, ethanol can affect the fate and transport of other compounds. For example, BTEX has been observed to travel farther in the subsurface in the presence of ethanol (Rasa et al., 2013; Corseuil et al., 2011; Corseuil et al., 2004; Powers et al., 2001; Heermann and Powers, 1998).

The presence of surfactants lowers fluid surface tension and increases solubility of organic chemicals. Surfactants can mobilize less soluble/less mobile organic chemicals. Two common surfactants reported in disclosures in the EPA FracFocus 1.0 project database were 2-butoxyethanol (CASRN 111-76-2, 21% of disclosures) and poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture) (CASRN 127087-87-0, 20% of disclosures). Additionally, surfactants can mobilize bacteria in the subsurface, which can increase the impact of pathogens on drinking water resources (Brown and Jaffé, 2001).

When chemicals are present as mixtures, one chemical can decrease or enhance the biodegradability of another through inhibition or co-metabolism. The process of inhibition can slow biodegradation of each of the chemicals present. For example, the biodegradation of ethanol and methanol can slow the biodegradation rate of BTEX or other organic chemicals present (Rasa et al., 2013; Powers et al., 2001). Co-metabolism can increase the biodegradation rate of other chemicals. For example, when methane or propane is present with tetrachloroethylene, the enzyme produced by bacteria to degrade methane also degrades tetrachloroethylene (e.g., Alvarez-Cohen and Speitel, 2001 and references therein). For the purposes of chemicals used in hydraulic fracturing, the presence of other chemicals in additives and hydraulic fracturing fluids could result in increased or decreased biodegradation if the chemicals are spilled.

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[1] A polar molecule is a molecule with a slightly positive charge at one part of the molecule and a slightly negative charge on another. The water molecule, H_2O, is an example of a polar molecule, where the molecule is slightly positive around the hydrogen atoms and negative around the oxygen atom.

[2] BTEX is an acronym for benzene, toluene, ethylbenzene, and xylenes. These chemicals are a group of single ringed aromatic hydrocarbons based on the benzene structure. These compounds are found in petroleum and are of specific importance because of their potential health effects.

5.8.6 Site and Environmental Conditions

Environmental conditions at and around the spill site affect the movement and transformation of chemicals. This section discusses the following: site conditions (e.g., proximity, land cover, and slope), soil conditions (e.g., permeability and porosity), and weather and climate.

The proximity of a spill to a drinking water resource, either laterally in the case of a surface water body or downward for groundwater, affects the potential for impact and its severity. Land cover will affect how readily a fluid moves over land. For example, more rugged land cover such as forest can impede flow, and an asphalt road can facilitate flow. A spill that occurs on or near a sloped site can move overland faster, increasing the potential to reach nearby surface water. Flatter surfaces result in a greater chance for infiltration to the subsurface, which could increase the potential for groundwater impact.

Soil characteristics that affect the transport and transformation of spill chemicals include soil texture (e.g., clay, silt, sand), permeability, porosity, and organic content.[1,2] Fluids will move more quickly through permeable soil (e.g., sand) than through less permeable soil (e.g., clay). A soil with a high porosity provides more volume to hold water and spilled chemicals. Another important factor for a site is the organic content, of which there are two competing types: soil organic carbon and dissolved organic carbon. Each type of carbon acts as a strong substance for chemicals to associate with. Soil organic carbon present in a solid phase, such as dead and decaying leaves and roots, is not mobile and slows the movement of chemicals through the soil. Dissolved organic carbon (DOC) moves with the water and can act as a shuttling mechanism to mobilize less soluble chemicals across the surface and through the subsurface. Chemicals may also associate and move with particulates and colloids.

Weather and climate conditions affect the fate and transport of a spilled chemical. After a spilled chemical stops moving, precipitation can remobilize the chemical. The amount, frequency, and intensity of precipitation will impact the volume, distance, and speed of chemical movement. Precipitation can carry chemicals downward or overland, and it can cause erosion, which can move sorbed chemicals overland.

5.8.7 Peer-Reviewed Literature on the Fate and Transport of Hydraulic Fracturing Fluid Spills

There has been limited peer-reviewed research investigating the fate and transport of chemicals spilled at hydraulic fracturing sites. Aminto and Olson (2012) modeled a hypothetical spill of 1,000 gal (3,800 L) of hydraulic fracturing fluid using equilibrium partitioning. The authors evaluated how 12 chemicals typically used for hydraulic fracturing in the Marcellus Shale would partition among different phases: air, water, soil, and biota.[3] They presented a ranking of

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[1] Permeability of a soil describes how easily a fluid can move through the soil. Under a constant pressure, a fluid will move faster in a high permeability soil than the same fluid in a low permeability soil.

[2] Porosity of a soil describes the amount of empty space for a given volume of soil. The porosity describes how much air, water, or hydraulic fluid a given volume of soil can hold.

[3] The chemicals they investigated included: sodium hydroxide, ethylene glycol, 4,4-dimethyl oxazolidine, 3,4,4-trimethyl oxazolodine, 2-amino-2-methyl-1-propanol, formamide, glutaraldehyde, benzalkonium chloride, ethanol, hydrochloric acid, methanol, and propargyl alcohol.

concentrations for each phase. In water, they showed that sodium hydroxide (a pH buffer), 4,4-dimethyl oxazolidine (a biocide), hydrochloric acid (a perforation clean-up additive), and 3,4,4-trimethyl oxazolidine (a biocide) had the highest simulated water concentrations; however, these concentrations depended on the chemicals included in the simulated mixture and the concentrations of each. Their analysis suggested that after a spill, a large fraction of the spill would volatilize and leave the soil; however, some constituents would be left behind in the water, soil, and biota compartments, which could act as long-term contamination sources. Aminto and Olson (2012) only studied this one scenario. Other scenarios could be constructed with different chemicals in different concentrations. These scenarios may result in different outcomes and impacts. Any spill would require site- and spill-specific modeling on a case-by-case basis. For this reason, we cannot make any general statement about fate and transport of hydraulic fracturing chemicals and fluids. For this reason, we cannot make any general statement about fate and transport of hydraulic fracturing chemicals and fluids.

Drollette et al. (2015) suggested a link between surface spills and groundwater contamination, possibly from hydraulic fracturing activity, because the chemicals detected were hydraulic fracturing additives. This work demonstrates the pathway for surface spills to impact groundwater sources. They detected low levels of gasoline related organic chemicals with elevated diesel range organic chemicals, which suggests that the former were degraded or volatilized, while the latter were more persistent and penetrated into the subsurface and into groundwater.

5.8.8 Potential and Documented Fate and Transport of Documented Spills

There is limited information on the fate and transport of hydraulic fracturing fluids and chemicals. This section highlights both potential and documented impacts for three reported spills (U.S. EPA, 2015m). In each case, we provide the documented and potential paths (surface, subsurface, or combination) and the associated fate and transport governing processes by which the spill has been documented or has the potential to have an impact on drinking water resources. The three cases involve a tank overflow with a reported surface water impact, a human error blender spill with a reported soil impact, and an equipment failure that had no reported impact. We specifically chose these three spills to highlight three different cases. One demonstrates a documented impact with a demonstrated pathway that had an observed effect on a nearby drinking water resource. The second case shows how a release can impact an environmental receptor with a pathway for potential impact on a drinking water resource, but there was no observed impact. The third example is a spill that was contained and cleaned up resulting in likely no impact. None of these chemical releases have any documented pre- or post-sampling. No information on the specific chemicals spilled or the concentrations or total mass of any chemical is provided. We cannot provide any quantitative assessment from these observed cases.

In the first documented spill, shown in Figure 5-17, a tank overflowed twice, releasing a total of 7,350 gal (980 ft^3, 28 m^3, or 27,800 L) of friction reducer and gel (PA DEP, 2012, ID#1830163).[1] The spill traveled across the land surface, crossed a road, and then continued to a nearby stream. The

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[1] We provide the total volume of the spill in gallons as well as cubic length (cubic feet and cubic meters), because it may be a little harder to visualize how far a volume of 7,300 gal (28,000 L) might travel.

spill affected wetlands and a stream, where fish were reported to have been killed. The fish kill indicates an observable impact. This represents a good example for how environmental conditions can affect the severity and timing of impact, due to the slope of the lands surface, the permeability of the soil, and the proximity to surface water. We are not aware of any measurements performed for soils, groundwater, surface water, sediments, or fish tissue. Based on the publicly available information, we do not know what chemicals were in the friction reducer and gel, which limits further assessment.

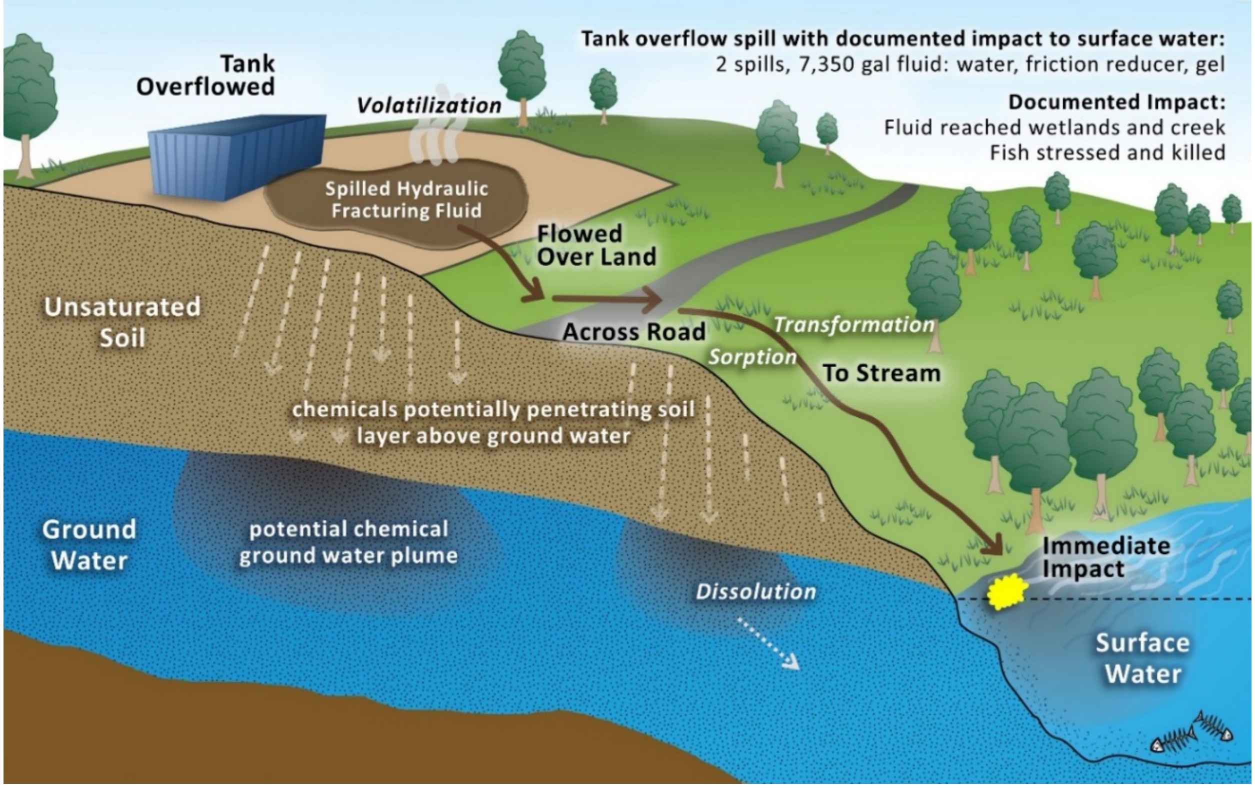


Figure 5-17. Fate and Transport Spill Example: Case 1.
Spills information from PA DEP (2012, ID#1830163).

For this first spill, the documented path was overland flow from the tank to the stream with a documented, immediate impact. There are also other potential paths for potential impacts on drinking water resources. The spilled chemicals could have penetrated into the soils or sorbed to soils and vegetation as the fluid moved across the ground towards the stream. Chemicals could then be mobilized during later precipitation, runoff, or erosion events. Chemicals that infiltrated the subsurface could serve as long-term sources, travel laterally across the unsaturated zone, or continue downwards to groundwater. Some chemicals could be lost to transformation processes. The absence of reported soil or groundwater sampling data prevents the ability to know if these potential paths occurred or not.

The second documented spill, shown in Figure 5-18, occurred when a cap was left off the blender, and 504 gal (70 ft^3 or 2 m^3) of biocide and hydraulic fracturing fluid were released (COGCC, 2012, ID#2608900). In addition, 294 gal (39 ft^3 or 1.1 m^3) were retained by a dike with a lined secondary containment measure, demonstrating the partial effectiveness of this containment mechanism. The remaining 210 gal (28 ft^3 or 0.8 m^3) of fluid (biocide and water) ran off-site. Of this, 126 gal were vacuumed, leaving 84 gal. There was no documented impact on surface or groundwater. However, potential impacts potentially could have occurred.

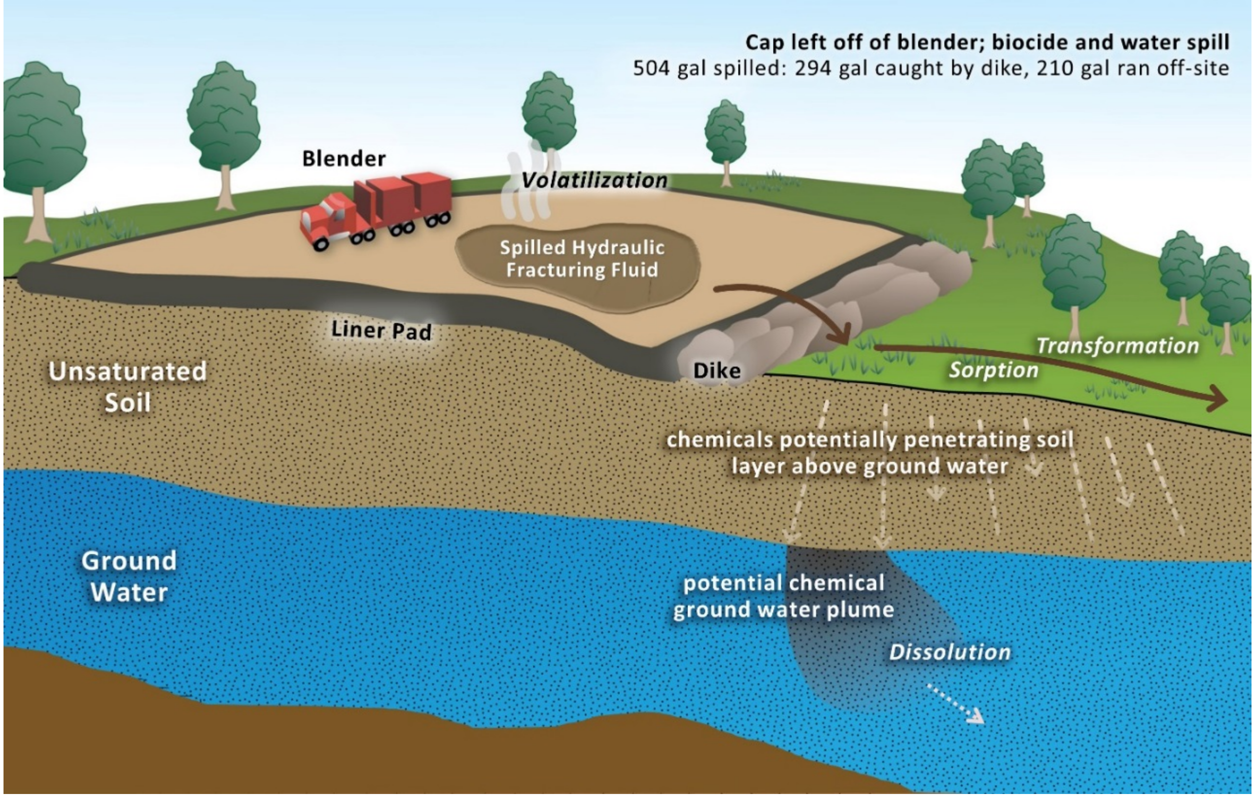


Figure 5-18. Fate and Transport Spill Example: Case 2.
Spills information from COGCC (2012, ID#2608900).

In this second case, the uncontained 84 gal could have infiltrated the subsurface, creating a potential path to groundwater. Highly mobile chemicals could have penetrated the soil more quickly than less mobile chemicals, which would have sorbed to soil particles. As the chemicals penetrated into the soil, some could have moved laterally in the unsaturated zone, or traveled downward to the groundwater table and moved with direction of groundwater flow. These chemicals could have served as a long-term contamination source. The chemicals also could have transformed into other chemicals with different physicochemical properties, and any volatile chemicals could have moved to the air as a loss process. As in the first case, there was no reported sampling of soil or groundwater, so there is no way to know if chemicals did or did not follow any of these pathways. We do not have any more information on the types of chemicals present or the concentrations with which they were present, which limits further assessment.

In the third documented spill, shown in Figure 5-19, 630 gal (84 ft^3 or 2.4 m^3) of crosslinker spilled onto the well pad when a hose wore off at the cuff (COGCC, 2012, ID#1395827). The spill was contained in the berm and an on-site vacuum truck was used to clean up the spill. No impact on soil or water was reported.

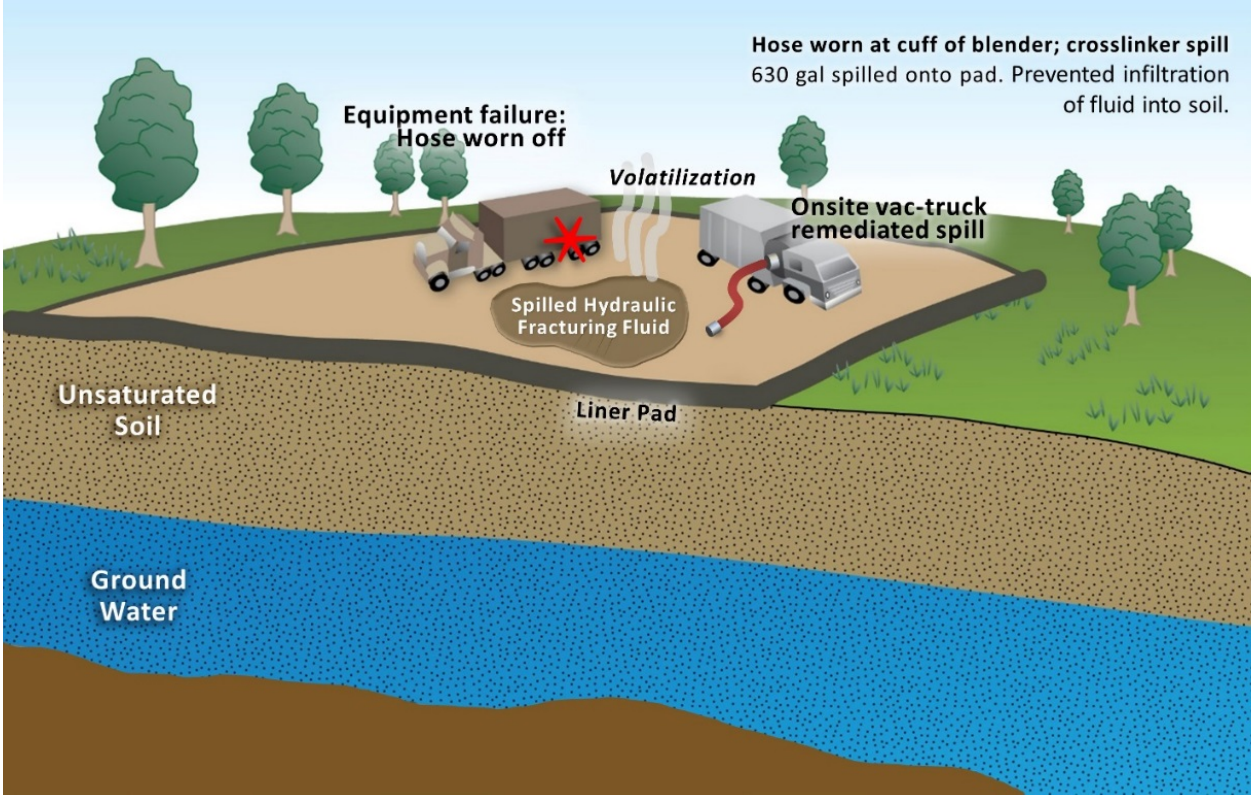


Figure 5-19 Fate and Transport Spill Example: Case 3.

The pad may or may not have had a liner. Spills information from COGCC (2012, ID#1395827).

For this third case, we do not have any information on whether the well pad was lined or not. If the site had a liner, the spill could have been fully contained and cleaned up. Without a liner or if the integrity of the liner was compromised (e.g., had a tear), any residual chemical that was not effectively cleaned up could have remained in the soil. This would create potential paths similar to those above in the second case, where the chemicals could have sorbed to the soils and penetrated into the subsurface and possibly reach groundwater. There was no reported sampling of soil or groundwater to determine whether or not chemicals migrated into the soil, and we do know the types of chemicals or the concentrations of the released chemicals.

5.8.9 Challenges with Unmonitored and Undetected Chemicals

One of the challenges confronting a thorough assessment of the fate and transport of spilled hydraulic fracturing chemicals lies in the lack of documented observations. It is difficult to prove absence of impact, and absence of observations does not necessarily imply lack of impact. Also, we know there are over 1,000 different chemicals reported used in hydraulic fracturing (Section 5.4), and this number is increasing. For many chemicals, there is not an analytical technique available to detect them in samples taken to a laboratory. Due to the lack of information on the chemicals used on site (some of which are claimed as CBI), one would not know what chemicals to include in the lab analysis. Hydraulic fracturing chemicals are typically present as complex mixtures, which also complicates sample analysis. Chemicals can transform upon release, which can result in different chemicals in the environment than those originally released. Even if chemicals are detected on-site, it can be difficult to demonstrate a direct linkage to hydraulic fracturing operations, since many of the chemicals used in hydraulic fracturing are also used for other purposes (such as gasoline or diesel from vehicles). Since there are currently no requirements for a detection–monitoring network to assess the occurrence and extent of chemical releases from the well pad, it is not possible to conclusively assess the frequency and impact of fluid releases during the chemical mixing process.

5.9 Trends in the Use of Hydraulic Fracturing Chemicals

Hydraulic fracturing science and engineering continues to advance. A part of this research includes using different chemicals. This section provides an overview of the changes in chemical use, with an emphasis on efforts to reduce potential impacts from surface spills by using fewer and safer chemicals. Reasons for changing the types of chemicals used can include: improving the fracturing process, using greener/safer chemicals, and reducing overall cost.

Representatives from oil and gas companies, chemical companies, and non-profits are working on strategies to reduce the number and volume of chemicals used and to identify safer chemicals (Waldron, 2014). Southwestern Energy Company, for example, is developing an internal chemical ranking tool (SWN, 2014), and Baker Hughes is working on a hazard ranking system designed for wide-scale external use (Baker Hughes, 2014; Brannon et al., 2012; Daulton et al., 2012; Brannon et al., 2011). Environmental groups, such as the Environmental Defense Fund, are also developing hazard rating systems (Penttila et al., 2013). Typical criteria used to rank chemicals include mobility, persistence, biodegradation, bioaccumulation, toxicity, and hazard characteristics. In this assessment, toxicity and a methodology to rank chemical hazards of hydraulic fracturing chemicals is discussed in Chapter 9.

Given that human error is the cause of 25% of chemical mixing related spills and spill prevention can never be 100% effective, changes to the types of chemicals used could reduce the frequency or the severity of potential impacts. Using chemicals with specific physicochemical properties that affect the fate and transport of chemicals could reduce their potential impacts. Less mobile chemicals could make cleanup of spills easier. For example, using dry chemicals that are hydrated on-site could minimize impacts if there were a container failure. Using chemicals with lower persistence and higher biodegradability, if spill prevention and cleanup are not fully effective, would lessen the severity of potential impact. Use of less hazardous chemicals could lessen impact in cases where a spill reaches a drinking water resource.

The EPA has not conducted a comprehensive review of efforts to develop safer hydraulic fracturing chemicals. However, the following are some specific examples of efforts that companies cite as part of their efforts toward safer chemical use:

- A renewable citrus-based replacement for conventional surfactants (Fisher, 2012);

- A crosslinked gel system comprised of chemicals designated as safe food additives by the U.S. Food and Drug Administration (Holtsclaw et al., 2011);
- A polymer-free gel additive (Al-Ghazal et al., 2013);
- A dry, hydrocarbon-free powder to replace liquid gel concentrate (Weinstein et al., 2009);
- Biodegradable polymers (Irwin, 2013);
- The use of ultraviolet light to control bacteria (Rodvelt et al., 2013);
- New chelating agents that reduce the use of strong acids (LePage et al., 2013);
- Eco-friendly viscoelastic surfactant (VES) polymer-free fluid reduces fracture cleanup time with 95% retrieved fluids compared to 40 – 60% and is less toxic than polymer-based fluids (AlKhowaildi et al., 2016); and
- The recovery and reuse of produced water as hydraulic fracturing fluids, which can reduce the need to add additional chemicals (Horn et al., 2013).

A review of the EPA's new chemicals program found that, from 2009 to April 2015, the Agency received pre-manufacturing notices (PMN) for about 110 chemicals that have the potential for use as additives. Examples include chemicals intended for use as clay control agents, corrosion inhibitors, gel crosslinkers, emulsifiers, foaming agents, hydrate inhibitors, scale inhibitors, and surfactants. At the time of PMN submission, these chemicals were not in commercial use in the United States. As of April 2015, the EPA had received 30 notices of commencement, indicating that some of the chemicals are now used commercially.

As different hydraulic fracturing fluids are developed, they have corresponding effects on different stages of the hydraulic fracturing water cycle. For example, in Figure 5-4(b) an example of an energized fluid uses a total water volume of 105,000 gal (397,000 L), which means less water is required in the water acquisition stage and less produced water results in less wastewater. Figure 5-4(a) shows slickwater with 4,763,000 gal (18,030,000 L) of water, yet a larger fraction of slickwater may be reused, reducing the need for more water for another frac job and requiring the treatment of less wastewater.

5.10 Synthesis

The chemical mixing stage includes the mixing of base fluid, proppant, and additives on the well pad to make hydraulic fracturing fluid. This chapter provided an analysis of the factors affecting potential impacts on drinking water resources during the chemical mixing stage of the hydraulic fracturing water cycle and the factors governing the frequency and severity of these impacts.

5.10.1 Summary of Findings

Reports have demonstrated that spills and releases of chemicals and fluids have occurred during the chemical mixing stage and have reached soils and surface water receptors. Spill reports have not documented impacts on groundwater related to the chemical mixing stage. Spill reports have little information on post-spill testing and sampling. Impacts on groundwater may remain undocumented. The potential pathway for impact on groundwater has been demonstrated and documented for chemicals spilled during other parts of the hydraulic fracture water cycle. (Evidence of groundwater impact from produced water spills is discussed Chapter 7.)

The hydraulic fracturing fluid generally consists of a base fluid (typically water), a proppant (typically sand), and additives (chemicals), although there is no standard or single composition of hydraulic fracturing fluid used. According to the analysis of the EPA FracFocus 1.0 project database, based on FracFocus disclosure data from January 2011 to February 2013, approximately 93% of hydraulic fracturing fluids use water as a base fluid. Non-aqueous fluids, such as nitrogen, carbon dioxide, and hydrocarbons, are also used as base fluids or used in combination with water as base fluids. The number of chemicals injected into a well typically ranges from 4 to 28, with a median of 14 (U.S. EPA, 2015a). In water-based hydraulic fracturing, the composition, by volume, of a typical hydraulic fracturing fluid is 90% to 97% water, 2% to 10% proppant, and 2% or less additives (Carter et al., 2013; Knappe and Fireline, 2012).

The EPA has identified 1,084 different chemicals used in chemical mixing. A recent study of FracFocus disclosure data, covering January 2011 to April 2015, has reported 263 new CASRNs, increasing the number of chemicals identified for use by approximately 24% (Konschnik and Dayalu, 2016). Hydraulic fracturing chemicals cover a wide range of chemical classes and a wide range of physicochemical properties. The chemicals include acids, aromatic hydrocarbons, bases, hydrocarbon mixtures, polymers, and surfactants. The use of 32 chemicals, excluding water, quartz, and sodium chloride, is reported in 10% or more of disclosures in the EPA FracFocus 1.0 project database. The ten most common chemicals (excluding quartz) are methanol, hydrotreated light petroleum distillates, hydrochloric acid, isopropanol, ethylene glycol, peroxydisulfuric acid diammonium salt, sodium hydroxide, guar gum, glutaraldehyde, and propargyl alcohol (U.S. EPA, 2015c). These chemicals can be present in multiple additives. Methanol, hydrotreated light petroleum distillates, and hydrochloric acid are the three chemicals reported to be used in more than half of all hydraulic fracturing jobs, with methanol being used at 72% of all sites.

An EPA analysis of spills data (January 2006 to April 2012, from nine states, nine service companies, and nine operators) identified over 36,000 spills, with 457 spills (~1%) that were on or near the well pad and definitively associated with hydraulic fracturing. Of these spills, 151 were of chemicals or hydraulic fracturing fluid and thus assumed to be associated with the chemical mixing stage. Chemical spills during the chemical mixing stage were primarily caused by equipment failure (34%), followed by human error (25%), although 26% spills had an unknown source. The remaining spills were caused by a failure of container integrity, weather, vandalism, and well communication. Reported spills covered a large range of volumes, from 5 to 19,320 gal (19 to 73,130 L), with a median of 420 gal (1,600 L) (U.S. EPA, 2015m).

The rate of reported spills during the hydraulic fracturing water cycle is estimated to range from 0.4 to 12.2 reported spills for every 100 wells, based on spills data from North Dakota, Pennsylvania, and Colorado, with a median rate of 2.6 reported spills for every 100 wells (See Appendix C). The estimated rates provide an approximate estimate of the potential frequency of the number of spills at a site. It is uncertain how representative these rates are of national spill rates or rates in other states. These numbers are not specific to the chemical mixing stage. In 2015, there are 2.6 reported spills occurring during the chemical mixing stage per 100 wells hydraulically fractured in North Dakota.

The total volume of chemicals used on site are estimated to range from 2,600 to 30,000 gal (9,800 to 114,000L). An estimate for the mean volume for any chemical used on-site is 650 gal (2,500 L) with a mean mass of 1500 kg (3,200 lb). An estimate of 2,300 to 6,500 gal (8,800 to 25,000 L) of additives are stored on site, typically in multiple totes of 200 to 375 gal (760 to 1,420 L). These volumes provide insight on how much potentially could spill at any given hydraulic fracturing site and what the volume of a spill might be depending on where/when it occurs during the chemical mixing process.

The potential of spills to reach drinking water resources depends on site and chemical properties. The fate and transport of spilled hydraulic fracturing chemicals is complex, particularly because chemicals are generally present as diverse, complex mixtures. There are different pathways for a spill to reach ground and surface water and to serve as a long term source. Roughly 40% of hydraulic fracturing chemicals are organic chemicals, which have physicochemical properties that cover the parameter space, from fully miscible to insoluble and from highly hydrophobic to highly hydrophilic. Of the 20 most frequently used chemicals used at hydraulic fracturing sites, three chemicals have low mobility: hydrotreated light petroleum distillates, heavy aromatic petroleum solvent naphtha, and naphthalene. These chemicals have the potential to act as long term sources of contamination if spilled on-site.

5.10.2 Factors Affecting the Frequency or Severity of Impacts

The specific factors that have the potential to affect the frequency and severity of impacts include the size and type of the fracturing operation; volume, mass, and concentration of chemicals spilled; type of chemicals and their properties; combination of chemicals spilled; environmental conditions; proximity to drinking water resources; employee training and experience; quality and maintenance of equipment; and spill containment and mitigation.

The size and type of a fracturing operation, including the number of wellheads, the depth of the well, the length of the leg(s), and the number of stages and phases, affect the potential frequency and severity spills. Larger operations can require larger volumes of chemicals, more storage containers, more equipment, and additional transfers between different pieces of equipment. Larger storage containers increase the maximum volume of a spill or leak from a storage container. Additional transfers between equipment increase the possibility of human error and potential frequency of spills.

The volume, mass, and concentration of spilled chemicals affect the frequency and severity of impacts. A larger volume increases the potential for a spill to travel a longer distance and reach a drinking water resource. The severity of the spill will be affected by the spill volume, the total mass of chemicals released, and the concentration with which it reaches the drinking water resource.

The type of chemicals spilled affects how the chemicals will move and transform in the environment and the type of impact it will have on a drinking water resource. More mobile chemicals move faster through the environment, which can increase the frequency of impact. More soluble chemicals can reach a drinking water resource at higher concentrations, thereby increasing the potential severity of an impact. Less mobile chemicals will move more slowly, and can have delayed and longer-term impacts at lower concentrations. The potential severity of impact is affected by how the chemical adversely impacts water quality. Some chemicals can have severe impacts at low concentrations, while some chemicals can have minimal impacts even at high concentrations. Water quality impacts can range from aesthetic effects (e.g., taste, smell) to adverse health effects.

The environmental conditions at and around the spill site affect the fate and transport of a given chemical and thus affect the frequency of impacts as well as potential severity. Conditions include soil properties, climate, weather, and terrain. Permeable soils allow for rapid transport of the spilled fluid through the subsurface and to groundwater. The presence of preferential flow paths (e.g., fractures, animal burrows) may provide rapid transport through the subsurface in what might appear to have low permeability. The presence of complexing agents and colloids may further increase transport of less soluble chemicals. Precipitation can re-mobilize trapped chemicals and move them over land or through the subsurface.

The proximity of a spill to drinking water resources affects the frequency and severity of impact. The closer a spill is to a drinking water resource, the higher the potential to reach it. As a fluid moves toward a drinking water resource, it can decrease in concentration, which can reduce the severity of an impact. The characteristics of the drinking water resource will also influence the severity of the impact of a spill. For example, a slow release into a fast moving stream will result in large dilution and lower concentrations of chemicals (less severe impact). The transport of a chemical to groundwater may have a more severe impact, as there may be less dispersion of the chemical (higher concentrations in the groundwater, more severe impact) and the chemical could serve as a long-term source of contamination (resulting in a chronic exposure versus an acute exposure).

Effective spill containment and mitigation measures can prevent or reduce the frequency and severity of impacts. Spill containment measures include well pad containment liners, diversion ditches, berms, dikes, overflow prevention devices, drip pans, and secondary containers. These may prevent a spill from reaching soil and water receptors. Spill mitigation, including removing contaminated soils, vacuuming up spilled fluids, and using sorbent materials can limit the severity of a spill. It is unclear how effective these practices are and to what extent they are implemented.

5.10.3 Uncertainties

The lack of information and the uncertainty around information having to do with the composition of additives and fracturing fluids, containment and mitigation measures in use, the proximity of chemical mixing to drinking water resources, and the fate and transport of spilled fluids limits our ability to fully assess potential impacts on drinking water resources and the factors affecting their frequency and severity.

There is no standard design for hydraulic fracturing fluids. Detailed information on the chemicals used is limited. Volumes, concentrations, and mass, as well as the identity of some of chemicals stored on-site, are generally not publicly available. The FracFocus national registry, which currently holds the most comprehensive information on water and chemicals used in hydraulic fracturing fluids, is structured so as to input chemical information as a maximum percentage of the mass of fracturing fluid and the given additive. This does not provide exact information on the volume of a chemical, the mass of a chemical, or the actual composition of an additive. The accuracy and completeness of original FracFocus disclosure information has not been verified. In applying the EPA-standardized chemical list to the ingredient records in the EPA FracFocus 1.0 project database, standardized chemical names were assigned to only 65% of the ingredient records from the more than 36,000 unique, fully parsed disclosures. The remaining ingredient records could not be assigned a standardized chemical name and were excluded from analyses (U.S. EPA, 2015a).

Operators may specify certain ingredients as confidential business information (CBI) and not disclose the chemical used. More than 70% of disclosures in the EPA FracFocus 1.0 project database contained at least one CBI chemical. Of disclosures with at least one CBI chemical, the average number of CBI chemicals per disclosure was five. Approximately 11% of all chemicals reported in the disclosures in the EPA FracFocus 1.0 project database were reported as CBI (U.S. EPA, 2015a). The rate of withholding in FracFocus 2.0 data has increased to 16.5% (Konschnik and Dayalu, 2016). No data are available in FracFocus disclosures for any chemical listed as CBI. Therefore, chemicals identified as CBI in FracFocus disclosures are not included in any of the analyses in this assessment including estimates of chemical volume, physicochemical properties, or frequency of use. It is feasible that the same chemicals are repeatedly reported as CBI. Each reported CBI chemical could also be unique, which would mean there is a very large number of chemicals that we know nothing about. This results in an unknown amount of uncertainty regarding CBI chemicals and their potential impact on drinking water resources.

Of the 1,084 hydraulic fracturing fluid chemicals identified by the EPA, 629 were inorganic chemicals, mixtures, or polymers, and thus they did not have estimated physicochemical properties reported in the EPI Suite™ database. Knowing the chemical properties of a spilled fluid is essential to predicting how and where it will travel in the environment. Although we can make some generalizations about the physicochemical properties of these chemicals and how spilled chemicals may move in the environment, the distribution of properties could change if we obtained data for all known fracturing fluid chemicals (as well as for those listed as CBI).

There has been limited research on the fate and transport of spilled chemicals on site. We have provided a limited overview discussing the processes that may be important, but the processes are complex. There is great uncertainty in how these chemicals will move in the environment. These processes are complicated by the data gaps in fluid characteristics, especially present in mixtures, and there is limited understanding on how chemicals act in mixture in the environment. Hydraulic fluid mixtures are different than other previously studied mixtures (like petroleums, coal tars, and polychlorinated biphenyls (PCBs). Those mixtures are of chemicals of similar classes, while hydraulic fracturing fluids are chemicals covering a range of different chemical classes.

There is a lack of field data at hydraulic fracturing sites. There is a lack of baseline ground and surface water quality data. This lack of data limits our ability to assess the relative change to water quality from a spill or attribute the presence of a contaminant to a specific source. There is a lack of publicly or readily accessible sampling of soils and groundwater after a fracturing job is complete. The lack of data and uncertainty on what chemicals are used for hydraulic fracturing makes it unclear what chemicals to measure. Further uncertainty lies in the limited analytical techniques for chemicals used in hydraulic fracturing.

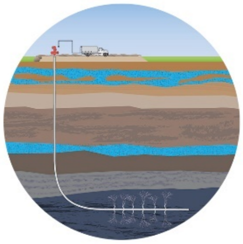
There are uncertainties and data gaps in the current information on spills. The EPA spills report included data from January 2006 to April 2012 from nine states, nine service companies, and nine oil and gas production well operators (U.S. EPA, 2015a). This data contained over 36,000 reported spills. From this data set, only 457 were determined to be definitively associated with hydraulic fracturing and occurred on or near the well pad. With these data, it is impossible to know if all these spill reports capture all spills occurring at hydraulic fracturing sites. The available data might not extrapolate to the rest of the nation. Spill reports had limited information on spill causes, containment and mitigation measures, and sources of spills. The actual chemicals spilled, the total mass, and the composition are generally not included. There are little available data on impacts of spills, due to a lack of baseline data and incomplete documentation of follow-up actions and testing.

In general, then, we are limited in our ability to fully assess potential impacts on drinking water resources from chemical spills, based on current available information. To improve our understanding we need: more information on the chemical composition of additives and fracturing fluids and the physicochemical properties of chemicals used; baseline monitoring and field studies of spilled chemicals; ground and surface water drinking water resources located and identified, with quality conditions performed before and after hydraulic fracturing; detailed site-specific environmental conditions; more information on containment and mitigation measures and their effectiveness; and more detail on the characteristics of spills, such as the exact chemicals and the amount spilled (mass, concentration, volume).

5.10.4 Conclusions

This chapter discusses the factors that affect the potential for the chemical mixing stage of the hydraulic fracturing water cycle to impact drinking water resources. Reports have demonstrated that spills and releases of chemicals and fluids have occurred during the chemical mixing stage and have reached soils and surface waters with the potential to reach groundwater. The potential for spilled fluids to reach, and therefore impact, ground or surface water resources depends on the composition of the spilled fluid, spill characteristics, spill response activities, and the fate and transport of the spilled fluid. There is no standard composition for a hydraulic fracturing fluid, which consists of base fluid, proppant, and additives. The EPA identified 1,084 chemicals that have been reported to be used nationwide, and these chemicals cover a wide variety of chemical classes and physicochemical properties, and this number is increasing. These chemicals cover a range of classes and physicochemical properties. The type of fluid and the number, volume, and type of chemicals used vary from site to site. Hydraulic fracturing fluids generally consist of a mixture of chemicals, which affects the potential for a release to reach a drinking water resource and the severity of the potential impact. State and industry spill data collected and reviewed by the EPA and others indicate that small (approximately 30 gal or 100 L) and large spills (greater than 1,000 gal or 4,000 L) can reach surface water resources. While small spills have reached surface water resources (and have the potential to reach groundwater resources), large volume spills are more likely to travel longer distances and thus have a greater potential to reach ground and surface water resources. Large volume spills, particularly of concentrated additives, also have a greater potential to result in more severe impacts on drinking water resources, because they can deliver a large quantity of potentially hazardous chemicals to ground or surface water resources.

Chapter 6. Well Injection



Abstract

The well injection stage of the hydraulic fracturing water cycle involves the injection of hydraulic fracturing fluids through the oil and gas production well and their movement in the production zone. Subsurface pathways created during this stage—including the production well and newly created fractures—can allow hydraulic fracturing fluids or naturally occurring fluids to reach groundwater resources.

This chapter examines two types of pathways by which hydraulic fracturing fluids and liquids and/or gases that exist in the subsurface can move to, and affect the quality of, subsurface drinking water resources. First, fluids can move via pathways adjacent to or through the production well as a result of inadequate design, construction, or degradation of the casing or cement. Second, fluid movement can occur within the subsurface geologic formations via fractures extending out of oil/gas-containing formations, by intersecting abandoned or active offset wells, or via naturally occurring faults and fractures.

The primary factors that can affect the frequency or severity of impacts to drinking water associated with injection for hydraulic fracturing are: (1) the condition of the well's casing and cement and their placement relative to drinking water resources, (2) the vertical separation between the production zone and formations that contain drinking water resources, and (3) the presence/proximity and condition of wells near the hydraulic fracturing operation.

We identified two cases where hydraulic fracturing activities affected the quality of drinking water resources due to well construction issues, including inadequate cement or ruptured casing. Additionally, there are places where oil and gas reservoirs and drinking water resources co-exist in the same formation and hydraulic fracturing operations occur, which results in the introduction of hydraulic fracturing fluids into the drinking water resource. There are other cases involving the migration of stray gas where hydraulic fracturing could be a contributing cause to impacts on drinking water resources.

While there is evidence that these pathways have formed and that groundwater quality has been impacted, there are limited nationally available data on the performance of wells used in hydraulic fracturing operations, pre- and post-hydraulic fracturing groundwater quality, and the extent of the fractures that develop during hydraulic fracturing operations.

These data limits, in combination with the geologic complexity of the subsurface environment and the fact that these processes cannot be directly observed, make determining the frequency of such impacts challenging.

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6. Well Injection

6.1 Introduction

In the well injection stage of the hydraulic fracturing water cycle, hydraulic fracturing fluids (primarily water, mixed with the types of chemicals and proppant described in Chapter 5) are injected into a well under pressure.[1] These fluids flow under pressure through the well, then exit the well and move into the formation, where they create fractures in the rock. This process is also known as a fracture treatment or a type of stimulation.[2] The fractures, which typically extend hundreds of feet away from the well, are designed to remain within the production zone to access as much oil or gas as possible by using an appropriate amount of water and chemicals to complete the operation.[3]

Production wells are sited and designed primarily to optimize production of oil or gas, which requires isolating water-bearing formations from hydrocarbon-bearing formations in order to prevent the water from diluting the hydrocarbons and to protect drinking water resources.[4] However, problems with the well's components or improperly sited, designed, or executed hydraulic fracturing operations (or combinations of these) could adversely impact the quality of drinking water resources. (Note that, due to the subsurface nature of activities in the well injection stage, the drinking water resources that may be directly impacted are groundwater resources; see Chapter 2 for additional information about groundwater.[5])

The well and the geologic environment in which it is located are a closely linked system. Wells are often designed with multiple barriers (i.e., isolation afforded by the well's casing and cement and the presence of subsurface rock formations) to prevent fluid movement between oil/gas zones and drinking water resources. Therefore, this chapter discusses (1) the well (including its construction and operation) and (2) the characteristics of or features in the subsurface geologic formations that could provide or have provided pathways for migration of fluids to drinking water resources. If present, and in combination with the existence of a fluid and a physical force that moves the fluid, these pathways can lead to impacts on the quality of drinking water resources throughout the life of the well, including during and after hydraulic fracturing.[6]

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[1] A fluid is a substance that flows when exposed to an external pressure; fluids include both liquids and gases.

[2] In the oil and gas industry, "stimulation" has two meanings—it refers to (1) injecting fluids to clear the well or pore spaces near the well of drilling mud or other materials that block or inhibit optimal production (i.e., matrix treatment) and (2) injecting fluid to fracture the rock to optimize the production of oil or gas. This chapter focuses on the latter.

[3] The "production zone" (sometimes referred to as the target zone or the targeted rock formation) refers to the portion of a subsurface rock zone that contains oil or gas to be extracted (sometimes using hydraulic fracturing). "Producing formation" refers to the larger geologic unit in which the production zone occurs.

[4] A subsurface formation (or "formation") is a mappable body of rock of distinctive rock type(s) and characteristics (such as permeability and porosity) with a unique stratigraphic position.

[5] Government agencies and other organizations use a variety of terms to describe potable groundwater and groundwater resources. In this chapter, we use the general term "groundwater resources" to refer to drinking water resources that occur underground. However, other terms are used in specific contexts to reflect the language used in cited materials.

[6] The primary physical force that moves fluids within the subsurface is a difference in pressure. Fluids move from areas of higher pressure to areas of lower pressure when a pathway exists. Density-driven buoyancy may also serve as a driving force; see Section 6.3 for more information.

Fluids can move via pathways adjacent to or through the production well that are created in response to the stresses exerted during hydraulic fracturing operations if the well is not able to withstand these stresses (Section 6.2). While wells are designed and constructed to isolate fluids and maximize the production of oil and gas, inadequate construction or degradation of the casing or cement can allow fluid movement that can impact drinking water quality. Potential issues associated with wells may be related to the following:

- Inadequate or degraded casing. This may be influenced by the number of casing strings and the depths to which they are set, compatibility with the geochemistry of intersected formations, the age of the well, whether re-fracturing is performed, and other operational factors.
- Inadequate or degraded cement. This may be influenced by a lack of cement in key subsurface intervals, poor-quality cement, improperly placed cement, or degradation of cement over time.

Fluid movement can also occur via induced fractures and/or other features within subsurface formations (Section 6.3). While the hydraulic fracturing operation may be designed so that the fractures will remain within the production zone, it is possible that, in the execution of the hydraulic fracturing treatment, fractures can extend beyond their designed extent. Four scenarios associated with induced fractures may contribute to fluid migration or communication between zones:

- Flow of injected and/or displaced fluids through pore spaces in adjacent rock formations out of the production zone due to pressure differences and buoyancy effects.
- Fractures extending out of oil/gas formations into drinking water resources or zones that are in communication with drinking water resources or fracturing into zones containing drinking water resources.
- Fractures intersecting artificial structures, including active (producing) or inactive offset wells near the well that is being stimulated (i.e., well communication) or abandoned or active mines.
- Fractures intersecting geologic features that can act as pathways for fluid migration, such as existing permeable faults and fractures.

This chapter describes the conditions that can contribute to or cause the development of the pathways listed above, the evidence for the existence of these pathways, examples of impacts on the quality of drinking water resources associated with these pathways that have been documented in the literature, and the factors that can affect the frequency or severity of those impacts. (See Chapter 10 for a discussion of factors and practices that can reduce the frequency or severity of impacts to drinking water quality.)

The interplay between the well and the subsurface features is complex and not directly observable; therefore, sometimes it is not possible to identify what specific element is contributing to or is the primary cause of an impact on drinking water resources. For example, concerns have been raised regarding stray gas detected in groundwater in natural gas production areas (for additional information about stray gas, see Sections 6.2.2 and 6.3.2.4).[1] Stray gas migration is a technically complex phenomenon, because there are many potential naturally occurring or artificially created routes for migration of gas into aquifers, including along production wells and via naturally existing or induced fractures. It is also challenging to determine the source of the natural gas and whether the mobilization is related to oil or gas production activities.

Furthermore, identifying cases where contamination of drinking water resources occurs due to oil and gas production activities—including hydraulic fracturing operations—requires extensive amounts of site and operational data, collected before and after hydraulic fracturing operations. (See Section 6.4 for additional information on data limitations.) Where such data do exist and provide evidence of contamination, we present it in the following sections. We do not attempt to predict which of these pathways is most likely to occur or to lead to a drinking water impact, or the magnitude of an impact that might occur as a result of migration via any single pathway, unless the information is available and documented based on collected data. However, a qualitative assessment of the factors that can affect the frequency or severity of impacts on drinking water quality associated with the well injection stage is possible; see Section 6.4.

6.2 Fluid Migration Pathways Within and Along the Production Well

In this section, we discuss pathways for fluid movement along or through the production well used in the hydraulic fracturing operation. While these pathways can form during other times within the life of an oil and gas well, the repeated high pressure stresses exerted during hydraulic fracturing operations can make maintaining the mechanical integrity of the well more difficult (Council of Canadian Academies, 2014).[2] Section 6.2.1 presents the purpose of the various well components and typical well construction configurations. Section 6.2.2 describes the pathways for fluid movement that can potentially develop within the production well and wellbore and the conditions that lead to pathway development, either as a result of the original design of the well, degradation over time or use, or hydraulic fracturing operations.

While we discuss casing and cement separately, it is important to note that these are related—inadequacies in one of these components can lead to stresses on the other. For example, flaws in cement may expose the casing to corrosive fluids. Furthermore, casing and cement work together in the subsurface to form a barrier to fluid movement, and it may not be possible to distinguish whether mechanical integrity problems are related to the casing, the cement, or both. For additional information on well design and construction, see Appendix D.

6.2.1 Overview of Well Construction

Production wells are constructed to transport hydrocarbon resources from the reservoirs in which they are found to the surface. They are also used to isolate fluid-bearing zones (containing oil, gas,

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[1] Stray gas refers to the phenomenon of natural gas (primarily methane) migrating into shallow drinking water resources or to the surface.

[2] Mechanical integrity of a well refers to the absence of significant leakage within the injection tubing, casing, or packer (referred to as internal mechanical integrity) or outside of the casing (referred to as external mechanical integrity).

or fresh water) from each other. Multiple barriers (i.e., casing and cement) are often present, and they act together to prevent both horizontal fluid movement (in or out of the well) and vertical fluid movement (along the wellbore from deeper oil- or gas-bearing formations to drinking water resources). Proper design and construction of the casing, cement, and other well components in the context of the location of drinking water resources and maintaining mechanical integrity throughout the life of a well are necessary to prevent migration of hydraulic fracturing fluids and formation fluids into drinking water resources.

A well is a multiple-component system that typically includes casing, cement, and a completion assembly, and it may be drilled vertically, horizontally, or in a deviated orientation (Figure 6-1).[1,2] These components work together to prevent unintended fluid movement into, out of, or along the well. Due to the presence of multiple barriers within the well and the geologic system in which it is placed, the existence of a pathway for fluid movement through a component of this system does not necessarily mean that an impact on a drinking water resource has occurred or will occur.

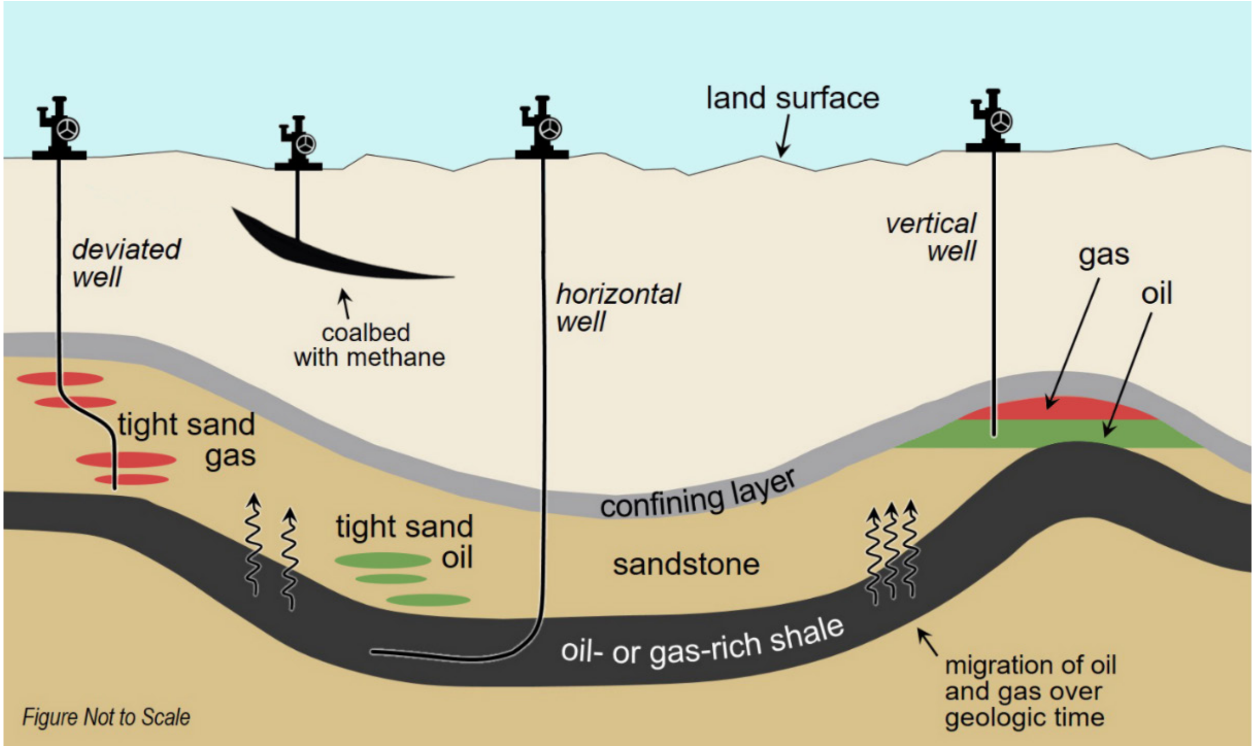

Figure 6-1. Schematic cross-section of general types of oil and gas resources and the orientations of production wells used in hydraulic fracturing.

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[1] Completion is a term used to describe the assembly of equipment at the bottom of the well that is needed to enable production from an oil or gas well. It can also refer to the activities and methods (including hydraulic fracturing) used to prepare a well for production following drilling.

[2] For the purposes of this assessment, a well's orientation refers to its inclination from verticality. Wells drilled straight downward are considered to be vertical, wells drilled directionally to end up parallel to the production zone's bedding plane are considered horizontal, and directionally drilled wells that are neither vertical nor horizontal are referred to as deviated. In industry usage, a well's orientation commonly refers both to its inclination from vertical and the azimuthal (compass) direction of a directionally drilled wellbores.

Casing primarily acts as a barrier to lateral movement of fluids, and cement primarily acts as a barrier to unintended vertical movement of fluids. Together, casing and cement are important in preventing fluid movement into drinking water resources, and are the focus of this section. Figure 6-2 illustrates the configurations and types of casing and cement and other features that may occur in oil and gas production wells. The figure depicts an idealized representation of the components of a production well; it is important to note that there is a wide variety in the design of hydraulically fractured oil and gas wells in the United States (U.S. EPA, 2015n), and the descriptions in the figure or in this chapter do not represent every possible well design.

6.2.1.1 Casing

Casing is steel pipe that is placed into the drilled wellbore to maintain the stability of the wellbore, to transport the hydrocarbons from the subsurface to the surface, and to prevent intrusion of other fluids into the well and wellbore (Hyne, 2012; Renpu, 2011). A long continuous section of casing is referred to as a casing string, which is composed of individual lengths of casing (known as casing joints) that are threaded together using casing collars. In different sections of the well, multiple concentric casing strings of different diameters can be used, depending on the construction of the well.

The presence of multiple layers of casing strings can isolate and protect geologic zones containing drinking water. In addition to conductor casing, which prevents the hole from collapsing during drilling, one to three other types of casing may be also present in a well. The types of casing include (from largest to smallest diameter) surface casing, intermediate casing, and production casing (GWPC, 2014; Hyne, 2012; Renpu, 2011). One or more of any of these types of casing (but not necessarily all of them) may be present in a well. Surface casing often extends from the wellhead down to the base (i.e., the bottom or lowest part) of the drinking water resource to be protected. Wells also may be constructed with production liners, which are anchored or suspended from inside the bottom of the previous casing string. Production liners serve the same purpose as production casing but extend only to the end of the previous casing, rather than all the way to the surface. Wells may also have production tubing, which is used to transport the hydrocarbons to the surface. Tie-back liners may be used to extend a production liner to the surface when downhole pressure or corrosive conditions warrant additional protection of the intermediate or production casing.

Among the wells represented by the Well File Review (described in Text Box 6-1), between one and four casing strings were present (the Well File Review did not evaluate conductor casings). A combination of surface and production casings was most often reported, followed by a combination of surface, intermediate, and production strings. All of the production wells used in hydraulic fracturing operations in the Well File Review had surface casing, while approximately 39% of the wells (an estimated 9,100 wells) had intermediate casing, and 94% (an estimated 21,900 wells) had production casing (U.S. EPA, 2015n).[1, 2]

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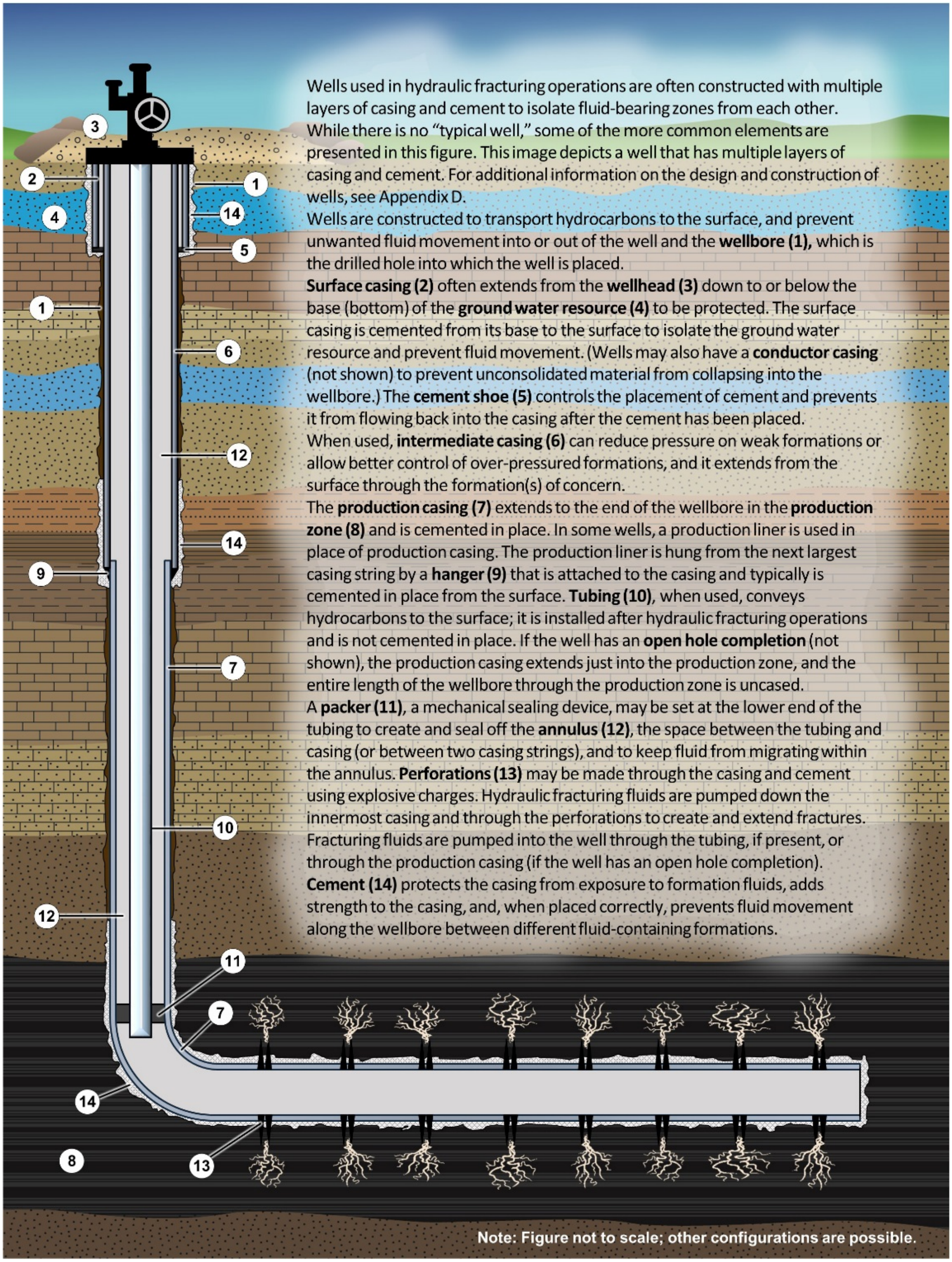
[1] 9,100 wells (95% confidence interval: 2,900 – 15,400 wells).

[2] 21,900 wells (95% confidence interval: 19,200 – 24,600 wells).



Wells used in hydraulic fracturing operations are often constructed with multiple layers of casing and cement to isolate fluid-bearing zones from each other. While there is no "typical well," some of the more common elements are presented in this figure. This image depicts a well that has multiple layers of casing and cement. For additional information on the design and construction of wells, see Appendix D.

Wells are constructed to transport hydrocarbons to the surface, and prevent unwanted fluid movement into or out of the well and the **wellbore (1),** which is the drilled hole into which the well is placed.

Surface casing (2) often extends from the **wellhead (3)** down to or below the base (bottom) of the **ground water resource (4)** to be protected. The surface casing is cemented from its base to the surface to isolate the ground water resource and prevent fluid movement. (Wells may also have a **conductor casing** (not shown) to prevent unconsolidated material from collapsing into the wellbore.) The **cement shoe (5)** controls the placement of cement and prevents it from flowing back into the casing after the cement has been placed.

When used, **intermediate casing (6)** can reduce pressure on weak formations or allow better control of over-pressured formations, and it extends from the surface through the formation(s) of concern.

The **production casing (7)** extends to the end of the wellbore in the **production zone (8)** and is cemented in place. In some wells, a production liner is used in place of production casing. The production liner is hung from the next largest casing string by a **hanger (9)** that is attached to the casing and typically is cemented in place from the surface. **Tubing (10)**, when used, conveys hydrocarbons to the surface; it is installed after hydraulic fracturing operations and is not cemented in place. If the well has an **open hole completion** (not shown), the production casing extends just into the production zone, and the entire length of the wellbore through the production zone is uncased.

A **packer (11)**, a mechanical sealing device, may be set at the lower end of the tubing to create and seal off the **annulus (12)**, the space between the tubing and casing (or between two casing strings), and to keep fluid from migrating within the annulus. **Perforations (13)** may be made through the casing and cement using explosive charges. Hydraulic fracturing fluids are pumped down the innermost casing and through the perforations to create and extend fractures.

Fracturing fluids are pumped into the well through the tubing, if present, or through the production casing (if the well has an open hole completion).

Cement (14) protects the casing from exposure to formation fluids, adds strength to the casing, and, when placed correctly, prevents fluid movement along the wellbore between different fluid-containing formations.

Note: Figure not to scale; other configurations are possible.

Figure 6-2. Overview of well construction.

Hydraulic fracturing operations impose a variety of stresses on the well components. In order to prevent the formation of pathways to drinking water resources, the casing should be designed with sufficient strength to withstand the stresses it will encounter during the installation, cementing, hydraulic fracturing, production, and post-production phases of the life of the well. These stresses, illustrated in Figure 6-3, include burst pressure (the interior pipe pressure that will cause the casing to burst), collapse pressure (the pressure applied to the outside of the casing that will cause it to collapse), tensile stress (the stress related to stretching exerted by the weight of the casing or tubing being raised or lowered in the hole), compression and bending (the stresses that result from pushing along the axis of the casing or bending the casing), and cyclic stress (the stress caused by frequent or rapid changes in temperature or pressure). While the injection stage represents a relatively brief portion of the life of a hydraulic fracturing well (Section 3.3), injection imposes the highest stresses the well is likely to encounter.

Text Box 6-1. The Well File Review.

The EPA conducted a survey of onshore oil and gas production wells that were hydraulically fractured by nine oil and gas service companies in the continental United States between approximately September 2009 and September 2010. This effort, known as the "Well File Review," produced two reports. The first report, *Review of Well Operator Files for Hydraulically Fractured Oil and Gas Production Wells: Well Design and Construction* (U.S. EPA, 2015n) describes well design and construction characteristics and their relationships to the location of operator-reported drinking water resources and the number and relative location of constructed barriers (i.e., casing and cement) that can block pathways for potential subsurface fluid movement. A second report, *Review of Well Operator Files for Hydraulically Fractured Oil and Gas Production Wells: Hydraulic Fracturing Operations* (U.S. EPA, 2016c) presents information on hydraulic fracturing job characteristics and the reported use of casing pressure tests, annular pressure monitoring, surface treating pressure monitoring, and microseismic monitoring conducted before or during hydraulic fracturing operations; it also explores the roles of well mechanical integrity and induced fracture growth as they relate to the potential for subsurface fluid movement to intersect protected groundwater resources.

The survey was based on a sample of 323 hydraulically fractured oil and gas production wells. Results of the research are presented as rounded estimates of the frequency of occurrence of hydraulically fractured production well design, construction, and operational characteristics with 95% confidence intervals (CIs). The results are statistically representative of an estimated 23,200 onshore oil and gas production wells hydraulically fractured in 2009 and 2010 by nine service companies where an estimated 28,500 hydraulic fracturing jobs were performed.

In addition, the casing must be resistant to corrosion from contact with the formations and any fluids that might be transported through the casing, including hydraulic fracturing fluids, brines, and oil or gas. Casing strength or corrosion resistance can be increased by using fiberglass or high-strength alloys or by increasing the thickness of the casing.

One way to ensure that the strength of the casing is sufficient to withstand the stresses imposed by hydraulic fracturing operations is to pressure test the casing. The casing can be pressurized to the pressure anticipated during hydraulic fracturing operations and shut-in periods; if the well can hold the pressure, it is considered to be leak-free and therefore should be able to withstand the pressures of hydraulic fracturing. However, if the test pressure is less than the hydraulic fracturing pressure, the casing is determined to be leak-free, but its suitability to resist the stresses associated with the planned fracturing operation is less certain.

The Well File Review (U.S. EPA, 2016c) found that pressure tests were performed prior to an estimated 15,600 of 28,500 hydraulic fracturing jobs the EPA studied, including cases where a frac string was pressure tested.[1] In 52% of those pressure tests performed (representing 28% of the hydraulic fracturing jobs studied), the well was tested to a pressure equal to or greater than the maximum pressure that occurred during the hydraulic fracturing job (U.S. EPA, 2016c).[2] Thus, in a significant number of hydraulic fracturing jobs (i.e., 72% of the wells studied), there are no data in the well files to indicate that the casing was tested in a manner that could ensure the adequacy of the casing to withstand the pressures of hydraulic fracturing. While, in some cases, casing may not have been pressure tested because a frac string was to be installed to protect the casing from the increased pressure, only 10% of fracturing jobs were conducted using a frac string.

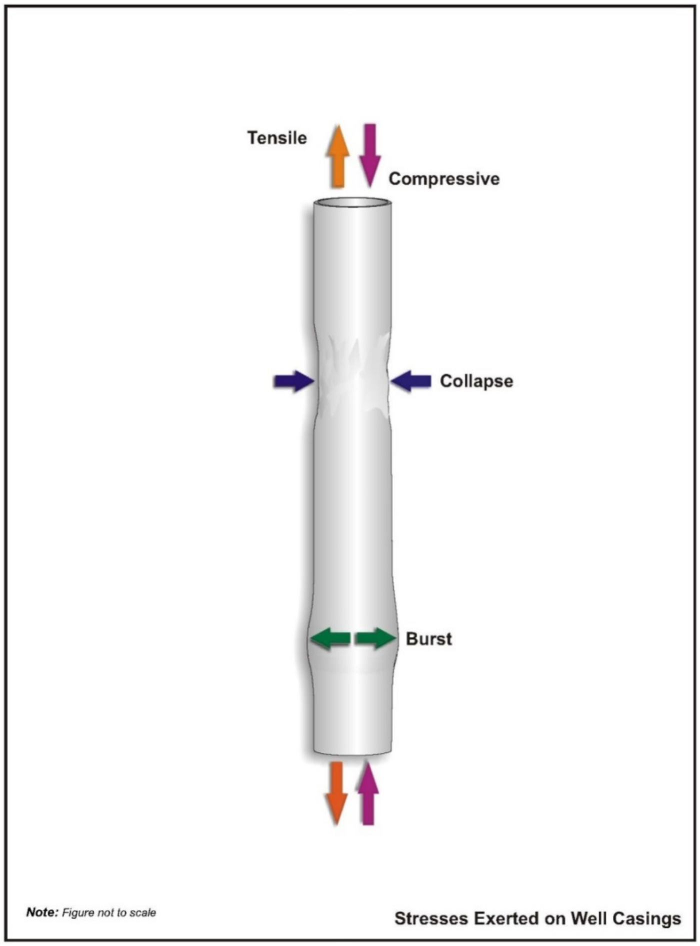


Figure 6-3. The various stresses to which the casing will be exposed.

In addition to the stresses illustrated, the casing will be subjected to bending and cyclic stresses. Source: U.S. EPA (2012d).

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[1] 15,600 jobs (95% confidence interval: 11,800 – 19,300 jobs).

[2] 52% of pressure tests (95% confidence interval: 20 – 82% of tests).

6.2.1.2 Cement

Cement is one of the most important components of a well for providing zonal isolation and reducing impacts on drinking water. Cement in the space between the casing and formation isolates fluid-containing formations from each other, protects the casing from exposure to formation fluids, and provides additional strength to the casing. The strength of the cement and its compatibility with the formation and fluids encountered are important for maintaining mechanical integrity throughout the life of the well.

A variety of methods are available for placing the cement, evaluating the adequacy of the cementing process and the resulting cement job, and repairing any identified deficiencies. Cement is most commonly emplaced by pumping the cement down the inside of the casing to the bottom of the wellbore and then up the space between the outside of the casing and the formation (or the next largest casing string). This method is referred to as the primary cement job and can be performed as a continuous event in a single stage (i.e., "continuous cementing") or in multiple stages (i.e., "staged cementing"). Staged cementing may be used when, for example, the estimated weight and pressure associated with standard cement placement could damage weak zones in the formation (Crook, 2008).

Deficiencies in the cementing process can result from poorly centered casing, poor removal of drilling mud behind the casing, cement shrinkage, premature gelation, excessive fluid loss, improper mixing, or lost cement.[1, 2] Cement deficiencies can be reduced by proper design of the cementing process including use of casing centralizers, proper design of the cement, proper mud removal, and use of cement additives (Kirksey, 2013).[3] If any deficiencies or defects in the primary cement job are identified, remedial cementing may be performed. See Text Box 6-2 for an example of an incident where cementing issues were studied as part of an evaluation of drinking water well impacts.

Text Box 6-2. Dimock, Pennsylvania.

In 2009, shortly after drilling and hydraulic fracturing in the Marcellus Shale commenced in the area, residents near the township of Dimock, Pennsylvania reported that natural gas was appearing or increasing in their water wells (Hammond, 2016; PA DEP, 2009a).

Water wells in the area largely draw from the Catskill Formation and range in depth from less than 50 ft (15 m) to more than 500 ft (150 m) (Molofsky et al., 2013). In this area, the Marcellus Shale is about 7,000 ft (2,000 m) below the surface and its natural gas is extracted through vertical and horizontal wells (Hammond, 2016). Methane exists naturally in the subsurface in this part of Pennsylvania, including in the Catskill Formation and the geologic formations below it (Baldassare et al., 2014; Molofsky et al., 2013; Molofsky et al., 2011).

(Text Box 6-2 is continued on the following page.)

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[1] Gelation is the process in the setting of the cement where it begins to solidify and lose its ability to transmit pressure to the formation.

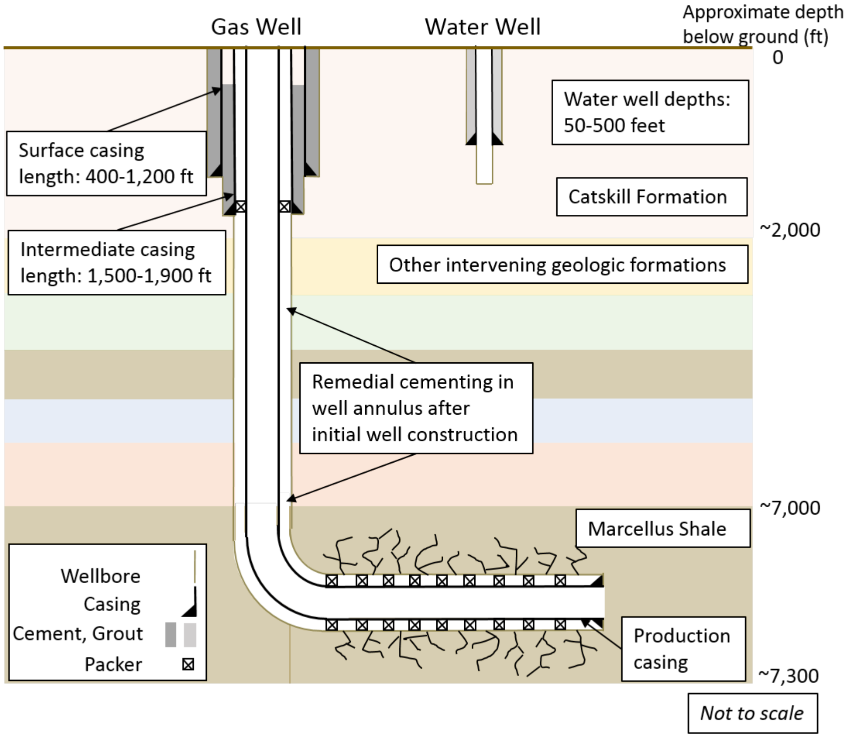
[2] Lost cement refers to a failure of the cement or the spacer fluid used to wash the drilling fluid out of the wellbore to be circulated back to the surface, indicating that the cement has escaped into the formation.

[3] Centralizers are used to keep the casing in the center of the hole and allow an even cement job.

Text Box 6-2 (continued). Dimock, Pennsylvania.

The Pennsylvania Department of Environmental Protection (PA DEP) investigated and made a determination that 18 water wells located within a 9 mi^2 (23 km^2) area had been negatively affected as a result of natural gas extraction activities. For approximately two years, during which there was a partial ban on gas well drilling and hydraulic fracturing in the vicinity, the gas company plugged four gas wells and undertook remedial construction actions at 18 additional gas wells (including remedial cementing at several wells, adding as much as 6,300 ft (1,900 m) of cement behind the production casings) (PA DEP, 2010b, d, 2009a).

The figure below presents a simplified geologic representation of water wells and one type of horizontal gas well completed within the geologic formations in the area. The location of remedial cementing performed in some gas wells is indicated.



Several studies in this and surrounding areas have focused on the geochemistry of the groundwater, in particular on gas composition, and noble and natural gas isotopes in the water. Results are consistent with an accumulation of stray gas originating from greater depth and moving to the Catskill Formation (Jackson et al., 2013c; Molofsky et al., 2013; Molofsky et al., 2011). However, the identity of the geologic formation(s) sourcing the natural gas is not always certain and may be consistent with sourcing from either the Marcellus (as suggested by Jackson et al. (2013c)), or the intervening geologic formations (Molofsky et al., 2013).

The role of hydraulic fracturing in the migration of gas to the Catskill Formation, and the specific pathways by which this migration occurred, is even less certain. Some investigators suspect that the initial gas well construction allowed natural gases from deeper formations to move upward along uncemented wellbores (Hammond, 2016; PA DEP, 2010b, d, 2009a). However, no publicly available information exists to document whether hydraulic fracturing may have aided fluid movement along wellbores to enter drinking water resources from greater depths. Reviews of information, such as hydraulic fracturing job reports showing the intervals hydraulically fractured, injection rates, and pressure monitoring, would support an evaluation of whether hydraulic fracturing might have played a role in the migration of natural gas to drinking water wells in the area.

Among the wells represented in the Well File Review, over 90% of cemented casings were cemented using primary cementing methods. Secondary or remedial cementing was used on an estimated 8% of casings (most often on surface and production casings and less often on intermediate casings).[1] The remedial cementing techniques employed in these wells included cement squeezes, cement baskets, and pumping cement down the annulus (U.S. EPA, 2015n). See Appendix D for more information on remedial cementing techniques.

The cement does not always need to be continuous along the entire length of the well to protect drinking water resources; rather, protection of drinking water resources depends on a good cement seal across the appropriate subsurface zones, including all fresh water- and hydrocarbon-bearing zones. One study of wells in the Gulf of Mexico found that, if at least 50 ft (15 m) of high quality cement was present, pressure differentials as high as 14,000 psi (97 MPa) would not lead to breakdown in isolation between geologic zones (King and King, 2013).

Most wells have cement behind the surface casing, which is a key barrier to contamination of drinking water resources. The surface casings in nearly all of the wells used in hydraulic fracturing operations represented in the Well File Review (93% of the wells, or an estimated 21,500 wells) were fully cemented.[2,3] None of the wells studied in the Well File Review had completely uncemented surface casings.

The length and location of cement behind intermediate and production casings can vary based on the presence and locations of over-pressured formations, formations containing fluids, or geologically weak formations (i.e., those that are prone to structural failure when exposed to changes in subsurface stresses). State regulations and economics also play a role.

In the Well File Review, the intermediate casings of most of the wells studied were fully cemented, although there were relatively wide 95% confidence intervals in the results. Among production casings, about half were partially cemented, about a third were fully cemented, and the remainder were either uncemented or their cementing status was undetermined. Among the approximately 9,100 wells represented in the Well File Review that are estimated to have intermediate casing, the intermediate casing was fully cemented in an estimated approximately 7,300 wells (80%) and partially cemented in an estimated 1,700 wells (19%).[4,5] Production casings were partially cemented in 47% of the wells, or approximately 10,900 wells (U.S. EPA, 2015n).[6]

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[1] 8% of casings (95% confidence interval: 3% – 14% of casings).

[2] The Well File Review defined fully cemented casings as casings that had a continuous cement sheath from the bottom of the casing to at least the next larger and overlying casing (or the ground surface, if surface casing). Partially cemented casings were defined as casings that had some portion of the casing that was cemented from the bottom of the casing to at least the next larger and overlying casing (or ground surface), but were not fully cemented. Casings with no cement anywhere along the casing, from the bottom of the casing to at least the next larger and overlying casing (or ground surface), were defined as uncemented.

[3] 21,500 wells (95% confidence interval: 19,500 – 23,600 wells).

[4] 9,100 wells (95% confidence interval: 2,900 – 15,400 wells).

[5] 7,300 wells (95% confidence interval: 600 – 13,900 wells).

[6] 10,900 wells (95% confidence interval: 6,900 – 14,900 wells).

The Well File Review also estimated the number of wells with a continuous cement sheath along the outside of the well. An estimated 6,800 of the wells represented in the study (29%) had cement from the bottom of the well to the ground surface, and approximately 15,300 wells (66%) had one or more uncemented intervals between the bottom of the well and the surface.[1,2] In the remaining wells, the location of the top of the cement was uncertain, so no determination could be made regarding whether the well had a continuous cement sheath along the outside of the well (U.S. EPA, 2015n).

A variety of logs are available to evaluate the quality of cement behind the well casing. Among wells in the Well File Review, the most common type of cement evaluation log run was a standard acoustic cement bond log (U.S. EPA, 2015n). Standard acoustic cement bond logs are used to evaluate both the extent of the cement placed along the casing and the cement bond between the cement, casing, and wellbore. Cement bond indices calculated from standard acoustic cement bond logs on the wells in the Well File Review showed a median bond index of 0.7 just above the hydraulic fracturing zone; this value decreased to 0.4 over a measured distance of 5,000 ft (2,000 m) above the hydraulic fracturing zone (U.S. EPA, 2015n).[3] While standard acoustic cement bond logs can give an average estimate of bonding, they cannot alone indicate zonal isolation, because they may not be properly run or calibrated (Boyd et al., 2006; Smolen, 2006). One study of 28 wells found that cement bond logs failed to predict communication between formations 11% of the time (Boyd et al., 2006). In addition, they cannot discriminate between full circumferential cement coverage by weaker cement and lack of circumferential coverage by stronger cement (King and King, 2013; Smolen, 2006). A few studies have compared cement bond indices to zonal isolation, with varying results. For example, Brown et al. (1970) showed that among 16 South American wells with varying casing size and cement bond indices, a cemented 5.5 in (14 cm) diameter casing with a bond index of 0.8 along as little as 5 ft (1.5 m) can act as an effective seal. The authors also suggest that an effective seal in wells having calculated bond indices differing from 0.8 are expected to have an inverse relationship between bond index and requisite length of the cemented interval, with longer lengths needed along casing having a lower bond index. Another study recommends that wells undergoing hydraulic fracturing should have a given cement bond over an interval three times the length that would otherwise be considered adequate for zonal isolation (Fitzgerald et al., 1985). Conversely, King and King (2013) concluded field tests from wells studied by Flournoy and Feaster (1963) had effective isolation when the cement bond index ranged from 0.31 to 0.75.

External mechanical integrity tests (MITs), including temperature logs, noise logs, and radioactive tracer logs, are another means to evaluate the zonal isolation performance of well cement. Instead of measuring the apparent quality of the cement, external MITs measure whether there is evidence of fluid movement along the wellbore (and potentially to a drinking water resource). An external MIT conducted before the hydraulic fracturing job can allow detection of channels in the cement that could allow injected fluids to move out of the production zone. An external MIT performed

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[1] 6,800 wells (95% confidence interval: 1,600 – 11,900 wells).

[2] 15,300 wells (95% confidence interval: 10,500 – 20,100 wells).

[3] Cement bond logs are used to calculate a bond index, which varies between 0 and 1, with 1 representing the strongest bond and 0 representing the weakest bond.

after hydraulic fracturing operations can detect any fluid movement resulting from cement damage caused by the hydraulic fracturing job. It is important to note that, if a well fails an MIT, this does not mean there is a failure of the well or that drinking water resources are impacted. An MIT failure is a warning that something needs to be addressed, and a loss of mechanical integrity is an event that can result in fluid movement from the well if remediation is not performed. More details on MITs are available in Appendix D.

Monitoring the treatment pressure of the hydraulic fracturing operation can also detect problems occurring during fracturing. Sudden changes in pressure during hydraulic fracturing operations can be indicative of failures in the cement or casing. This type of monitoring is performed in nearly all hydraulic fracturing jobs: the Well File Review (U.S. EPA, 2016c) found that the treatment pressure was monitored in 97% (or 27,700) of all hydraulic fracturing jobs studied.[1]

6.2.1.3 Well Orientation

A well can be drilled and constructed with any of several different orientations: vertical, horizontal, and deviated. The well's orientation can be important, because it affects the difficulty of drilling, constructing, and cementing the well. In particular, as described in Section 6.2.2, constructing and cementing horizontal wells present unique challenges (Sabins, 1990). In a vertical well, the wellbore is vertical throughout its entire length, from the wellhead at the surface to the production zone. Deviated wells are usually drilled vertically in the shallowest part of the well but are then drilled directionally, deviating from the vertical direction at some point such that the bottom of the well is at a significant lateral distance away from the point in the subsurface directly under the wellhead. In a horizontal well, the well is drilled vertically to a point known as the kickoff point, where the well turns toward the horizontal, extending into and parallel with the approximately horizontal targeted producing formation (Figure 6-2).

Among wells evaluated in the Well File Review, about 65% were vertical, 11% were horizontal, and 24% were deviated wells (U.S. EPA, 2015n).[2] This is generally consistent with information available in industry databases—of the approximately 16,000 oil and gas wells used in hydraulic fracturing operations in 2009 (one of the years for which the data for the Well File Review were collected), 39% were vertical, 33% were horizontal, and 28% were either deviated or the orientation was unknown (DrillingInfo, 2014b). See Section 3.3 for additional information on the use of horizontal wells in the United States.

6.2.1.4 Well Completion

Another important aspect of well construction is the way in which the well is completed into the production zone, because the well's completion is part of the system of barriers and must be intact for the well to operate properly. A variety of completion configurations are available. The most common configuration is for casing to extend to the end of the wellbore and be cemented in place (U.S. EPA, 2015n; George et al., 2011; Renpu, 2011). In these cased and cemented completions, the

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[1] 27,700 jobs (95% confidence interval: 24,800 – 30,600 jobs).

[2] The Well File Review considered any non-horizontal well in which the well bottom was located more than 500 ft (152 m) laterally from the wellhead as being deviated.

cement provides the primary containment of fluids to the production zone. Before hydraulic fracturing begins, perforations are made through the casing and cement into the production zone. It is through the perforated casing and cement that hydraulic fracturing is conducted. In some cases, a smaller temporary casing, known as a temporary frac string, is inserted inside the production casing to protect the casing from the high pressures imposed during hydraulic fracturing operations.

A different type of a cased completion uses production casing set on formation packers, where the production casing extends through the production zone and the length of the casing extending through the drilled horizontal wellbore is left uncemented, but has a series of formation packers that swell to seal the annulus between the casing and the formation.[1] With these completions, the production zone is fractured in separate stages through ports that open between the formation packers. When formation packers are used, they provide the primary isolation of hydraulic fracturing fluids during hydraulic fracturing.

Another type of completion is an open hole completion. When open hole completions are used, the entire production zone is fractured all at once in a single stage or may be fractured in separate stages using a temporary frac string set on one or more temporary formation packers that are positioned to a different interval for each stage. If a temporary frac string is used in an open hole completion, its packer(s) provide the primary isolation of hydraulic fracturing fluids during hydraulic fracturing and if no temporary frac string is used, then the next higher casing in the well provides the primary isolation of hydraulic fracturing fluids during the treatment.

Among wells represented in the Well File Review, an estimated 6% of wells (1,500 wells) had open hole completions, 6% of wells (1,500 wells) used formation packers, and the rest were cased and cemented (U.S. EPA, 2015n).[2,3]

In some cases, wells may be re-completed after the initial construction, with re-fracturing if production has decreased (Vincent, 2011). Re-completion also may include additional perforations in the well at a different interval to produce from a new formation, lengthening the wellbore, or drilling new laterals from an existing wellbore. In 95% of the re-completions represented in the Well File Review, hydraulic fracturing occurred at shallower depths than the previous job (U.S. EPA, 2016c).[4]

6.2.2 Factors that can Affect Fluid Movement to Drinking Water Resources

The following sections describe the pathways for fluid movement that can develop within the production well and wellbore. We also describe the conditions leading to the development of fluid movement pathways and, where available, evidence that a pathway has allowed fluid movement to

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[1] A formation packer is a specialized casing part that has the same inner diameter as the casing but whose outer diameter expands to make contact with the formation and seal the annulus between the uncemented casing and formation, preventing migration of fluids.

[2] 1,500 wells with open hole completions (95% confidence interval: 10 – 4,800 wells).

[3] 1,500 wells using formation packers (95% confidence interval: 1,400 – 1,600 wells).

[4] 95% of jobs (95% confidence interval: 75 – 99% of jobs).

occur within the casing or cement, and—in the case of sustained casing pressure (Section 6.2.2.4)—a combination of factors within the casing and cement. (See Figure 6-4 for an illustration of potential fluid movement pathways related to casing and cement.)

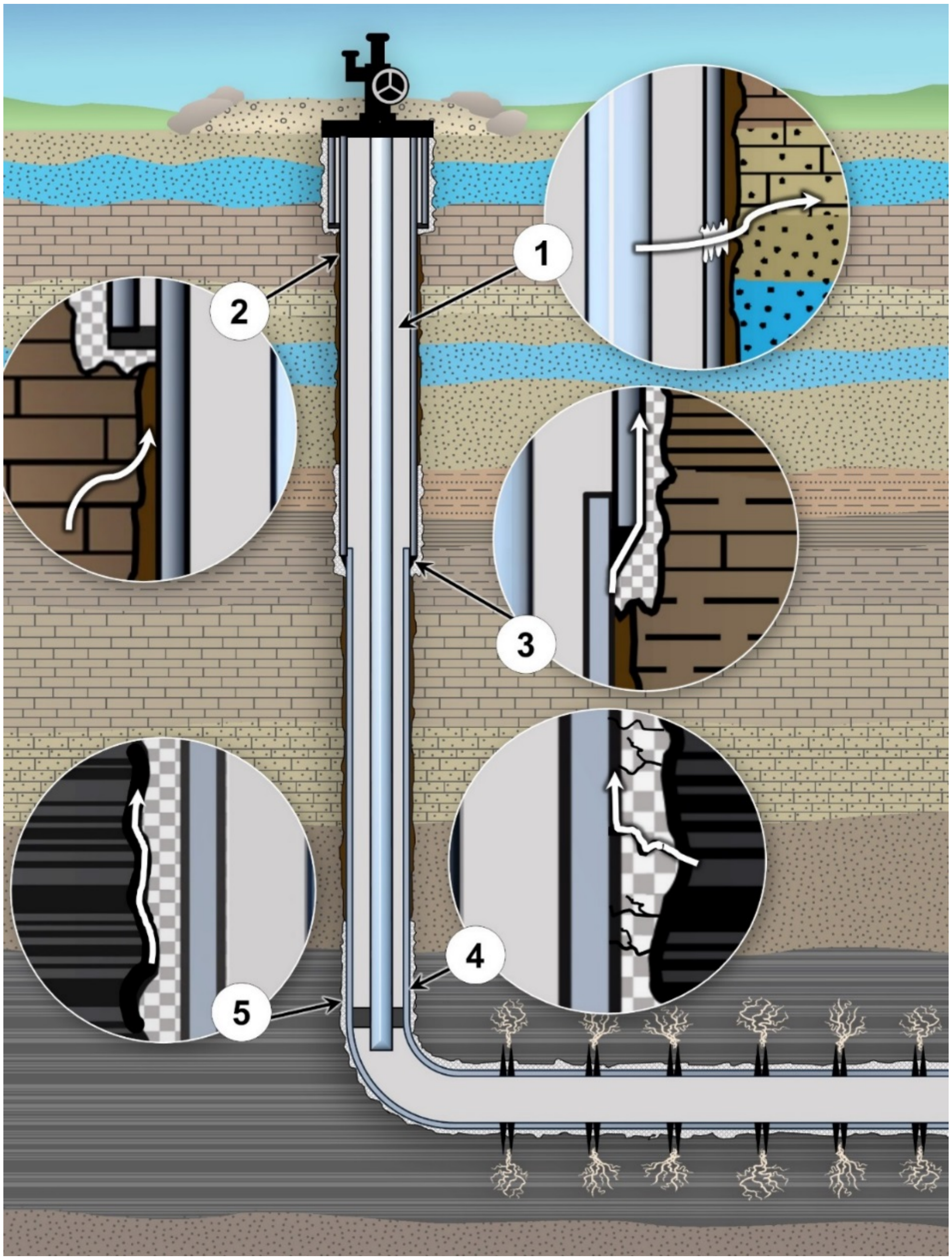

Figure 6-4. Potential pathways for fluid movement in a cemented wellbore.

These pathways (represented by the white arrows) include: (1) casing and tubing leak into a permeable formation, (2) migration along an uncemented annulus, (3) migration along microannuli between the casing and cement, (4) migration through poor cement, and (5) migration along microannuli between the cement and formation. Note: the figure is not to scale and is intended to provide a conceptual illustration of pathways that may develop within the well.

We describe information regarding the rate at which these pathways have been identified in hydraulic fracturing wells when it is available. Where such information does not exist, we present the results of research on oil and gas production wells in general or on injection wells, including those used for the geologic sequestration of carbon dioxide.[1] Publicly accessible information is insufficient to determine whether wells intended for hydraulic fracturing are constructed differently from production wells where no fracturing is conducted. See Chapter 10 for additional discussion of data gaps. It is not generally possible, based on the literature reviewed for this assessment, to determine the precise degree to which hydraulic fracturing created, or moved fluids along, the pathways described or whether all of the wells studied were hydraulically fractured. Nor is it generally possible to estimate the degree to which wells that were hydraulically fractured have a significantly different number of redundant barriers to protect drinking water resources than other production wells. However, given the applicability of well construction technology to address the subsurface conditions encountered in hydraulic fracturing operations and production or injection operations in general, the information presented here is considered relevant to the assessment.

6.2.2.1 Pathways Related to Well Casing

High pressures associated with hydraulic fracturing operations can damage casing and lead to fluid movement that can impact drinking water quality. As noted above, the casing string through which hydraulic fracturing fluids are injected is subject to higher internal pressures during hydraulic fracturing operations than during other phases in the life of a production well. To withstand the stresses created by the high pressure of hydraulic fracturing, the well and its components must have adequate strength and elasticity. If the casing is compromised or is otherwise not strong enough to withstand these stresses (Figure 6-3), a casing failure can result. If undetected or not repaired, casing failures can serve as pathways for hydraulic fracturing fluids to leak out of the casing. Below we present data or information suggesting that pathways along the casing are present or allowing fluid movement. See Chapter 10 for more information on factors that can increase or decrease the frequency or severity of impacts to drinking water quality associated with well construction.

Hydraulic fracturing fluids or fluids present within the well casing could flow into other zones in the subsurface if there is a leak in the casing, and cement is inadequate or not present. As described below, pathways for fluid movement associated with well casing can be related to the original design or construction of the well, degradation of the casing over time, or problems that can arise through extended use as the casing succumbs to stresses.

Casing failure can also occur if the wellbore passes through a structurally weak geologic zone that shears and deforms the well casing. Such shearing is common when drilling through zones containing salt (Renpu, 2011). The changes in the pressure field in the portions of the formation near the wellbore during hydraulic fracturing can also cause mechanically weak formations to shear, potentially damaging the well's casing or cement. Palmer et al. (2005) demonstrated through modeling that hydraulic fracturing within coal that had a low unconfined compressive strength

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[1] An injection well is a well into which fluids are being injected (40 Code of Federal Regulations (CFR) 144.3).

could cause shear failure of the coalbeds surrounding the wellbore. Shearing of the coalbed layers can cause the casing to deform and potentially fail.

Corrosion in uncemented zones is the most common cause of casing failure. This can occur if uncemented sections of the casing are exposed to corrosive substances such as brine or hydrogen sulfide (Renpu, 2011). Corrosion commonly occurs at the collars that connect sections of casing or where equipment is attached to the casing. Corrosion at collars can exacerbate problems with loose or poorly designed connections, which are another common cause of casing leaks (Agbalagba et al., 2013; Brufatto et al., 2003). Watson and Bachu (2009) found that 66% of all casing corrosion occurred in uncemented well sections, as shown in Pathway 1 of Figure 6-4.

As noted above, the casing and cement work together to strengthen the well and provide zonal isolation. Uncemented casing does not necessarily lead to fluid migration. However, migration can occur if the casing in an uncemented zone fails during hydraulic fracturing operations.

Other mechanical integrity problems have been found to vary with the well environment, particularly environments with high pressures and temperatures. Wells in high pressure/high temperature environments, wells with thermal cycling, and wells in corrosive environments can have life expectancies of less than 10 years (Agbalagba et al., 2013).

The depth of the surface casing relative to the base of the drinking water resource to be protected is an important factor in protecting the drinking water resource. In a limited risk modeling study of selected injection wells in the Williston Basin, Michie and Koch (1991) found the risk of aquifer contamination from leaks from the inside of the well to the drinking water resource was seven in 1,000,000 injection wells if the surface casing was set deep enough to cover the drinking water resource, and that the risk increased to six in 1,000 wells if the surface casing was not set deeper than the bottom of the drinking water resource. An example where surface casing did not extend below drinking water resources comes from an investigation of 14 selected drinking water wells with alleged water quality problems in the Wind River and Fort Union formations near Pavillion, Wyoming (WYOGCC, 2014b). The state found that the surface casing of oil and gas wells was shallower than the depth of three of the 14 drinking water wells. Some of the oil and gas wells with shallow surface casing had elevated gas pressures in their annuli (WYOGCC, 2014b). The presence of gas in the annuli, combined with surface casing that is set above the lowest drinking water resource, could allow migration of gas into drinking water resources.

Fleckenstein et al. (2015) found that the depth of surface casing and the presence of uncemented gas zones are major factors in determining the likelihood of well failures and contamination. Their study in the Wattenberg field in Colorado classified the wells in the field into seven categories based on the depth of surface casing, the presence of cement, and the presence of intermediate gas zones above the production zone (Table 6-1). The categories were arranged in order of risk, with category 1 wells being at the highest risk of allowing fluid migration and category 7 wells being the least likely to allow migration. The overall barrier failure rate was 2.4% of all wells, and the overall catastrophic failure rate was 0.06% of all wells. A remediation effort was made in order to decrease the likelihood of fluid migration, which included the plugging of 1,103 of the 17,948 wells studied. All the wells shown in the table are vertical wells that were drilled between 1970 and 2013. Similar categories were created for the 973 horizontal wells in the field. No failures were recorded for any of the horizontal wells.

Table 6-1. Failure rates of vertical wells in the Wattenberg field, Colorado.
From Fleckenstein et al. (2015).

Category and description[a, b]	Total wells	Wells with barrier failures[c]	Wells with catastrophic failures[d]
1--Shallow surface casing and exposed (uncemented) over-pressured intermediate gas zones	399	92 (23.06%)	3 (0.75%)
2 – Shallow surface casing and exposed under-pressured intermediate gas zones	7,811	276 (3.53%)	6 (0.08%)
3 – Shallow surface casing but no exposed gas zones	3,407	20 (0.59%)	1 (0.03%)
4 – Shallow surface casing with production casing cemented to bottom of surface casing	1,063	0 (0%)	0 (0%)
5 – Deep surface casing with production casing cement below top of gas	1,374	13 (0.95%)	0 (0%)
6 – Deep surface casing with production casing cement above top of gas	2,069	0 (0%)	0 (0%)
7 – Deep surface casing with production casing cement to bottom of surface casing	705	0 (0%)	0 (0%)
Total	16,828	401 (2.4%)	10 (0.06%)

[a] The study defined shallow surface casing as casing that did not extend below the Fox Hills Aquifer, a deep aquifer that had not been identified and protected by the state prior to 1994.

[b] Uncemented zones could be located along the intermediate or production casings.

[c] Barrier failures were considered to have occurred when there were signs of a failure, but no contamination.

[d] A catastrophic failure was considered to have occurred where there was contamination of drinking water aquifers (i.e., the presence of thermogenic gas in a drinking water well) and evidence of a well defect such as exposed intermediate gas zone or casing leaks.

Sherwood et al. (2016) examined complaint records in the same field. They reviewed 29 Colorado Oil and Gas Commission complaint records associated with 32 incidents at 42 drinking water wells in which thermogenic methane was detected. (See Text Box 6-3 for more information on thermogenic and biogenic methane.) Of the 29 complaints, 10 were determined to be caused by oil and gas wellbore failures, one was suspected of being a wellbore failure but not confirmed, three were settled in court with documents being sealed, and the remaining 15 were unresolved.[1] If all 32 cases are assumed to be associated with an individual oil and gas well, that would result in a failure rate of 0.06% of all oil and gas wells in the basin, the same failure rate as found in the Fleckenstein et al. (2015) study. As in the Fleckenstein study, surface casing that was set too shallow and

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[1] This paper defined a wellbore failure as the failure of one or more barriers to fluid movement in the wellbore (e.g., cement, casing, etc.).

uncemented intermediate zones were the main contributing factors to wellbore failure. All 11 of the confirmed or suspected wellbore failures involved vertical wells that were drilled before 1933 and had surface casing shallower than nearby aquifers. Of these wells, seven had been hydraulically fractured. The study noted that the failure rate was fairly constant over time with about two new cases per year since 2000 and that the rate had not changed since high rates of hydraulic fracturing of horizontal wells became prevalent around 2010. This is consistent with the study's finding of no failures in horizontal wells.

During hydraulic fracturing operations in September of 2010 near Killdeer, in Dunn County, North Dakota, the production, surface, and conductor casing of the Franchuk 44-20 SWH well ruptured, causing fluids to spill to the surface (Jacob, 2011). The rupture occurred during the 5th of 23 planned stages of hydraulic fracturing when the pressure spiked to over 8,390 psi (58 MPa). Ruptures were found in two locations along the production casing—one just below the surface and one at about 55 ft (17 m) below ground surface. The surface casing ruptured in three places down to a depth of 188 ft (57 m), and the conductor casing ruptured in one place. Despite a shutdown of the pumps, the pressure was still sufficient to cause fluid to travel through the ruptured casings and to flow to the surface. Ultimately, over 166,000 gal (628,000 L) of fluids and approximately 2,860 tons (2,595 metric tons) of contaminated soil were removed from the site (Jacob, 2011).

The EPA investigated the Killdeer site as part of its Retrospective Case Study in Killdeer, North Dakota: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources (U.S. EPA, 2015i). As part of the study, water quality samples were collected from three domestic wells, nine monitoring wells, two supply wells, one municipal well, and one state well in July 2011, October 2011, and October 2012. Two study wells installed less than 60 ft (20 m) from the production well (NDGW08 and NDGW07) had significant differences in water quality compared to the remaining study wells.[1] These two wells showed differences in ion concentrations (e.g., chloride, calcium, magnesium, sodium, strontium) and tert-butyl alcohol (TBA). The sampling identified brine contamination that was consistent with mixing of local groundwater with brine from Madison Group formations, which the well had penetrated. The TBA was consistent with degradation of tert-butyl hydroperoxide, a component of the hydraulic fracturing fluid used in the Franchuk well. Based on the analysis of potential sources of contamination, the EPA determined that the only potential sources of TBA were gasoline spills, leaky underground storage tanks, and hydraulic fracturing fluids. However, the lack of MTBE and other signature compounds associated with gasoline or fuels strongly suggests that the rupture (blowout) was the only source consistent with findings of high brine and TBA concentrations in the two wells.[2] For additional information about impacts at the Killdeer site, see Section 6.3.2.2.

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[1] Based on comparison with historical Killdeer aquifer water quality data, the remaining study wells were in general consistent with historical background data; these wells were then used for the data analysis as background wells. Comparisons of TBA between the study data and historical data could not be made since no historical data for TBA were found for the Killdeer aquifer.

[2] A well blowout is the uncontrolled flow of fluids out of a well.

Inadequate casing or cement can respond poorly when blowout preventers activate.[1] When blowout preventers are activated, they immediately stop the flow in the well, which can create a sudden pressure increase in the well. If the casing or cement are not strong enough to withstand the increased pressure when this occurs, well components can be damaged (The Royal Society and the Royal Academy of Engineering, 2012) and the potential for fluid release and migration in the subsurface increases. Blowouts can also occur during the production phase, and cause spills on the surface that can affect drinking water resources; see Section 7.4.2.2.

While well construction and hydraulic fracturing techniques continue to change, the pressure- and temperature-related stresses associated with hydraulic fracturing remain as factors that can affect the integrity of the well casing. Tian et al. (2015) investigated one such case where temperature effects led to casing damage in China. In the Changning-Weiyuan basin in China, 13 of 33 wells (39.4%) suffered casing damage, with most of the wells experiencing the damage after fracturing. The authors found that injection of the cooler hydraulic fracturing fluid led the casing temperature to drop from the formation temperature of 212°F to 64°F (100°C to 18°C) in some cases. This drop in temperature, in turn, caused pockets of high pressure fluid outside the casing to contract. If the temperature dropped below 136°F (58°C), the effect was sufficient to form a vacuum outside the casing, potentially leading to casing deformation. Areas of the casing with severe doglegs (i.e., bends in the well) and where there was a smaller space between the casing and formation were more prone to this type of damage. While the conditions in this Chinese basin may or may not represent conditions in U.S. basins, they do demonstrate that temperature changes during hydraulic fracturing can place additional stress on the well and highlight their importance as a consideration in casing design. In the case mentioned, increasing the space around the casing, decreasing dogleg angles, properly removing drilling mud, and using high strength, low elasticity cement were found to improve performance.

Sugden et al. (2013) used numerical simulation to examine a similar problem using parameters chosen to represent the Haynesville Shale. They found that injecting a fluid at 70°F (21°C) could cool the wellbore temperature from 320°F to 96°F (160°C to 36°C). The temperature change was 90% complete within the first half hour of hydraulic fracturing operations. They also found that a well with a 20 degree per 100 ft (31 m) dogleg decreased the pressure required to damage the well casing by 850 psi (5.9 MPa). The study also reported that cooling of fluids in voids in the cement can lead to contraction of the fluids. In low permeability shales, fluid cannot flow in fast enough to compensate, and the pressure in the void can drop significantly. Sugden et al. (2013) report that such cement voids can reduce the pressure needed to rupture the casing by 40%.

Emerging isotopic techniques can be used to identify the extent to which stray gas occurring in drinking water resources is linked to casing failure. (See Text Box 6-3 for more information on stray gas.) Darrah et al. (2014) used hydrocarbon and noble gas isotope data to investigate the source of gas in eight identified “contamination clusters” that occurred in the Marcellus and Barnett shales. Seven of these clusters were stripped of atmospheric gases (Argon-36 and Neon-20) and were

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[1] A blowout preventer (BOP) is casinghead equipment that prevents the uncontrolled flow of oil, gas, and mud from the well by closing around the drill pipe or sealing the hole (Oil and Gas Mineral Services, 2010). BOPs are typically a temporary component of the well, in place only during drilling and perhaps through hydraulic fracturing operations.

enriched in crustal gases, indicating the gas migrated quickly from depth without equilibrating with intervening formations. The rapid transport was interpreted to mean that the migration did not occur along natural fractures or pathways, which would have allowed equilibration to take place. Based on the isotopic results, the authors also ruled out the possibility that the gas was carried upward (relative to the surface) as the geologic formation in which it formed was uplifted over geologic time. Possible explanations for the rapid migration include transport up the well and through a leaky casing (Pathway 1 in Figure 6-4) or along uncemented or poorly cemented intervals from shallower depths (Pathways 2 through 5 in Figure 6-4). In four Marcellus Shale clusters, gas found in drinking water wells had isotopic signatures and ratios of ethane to methane that were consistent with those in the producing formation. The authors conclude that this suggests that gas migrated along poorly constructed wells from the producing formation, likely with improper, faulty, or failing production casings. In three clusters, the isotopic signatures and ethane to methane ratios were consistent with formations overlying the Marcellus. The authors suggest that this migration occurred from the shallower gas formations along uncemented or improperly cemented wellbores. In another Marcellus cluster in the study, deep gas migration was linked to a subsurface well, likely from a failed well packer.

Text Box 6-3. Stray Gas Migration.

Stray gas refers to the phenomenon of natural gas (primarily methane) migrating into shallow drinking water resources, into water wells or other types of wells, to the surface, or to near-surface features (e.g., basements, streams, or springs). The source of the migrating gas can be natural gas reservoirs (either conventional or unconventional), or from coal mines, landfills, leaking gas wells, leaking gas pipelines, buried organic matter, or natural microbial processes (Li and Carlson, 2014; Baldassare, 2011). Although methane is not a regulated drinking water contaminant, its presence in drinking water resources can initiate chemical and biological reactions that release or mobilize other contaminants. Over time, it can promote more reducing conditions in groundwater, potentially leading to reductive dissolution of iron and manganese and the possible liberation of naturally occurring contaminants, such as arsenic, that are potentially associated with iron and manganese (U.S. EPA, 2014f). In addition, methane can accumulate to explosive levels in confined spaces (like basements or cellars) if it exsolves (degases) from groundwater into those spaces. (See Section 9.5.5 for information about the hazards associated with methane exposure.)

Detectable levels of dissolved natural gas exist in some aquifers, even in the absence of human activity (Gorody, 2012). In northern Pennsylvania and New York, low levels of methane are frequently found in water wells in baseline studies, prior to commercial oil or gas development (Christian et al., 2016; Kappel, 2013; Kappel and Nystrom, 2012); for example, one USGS study detected methane in 80% of sampled wells in Pike County, Pennsylvania (Senior, 2014). The origin of methane in groundwater can be either thermogenic (produced by high temperatures and pressures in deeper formations, such as the gas found in the Marcellus Shale) or biogenic (produced in shallower formations by bacterial activity in anaerobic conditions).

Gas occurrence is linked to local and regional geologic characteristics. In some cases, thermogenic methane occurs naturally in shallow formations because the formation itself was uplifted (relative to the surface) over geologic time. In other cases, it has migrated there via one or more pathways. For example, Brantley et al. (2014) suggest that northern Pennsylvania's glacial history can help explain why stray gas is more common

(Text Box 6-3 is continued on the following page.)

Text Box 6-3 (continued). Stray Gas Migration.

there than in the southern part of the state. Christian et al. (2016), Mcphillips et al. (2014), Molofsky et al. (In Press), and Wilson (2014) all identified correlations between the presence of methane in water wells and certain geologic, hydrographic, and geochemical parameters, such as valley locations and the presence of coal beds.

Stray gas migration can be a technically complex phenomenon to study, in part because there are many potential sources and routes for migration. When a particular site lacks detailed monitoring data, especially baseline measurements, determination of sources and migration routes is complicated and challenging. Examining the concentrations and isotopic compositions of methane and higher molecular weight hydrocarbons such as ethane and propane can aid in determining the source of stray gas (Tilley and Muehlenbachs, 2012; Baldassare, 2011; Rowe and Muehlenbachs, 1999). Isotopic composition and methane-to-ethane ratios can help determine whether the gas is thermogenic or biogenic in origin and whether it is derived from shale or other formations (Gorody, 2012; Muehlenbachs et al., 2012; Barker and Fritz, 1981). Isotopic analysis can also be used to identify the strata where the gas originated and provide evidence for migration mechanisms (Darrah et al., 2014). For example, isotope-based techniques have been used to investigate the potential sources of methane in drinking water wells in Dimock, Pennsylvania (Hammond, 2016), and Jackson et al. (2013c) found evidence of potential Marcellus gas contamination in some Pennsylvania drinking water wells using stable-isotopic ratios, while other wells in the area appeared to be contaminated by shallower sources (not associated with gas production).

However, determining the source of methane does not necessarily establish the migration pathway. Multiple researchers (e.g., Siegel et al., 2015; Jackson et al., 2013c; Molofsky et al., 2013; Révész et al., 2012; Osborn et al., 2011) have described biogenic and/or thermogenic methane in groundwater supplies in Marcellus gas production areas, although the sources and pathways of migration are generally unknown. Well casing and cementing issues may be an important source of stray gas problems (Jackson et al., 2013c); however, other potential subsurface pathways are also discussed in the literature. Zhang and Soeder (2016) suggested that air-drilling practices used to construct the vertical component of gas wells can affect methane migration by creating groundwater surges in the shallow subsurface. The type of well may also play a role; in one study, deviated gas wells in Canada were three to four times more likely than vertical wells to have evidence of gas migration to the surface (Jackson et al., 2013b).

In the absence of data on specific pathways, some researchers have investigated geographic correlations. Jackson et al. (2013c) and Osborn et al. (2011) found that thermogenic methane concentrations in well water increased with proximity to Marcellus Shale production sites. In contrast, Molofsky et al. (2013) found the presence of gas to be more closely correlated with topography and elevation, and (Siegel et al., 2015)found no correlation between methane in groundwater and proximity to production wells. Kresse et al. (2012) investigated methane concentration and isotopic geochemistry in shallow groundwater in the Fayetteville Shale area, and found no evidence that the water had been influenced by shale gas activities. Similarly, Li and Carlson (2014), while not ruling out potential leakage pathways from deeper reservoirs, found no systematic correlation between increasing well drilling density in the Wattenberg Field in Colorado and near-surface stray gas concentrations.

EPA conducted retrospective case studies to investigate stray gas in northeastern Pennsylvania and the Raton Basin of Colorado. As described in the northeastern Pennsylvania case study report, *Retrospective Case Study in Northeastern Pennsylvania: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (U.S. EPA, 2014f), 27 of 36 drinking water wells within the study area (75%) contained elevated methane concentrations. For some of the wells, the EPA concluded that the methane (of both thermogenic and biogenic origin) was naturally occurring gas, not attributable to gas exploration activities. In others, it

(Text Box 6-3 is continued on the following page.)

Text Box 6-3 (continued). Stray Gas Migration.

appeared that methane had entered the water wells following well drilling and hydraulic fracturing. In most cases, the methane in the wells likely originated from intermediate formations between the production zone and the surface; however, in some cases, the methane appears to have originated from deeper layers such as those where the Marcellus Shale is found (U.S. EPA, 2014f). The Raton Basin case study examined the Little Creek Field, where potentially explosive quantities of methane entered drinking water wells in 2007. As described in the EPA's *Retrospective Case Study in the Raton Basin, Colorado: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (U.S. EPA, 2015k), the methane was found to be primarily thermogenic in origin, modified by biologic oxidation (U.S. EPA, 2015k). Secondary biogeochemical changes related to the migration and reaction of methane within the shallow drinking water aquifer were reflected in the characteristics of the Little Creek Field groundwater (U.S. EPA, 2015k).

The sources of methane in the two studies could be determined with varying degrees of certainty. Narrowly identifying the most likely pathway(s) of migration has been more difficult. In northeastern Pennsylvania, while the sources could not be definitively determined, the Marcellus Shale could not be excluded as a potential source in some wells based on isotopic signatures, methane-to-ethane ratios, and isotope reversal properties (U.S. EPA, 2014f). The Pennsylvania Department of Environmental Protection (PA DEP) cited at least two operators for failure to prevent gas migration at wells within the study area. Evidence cited by the state included isotopic comparison of gas samples from drinking water wells, water bodies, and gas wells; inadequate cement jobs; and sustained casing pressure (although, under Pennsylvania law, oil or gas operators can be cited if they cannot disprove the contamination was caused by their well using pre-drilling samples) (Llewellyn et al., 2015). A separate study (Ingraffea et al., 2014) showed that wells in this area had higher incidences of mechanical integrity problems relative to wells in other parts of Pennsylvania. While the study did not definitively show that stray gas was linked to construction problems, it does imply that there may be more difficulties in constructing wells in this area. In the Little Creek Field in the Raton Basin, the source of methane was identified as the Vermejo coalbeds. While the nature of the migration pathway is unknown, modeling suggests that it could have occurred along natural rock features in the area and/or along a gas production well (U.S. EPA, 2015k). Because the production wells were shut in shortly after the incident began, the wells could not be inspected to determine whether a mechanical integrity failure in the wellbore was a likely cause of the migration.[1]

These two case studies illustrate the considerations involved with understanding stray gas migration and the difficulty in determining sources and migration pathways. To more conclusively determine sources and migration pathways, studies in which data are collected on mechanical integrity and hydrocarbon gas (e.g., methane, ethane) concentrations both before and after hydraulic fracturing operations, in addition to the types of data summarized above, would be needed.

In the Wattenberg Field in Colorado, Li et al. (2016a) investigated the concentration of various ions in water from an uncontaminated aquifer, an aquifer containing thermogenic methane, and produced water from oil and gas wells to understand the transport of aqueous- and gas-phase fluids at the site. The results indicated that the methane that was contaminating water wells was not transported with aqueous phase fluids; the authors suggested that this can provide evidence for migration mechanisms, because certain pathways (e.g., migration from improperly sealed well

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[1] Shutting in a well refers to sealing off a well by either closing the valves at the wellhead, a downhole safety valve, or a blowout preventer.

casings) could potentially result in gas-phase but not aqueous-phase migration. See Text Box 6-4 for another example of an investigation into the occurrence of stray gas in drinking water wells.

Text Box 6-4. Parker County, Texas.

Peer-reviewed studies have been conducted within the Barnett Shale area, which includes Parker County, Texas. These include sampling studies of private water well composition, noble gas content, and isotopic signatures of natural gases, as well as analysis of existing water sample data. Disagreement exists about the origin of the increased natural gas in private well water.

One suggested possibility is that production casing annuli could serve as a migration pathway for natural gas from formations located between the Barnett and the Trinity to reach overlying intervals (including the Trinity aquifer) (Darrah et al., 2014). However, using measurements of hydrocarbon and noble gas isotopes, Wen et al. (2016) suggests the source of methane in the Trinity aquifer water wells is directly from the underlying Strawn Formation and not from pathways associated with the gas production wells although the timing of methane entry into the Strawn is not known.

6.2.2.2 Pathways Related to Cement

Fluid movement can result from inadequate well design or construction (e.g., cement loss or other problems that arise in cementing of wells) or degradation of the cement over time (e.g., corrosion or the formation of microannuli), which may, if undetected and not repaired, cause the cement to succumb to the stresses exerted during hydraulic fracturing.[1] The well cement must be able to withstand the subsurface conditions and the stresses encountered during hydraulic fracturing operations. This section presents data and information that can help indicate that pathways within the cement are present or allowing fluid movement.

Uncemented zones can allow fluids or brines to move into drinking water resources. If a fluid-containing zone is left uncemented, the open annulus between the formation and casing can act as a pathway for migration of that fluid. Fluids can enter the wellbore along any uncemented section of the wellbore if a sufficient pressure gradient is present. Once the fluids have entered the wellbore, they can travel up along the entire uncemented length of the wellbore as shown in Pathway 2 of Figure 6-4.

As mentioned in Section 6.2.2.1, Fleckenstein et al. (2015) found uncemented gas zones to be a significant factor in barrier failures in wells in the Wattenberg basin in Colorado. A report on the Pavillion field by AME (2016) identified a similar set of risk factors for fluid migration including: uncemented production casing, shallow surface casing, and the presence of both an intermediate pressurized gas zone and a permeable groundwater zone encountered in the same production wellbore.

Because of their low density and buoyancy, gaseous fluids such as methane will migrate up the wellbore if an uncemented wellbore is exposed to a gas-containing formation. Gas may then be able

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[1] Microannuli are very small openings that form between the cement and its surroundings and that may serve as pathways for fluid migration to drinking water resources.

to enter other formations (including drinking water resources) if the wellbore is uncemented and the pressure in the annulus is sufficient to force fluid into the surrounding formation (Watson and Bachu, 2009; Harrison, 1985). The rate at which the gas can move will depend on the difference in pressure between the annulus and the formation (Wojtanowicz, 2008). See Chapter 10 for a discussion of practices, such as well testing, that can decrease the frequency of such gas migration that could impact drinking water quality.

In several cases, poor or failed cement has been linked to stray gas migration (Text Box 6-3). A Canadian study found that uncemented portions of casing were the most significant contributors to gas migration (Watson and Bachu, 2009). The same study also found that 57% of all casing leaks occurred in uncemented segments. In the study by Darrah et al. (2014) (Section 6.2.2.1), using isotopic data, four clusters of gas contamination were linked to poor cementing. In three clusters in the Marcellus and one in the Barnett, gas found in drinking water wells had isotopic signatures consistent with intermediate formations overlying the producing zone. This suggests that gas migrated from the intermediate units along the well annulus, along uncemented portions of the wellbore, or through channels or microannuli.

Cementing of the surface casing is the primary aspect of well construction intended to protect drinking water resources. Most states require the surface casing to be set and cemented from the level of the lowermost drinking water resource to the surface (GWPC, 2014). Most wells—including those used in hydraulic fracturing operations—have such cementing in place. Among the wells represented in the Well File Review, surface casing was found to be fully cemented in 93% of wells. Of these, an estimated 55% of wells (12,600 wells) were cemented to below the operator-reported protected groundwater resource; in an additional 28% of wells (6,400 wells), the operator-reported protected groundwater resources were fully covered by the next cemented casing string.[1,2,3] A portion of the annular space between the casing and the operator-reported protected groundwater resources was uncemented in at least 3% of wells (600 wells) (U.S. EPA, 2015n).[4]

Improper placement of cement can lead to defects in external mechanical integrity. For example, an improper cement job can be the result of loss of cement during placement into a formation with

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[1] In the Well File Review, protected groundwater resources were as reported by well operators. For most wells represented in the Well File Review, protected groundwater resources were identified based on state or federal authorization documents. Other data sources used by well operators included aquifer maps, data from offset production wells, open hole log interpretations by operators, operator experience, online databases, and references to a general requirement by the oil and gas agency.

[2] The research that the EPA reviewed used various terms to describe subsurface water resources that are used/potentially used for drinking water. Where another term is relevant to describing the author's research, we use that term; for the purpose of this assessment, all of these terms are considered to fall within the assessment's definition of "drinking water resources." See Chapter 2 for additional information on the definition of a drinking water resource.

[3] 6,400 wells (95% confidence interval: 500 – 12,300 wells).

[4] 600 wells (95% confidence interval: 10 – 1,800 wells). The well files representing an estimated 8% of wells in the Well File Review did not have sufficient data to determine whether the operator-reported protected groundwater resource was uncemented or cemented. In these cases, there was ambiguity either in the depth of the base or the top of the operator-reported protected groundwater resource. An additional 6% of wells represented had surface casing set below the reported protected groundwater resource depth, but because the protected groundwater depth was based on a nearby water well depth, the true base of the protected groundwater resource may be deeper, leaving uncertainty as to whether the surface casing in these wells is set deeper than the base of the protected groundwater resource.

high porosity or fractures, causing a lack of adequate cement across a water- or brine-bearing zone. Additionally, failure to use cement that is compatible with the anticipated subsurface conditions, failure to remove drilling fluids from the wellbore, and improper centralization of the casing in the wellbore can all lead to the formation of channels (i.e., small connected voids) in the cement during the cementing process (McDaniel et al., 2014; Sabins, 1990). If the channels are small and isolated, they may not lead to fluid migration. However, if they are long and connected, extending across multiple formations, or connecting to other existing channels or fractures, they can present a pathway for fluid migration. Figure 6-4 shows a variety of pathways for fluid migration that are possible from failed cement jobs.

One example of how hydraulic fracturing of a well with insufficient and improperly placed cement led to contamination occurred in Bainbridge Township, Ohio. This incident was well studied by the Ohio Department of Natural Resources (ODNR, 2008) and by an expert panel (Bair et al., 2010). The level of detail available for this case is not typically found in studies of such events but was collected because of the severity of the impacts and the resulting legal action. The English #1 well was drilled to a depth of 3,900 ft (1,200 m) below ground surface (bgs) in October 2007 with the producing formation located between 3,600 and 3,900 ft (1,100 and 1,200 m) bgs. Overlying the producing formation were several uneconomic formations containing over-pressured gas (i.e., gas at pressures higher than the hydrostatic pressure exerted by the fluids within the well).[1] The original cement design required the cement to be placed 700 – 800 ft (210 – 240 m) above the producing formation to seal off these areas. During cementing, however, both the spacer fluid and cement were lost in the subsurface, and the cement did not reach the intended height.[2] Despite the lack of sufficient cement, the operator proceeded with hydraulic fracturing.

During the hydraulic fracturing operation in November 2007, about 840 gal (3,200 L) of fluid flowed up the annulus and out of the well. When the fluid began flowing out of the annulus, the operator immediately ceased operations and shut in the well; this caused the pressure in the wellbore to increase. About a month later, there was an explosion in a nearby house where methane had entered from an abandoned and unplugged drinking water well connected to the cellar (Bair et al., 2010). In addition to the explosion, the over-pressured gas entering the aquifer resulted in the contamination of 26 private drinking water wells with methane. The wells, some of which had histories of elevated methane prior to the incident, were taken off-line. By 2010, all of the well owners had been connected to a public water supply (Tomastik and Bair, 2010).

Contamination at the Bainbridge Township site was the result of inadequate cement. The ODNR determined that failure to cement the over-pressured gas formations, proceeding with the hydraulic fracturing operation without adequate cement, and the extended period during which the well was shut in all contributed to the contamination of the aquifer with stray gas (ODNR, 2008). Cement logs found the cement top was at 3,640 ft (1,110 m) bgs, leaving the uneconomic gas-producing formations and a portion of the production zone uncemented. The surface casing was 253 ft (77 m) deep and cemented to the surface. Hydraulic fracturing fluids flowing out of the

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[1] Hydrostatic pressure is the pressure exerted by a column of fluid at a given depth. Here, it refers to the pressure exerted by a column of drilling mud or cement on the formation at a particular depth.

[2] Spacer fluid is a fluid pumped before the cement to clean drilling mud out of the wellbore.

annulus provided an indication that hydraulic fracturing had created a path from the producing formation to the well annulus in addition to the uncemented gas zones. Because the well was shut in, the pressure in the annulus could not be relieved, and the gas eventually traveled through natural fractures surrounding the wellbore into local drinking water aquifers (during the time the well was shut in, natural gas seeped into the well annulus and pressure built up from an initial pressure of 90 psi (0.6 MPa) to 360 psi (2.5 MPa)). From the aquifer, the gas moved into drinking water wells and from one of those wells into a cellar, resulting in the explosive accumulation of gas.

The Well File Review found that 3% of all hydraulic fracturing jobs (800 jobs) reported a mechanical integrity failure that allowed fluid to enter an annular space (U.S. EPA, 2016c).[1] The mechanical integrity failures generally resulted in hydraulic fracturing fluid entering the annular space between the casing and formation or between two casings, and were generally noted by increases in annular pressure or fluid bubbling to the surface. Other possible mechanisms for the failures include casing leaks, cement failure, and fractures extending above the height of the cement. (See Section 6.3.2.2 for additional information on fracture overgrowth.) While failures were noted, these do not necessarily indicate there was movement of fluid into a drinking water resource. In most cases, when problems occurred, the hydraulic fracturing operation was stopped and operators addressed the cause of the failure before hydraulic fracturing operations resumed; however, in 0.5% of the hydraulic fracturing jobs (100 jobs) with identified failures, there was no additional barrier between the annular space with fluid and protected drinking water resources.[2] While it could not definitively be determined whether fluid movement into the protected drinking water resource occurred, in these cases, all of the protective barriers intended to prevent such fluid migration failed, leaving the groundwater resource vulnerable to contamination.

While limited literature is available on construction (including cementing) flaws in hydraulically fractured wells, several studies have examined construction flaws in oil and gas wells in general. One study that examined reported drinking water contamination incidents in Texas identified 10 incidents related to drilling and construction activities among 250,000 oil and gas wells (Kell, 2011). The study noted that many of the contamination incidents were associated with wells that were constructed before Texas revised its regulations on cementing in 1969 (it is not clear how old the wells were at the time the contamination occurred). Because this study relied on reported incidents, it is possible that other wells exhibited mechanical integrity issues but did not result in contamination of a drinking water well or were not reported. Therefore, this should be considered a low-end estimate of the number of mechanical integrity issues that could be tied directly to drilling and construction activities. It is important to note that the 10 contamination incidents identified were not associated with wells that were hydraulically fractured (Kell, 2011).

Several investigators have studied violations information from the PA DEP online violation database to evaluate the rates of and possible factors contributing to mechanical integrity problems, including those related to cement. The results of these studies are summarized in Table 6-2.

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[1] 800 jobs (95% confidence interval: 10 – 1,700 jobs).

[2] 100 jobs (95% confidence interval: 10 – 300 jobs).

Table 6-2. Results of studies of PA DEP violation data that examined mechanical integrity failure rates.

Study	Violations investigated	Wells studied	Data timeframe	Key findings[a]
Considine et al. (2012)	Violations resulting in environmental damage	3,533	2008–2011	Of 845 environmental damage incidents (which resulted in 1,144 violations), approximately 10% were related to casing or cement problems. The overall violation rate dropped from 52.9% of all wells in 2008 to 20.8% of all wells in 2011.
Davies et al. (2014)	Failure of one of the barriers preventing fluid migration	8,030	2005–2013	Approximately 5% of wells received this type of violation. The incident rate increased to 6.3% when failures noted on forms, but not resulting in violations, were included.
Ingraffea et al. (2014)	Violations and inspection records indicating structural integrity loss	3,391	2000–2012	Wells in unconventional reservoirs experienced a rate of structural integrity loss of 6.2%, while the rate for conventional wells was 1%.
Vidic et al. (2013)	Construction violations related to casing or cement	6,466	2008–2013	Approximately 3.4% of wells received this type of violation.
Olawoyin et al. (2013)	All violations	2,001	2008–2010	Analysis of 2,601 violations from 65 operators based on weighted risks found that potentially risky violations increased 342% over the study period, while total violations increased 110%.
Brantley et al. (2014)	Violations related to well construction issues	7,234	2005 – 2013	Over the period studied, a total of 3.4% of well operators received violations for construction issues. Violations in any given year ranged from 0.6% to 10.8%. Also, 0.24% of wells were cited for methane migration.

[a] While all of these studies used the same database, their results vary because they studied different timeframes and used different definitions of what violations constituted a mechanical integrity problem or failure.

Because a significant portion of Pennsylvania's recent oil and gas activity is in the Marcellus Shale, many of the wells in these studies were most likely used for hydraulic fracturing. For example, Ingraffea et al. (2014) found that approximately 16% of the oil and gas wells drilled in the state between 2000 and 2012 were completed in unconventional reservoirs, and nearly all of these wells were used for hydraulic fracturing. Wells drilled in unconventional reservoirs experienced higher rates of structural integrity loss, as defined by the authors, than conventional wells drilled during the same time period (Ingraffea et al., 2014). The authors did not compare rates of structural integrity loss in conventional wells that were and were not hydraulically fractured; they assumed that unconventional wells were hydraulically fractured and conventional wells were not.

Violation rates resulting in environmental damage among all Pennsylvania wells dropped from 52.9% in 2008 to 20.8% in 2011 (Considine et al., 2012), and the drop may be due to a number of factors. Violations related to failure of cement or other well components represented a minority of all well violations (i.e., among wells that were and were not hydraulically fractured). Of 845 events that caused environmental damage, including but not limited to contamination of drinking water resources, Considine et al. (2012) found that about 10% (85 events) were related to casing and cement problems. The rest of the incidents were related to site restoration and spills; the violations noted are confined to those incidents that caused environmental damage (i.e., the analysis excluded construction flaws that did not have adverse environmental effects). In addition, two wells (0.06%) were found to have contributed to methane migration into drinking water. Ingraffea et al. (2014) identified a significant increase in mechanical integrity problems such as casing leaks, sustained casing pressure, and insufficient cement from 2009 to 2011, rising from 5% to 6% of all newly drilled oil and gas wells, followed by a decrease beginning in 2012 to about 2% of all wells, a reduction of approximately 100 violations among 3,000 wells from 2011 to 2012. The rise in mechanical integrity problems between 2009 and 2011 coincided with an increase in the number of wells in unconventional reservoirs.

While all of the studies shown in the table used the same database, their results vary, not only because of the different timeframes studied, but also because they used different definitions of what violations constituted a mechanical integrity problem or failure. For example, Considine et al. (2012) considered all events resulting in environmental damage—including effects such as erosion—and found a relatively high violation rate. Davies et al. (2014) and Ingraffea et al. (2014) investigated violations related to mechanical integrity, while Vidic et al. (2013) looked only at mechanical integrity violations resulting in fluid migration out of the wellbore; these more specific studies found relatively lower violation rates. Olawoyin et al. (2013) performed a statistical analysis that weighted violations based on risk and found that the most risky violations included those involving pits, erosion, waste disposal, and blowout preventers.

Another source of information on contamination caused by wells is positive determination letters (PDLs) issued by the PA DEP. PDLs are issued in response to a complaint when the state determines that contamination did occur in proximity to oil and gas activities. The PDLs take into account the impact, timing, mechanical integrity, and formation permeability; liability is presumed for wells within a given distance if the oil and gas operator cannot refute that they caused the contamination, based on pre-drilling sampling (Brantley et al., 2014).[1] Brantley et al. (2014) examined these PDLs, and concluded that, between 2008 and 2012, the water supplies of approximately seven properties were impacted; depending on the assumptions used to determine how many unconventional gas wells affected a single property; this equates to a rate of 0.12 to 1.1% of the 6,061 wells begun in that timeframe. While these oil and gas wells were linked to contamination of wells and springs, the

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[1] Under Pennsylvania's Oil and Gas Act, operators of oil or gas wells are presumed liable if water supplies within 1,000 ft (305 m) were impacted within 6 months of drilling, unless the claim is rebutted by the operator; this was expanded to 2,500 ft (762 m) and 12 months in 2012.

mechanisms for the impacts (including whether fluids may have been spilled at the surface or if there was a pathway through the well or through the subsurface rock formation to the drinking water resource) were not described by Brantley et al. (2014).

While the studies discussed above present possible explanations for higher violation incidences in unconventional wells that are likely to be hydraulically fractured, it should be noted that other explanations not specific to hydraulic fracturing are also possible. These could include different inspection protocols and different formation types.

Cementing in horizontal wells, which are commonly hydraulically fractured, presents challenges that can contribute to higher rates of mechanical integrity issues. The observation by Ingraffea et al. (2014) that wells drilled in unconventional reservoirs (which are horizontal in Pennsylvania) experience higher rates of structural integrity loss than conventional wells is supported by conclusions of Sabins (1990), who noted that horizontal wells have more cementing problems because they are more difficult to center properly and can be subject to settling of solids on the bottom of the wellbore. Cementing in horizontal wells presents challenges that can contribute to higher rates of mechanical integrity issues.

Thermal and cyclic stresses caused by intermittent operation also can stress cement (King and King, 2013; Ali et al., 2009). Increased pressures and cyclic stresses associated with hydraulic fracturing operations can contribute to cement integrity losses and, if undetected, small mechanical integrity problems can lead to larger ones. Temperature differences between the (typically warmer) subsurface environment and the (typically cooler) injected fluids, followed by contact with the (typically warmer) produced water, can lead to contraction of the well materials (both casing and cement), which introduces additional stresses. Similar temperature changes may occur when multiple fracturing stages are performed. Because the casing and cement have different mechanical properties, they may respond differently to these stress cycles and debond.

Several studies illustrate the effects of cyclic stresses. Dusseault et al. (2000) indicate that wells that have undergone several cycles of thermal or pressure changes will almost always show some debonding between cement and casing. Another laboratory study by De Andrade et al. (2015) found that cycling temperatures between 61°F and 151°F (16°C and 66°C) at 35 bar pressure (2.5 MPa) led to the formation of cracks in cement across both shale and sandstone formations. Cement damage was more significant in sandstone formations and worsened with each thermal cycle. A similar study by Roy et al. (2016) at ambient pressure did not find any cracks larger than 200 microns with temperature fluctuation between -40°F and 158°F (-40°C and 70°C), although numerical modeling of the same scenario predicted that cracks up to 1 to 10 microns would form, which would not have been detected by the methods used. Microannuli formed by this debonding can serve as pathways for gas migration, in particular because the lighter density of gas provides a larger driving force for migration through the microannuli than for heavier liquids.[1] One laboratory study indicated that microannuli on the order of 0.01 in (0.25 mm) could increase effective cement permeability from 1 nD (1×10^{-21} m^2) in good quality cement up to 1 mD (1×10^{-15} m^2) (Bachu and Bennion, 2009). This six-order magnitude increase in permeability shows that even small

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[1] Microannuli can also form due to an inadequate cement job, e.g., poor mud removal or improper cement placement rate.

microannuli can significantly increase the potential for flow through the cement. Typically, these microannuli form at the interface between the casing and cement or between the cement and formation. Debonding and formation of microannuli can occur through intermittent operation, pressure tests, and workover operations (Dusseault et al., 2000).[1] While a small area of debonding may not lead to fluid migration, the microannuli in the cement resulting from the debonding can serve as initiation points for fracture propagation if re-pressurized gas enters the microannulus (Dusseault et al., 2000).

A number of modeling studies have indicated that fractures can propagate upwards from existing defects in cement or areas with poorer bonding (Kim et al., 2016; Roy et al., 2016; De Andrade et al., 2015). Feng et al. (2015) showed that fractures in cement tended to propagate upwards along the wellbore instead of radially. Modeling studies have also shown that cements with lower Young's modulus tend to propagate fractures more slowly than stiffer cements (Kim et al., 2016; Feng et al., 2015).[2]

The Council of Canadian Academies (2014) found that the repetitive pressure surges occurring during the hydraulic fracturing process would make maintaining an intact cement seal more of a challenge in these wells. Wang and Dahi Taleghani (2014) performed a modeling study, which concluded that hydraulic fracturing pressures could initiate annular cracks in cement. Another study of well data indicated that cement failure rates are higher in intermediate casings compared to other casings (McDaniel et al., 2014). The failures occurred after drilling and completion of wells, and the authors surmised that the cement failures were most likely due to cyclic pressure stresses caused by drilling. Theoretically, similar cyclic pressure events could also be experienced in the production casing during multiple stages of hydraulic fracturing. Mechanical stresses associated with well operation or workovers and pressure tests also may lead to small cracks in the cement, which may provide migration pathways for fluid.

Corrosion can lead to cement failure. Cement can fail to maintain integrity as a result of degradation of the cement after the cement is set. Cement degradation can result from attack by corrosive brines or chemicals such as sulfates, sulfides, and carbon dioxide that exist in formation fluids (Renpu, 2011). These chemicals can alter the chemical structure of the cement, resulting in increased permeability or reduced strength and leading to loss of cement integrity over time. Additives or specialty cements exist that can decrease cement susceptibility to specific chemicals.

6.2.2.3 Well Age

Hydraulic fracturing within older (legacy) wells has the potential to impact drinking water resources, either due to inadequate design and construction or degradation of the well components over time that afford pathways for the unintended migration of fluids. While new wells can be specifically designed to withstand the stresses associated with hydraulic fracturing operations,

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[1] A workover refers to any maintenance activity performed on a well that involves ceasing operations and removing the wellhead. Depending on the purpose of the workover and the tools used, workovers may induce pressure changes in the well.

[2] Young's modulus, a ratio of stress to strain, is a measure of the rigidity of a material.

older wells, which are sometimes used in hydraulic fracturing operations, may not have been designed to the same specifications, and their reuse for this purpose could be a concern.

Aging and extended use of a well contribute to casing corrosion and degradation, and the potential for fluid migration related to compromised casing tends to be higher in older wells. For example, exposure to corrosive chemicals such as hydrogen sulfide, carbonic acid, and brines can accelerate corrosion (Renpu, 2011). Ajani and Kelkar (2012) studied wells in Oklahoma and found a correlation between well age and mechanical integrity issues. Specifically, in wells spaced between 1,000 and 2,000 ft (300 and 600 m) from a well being fractured, the likelihood of impact on the well (defined in the study as a loss of gas production or increase in water production) rose from approximately 20% to 60% as the well's age increased from 200 days to over 600 days. Age was also found to be a factor in mechanical integrity problems in a study of wells drilled offshore in the Gulf of Mexico (Brufatto et al., 2003).

The Well File Review (U.S. EPA, 2016c, 2015n) provides evidence that fracturing does occur in older wells, including re-entering existing wells to fracture them for the first time or re-fracturing in wells that have been previously fractured. The Well File Review found that the median age of wells being initially fractured was 45 days, with well ages at time of fracturing ranging from 8 days to nearly 51 years. While 64% of the wells studied in the Well File Review were fractured within 6 months of the well spud date, the median age for wells being re-fractured was 6 years.[1,2] An estimated 11% of fracture jobs studied in the Well File Review were re-completions in a different zone than the original fracture job and 8% were re-fractures in the same zone as the original fracture job.[3,4]

The Well File Review also found that well component failures appeared to occur more frequently in older wells that were being re-completed or re-fractured.[5] The failure rate in hydraulic fracturing jobs involving re-completions and re-fractures was 6%, compared to 2% for hydraulic fracturing jobs in wells that had not been previously fractured.[6,7] While the confidence levels overlap, there is an indication that re-fractured and re-completed wells are more likely to suffer a failure of one or more components during hydraulic fracturing operations.

Frac strings, which are specialized pieces of casing inserted inside the production casing, can be used to protect older casing during fracturing. However, the effect of hydraulic fracturing on the cement on the production casing in older wells is unknown. One study on re-fracturing of wells noted that the mechanical integrity of the well was a key factor in determining the success or failure of the fracture treatment (Vincent, 2011). The Well File Review (U.S. EPA, 2016c) found that

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[1] Spudding refers to starting the well drilling process by removing rock, dirt, and other sedimentary material with the drill bit.

[2] 64% of wells (95% confidence interval: 48 – 77% of wells).

[3] 11% of jobs (95% confidence interval: 5 – 23% of jobs).

[4] 8% of jobs (95% confidence interval: 5 – 12% of jobs).

[5] The Well File Review defines a failure as a defect in a well component that allows fluid to flow into an annular space.

[6] 6% failure rate (95% confidence interval: 2 – 19% failure rate).

[7] 2% failure rate (95% confidence interval: 0.5 – 8% failure rate).

failures occurred more frequently in completions using frac strings, with failures occurring 20% of the time, compared to failures occurring 0.9% of the time when a frac string was not used.[1,2]

Note that there are also potential issues related to *where* these older wells are sited. For example, some wells could be in areas with naturally occurring subsurface faults or fractures that could not be detected or fully characterized with the technologies available at the time of construction. It is also possible that, in areas of historic petroleum exploration, old abandoned wells can be present which may have been improperly plugged or have degraded over time.[3] These wells could serve as pathways for fluid migration if they are located within the fracture network of the well; see Section 6.3.2.

6.2.2.4 Sustained Casing Pressure

Sustained casing pressure illustrates how the issues related to casing and cement discussed in the preceding sections can work together and be difficult to differentiate.[4] It is an indicator that pathways within the well related to the well's casing, cement, or both allowed fluid movement to occur. Sustained casing pressure can result from casing leaks, uncemented intervals, microannuli, or some combination of the three, which can be an indication that a well has lost mechanical integrity. Sustained casing pressure can be observed when an annulus (either the annulus between the tubing and production casing or between any two casings) is exposed to a source of nearly continuous elevated pressure. Goodwin and Crook (1992) found that sudden increases in sustained casing pressure occurred in wells that were exposed to high temperatures and pressures. Subsequent logging of these wells showed that the high temperatures and pressures led to shearing of the cement/casing interface and a total loss of the cement bond. Aly et al. (2015) demonstrated methods using a combination of chemical analysis, isotopic analysis, well logs, and drilling records to identify the most likely source of fluids causing sustained casing pressure.

Sustained casing pressure occurs more frequently in older wells and horizontal or deviated wells. One study found that sustained casing pressure becomes a greater concern as a well ages. Sustained casing pressure was found in less than 10% of wells that were less than a year old, but was present in up to 50% of 15-year-old wells (Brufatto et al., 2003). While these wells may not have been hydraulically fractured, the study demonstrates that older wells can exhibit more mechanical integrity problems. Fleckenstein et al. (2015) also found that older wells exhibited more barrier failures, including sustained casing pressure. They reported that 3.53% of the wells in the study with under-pressured intermediate gas zones developed sustained casing pressure, although it is likely the sustained casing pressure was due to poor well design (i.e., under older standards) rather

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[1] 20% failure rate (95% confidence interval: 10 – 36% failure rate).

[2] 0.9% failure rate (95% confidence interval: 0.8 – 1.0% failure rate).

[3] An abandoned well refers to a well that is no longer being used, either because it is not economically producing or it cannot be used because of its poor condition.

[4] Sustained casing pressure is pressure in any well annulus that is measurable at the wellhead and rebuilds after it is bled down, not caused solely by temperature fluctuations or imposed by the operator (Skjerven et al., 2011). If the pressure is relieved by venting natural gas from the annulus to the atmosphere, it will build up again once the annulus is closed (i.e., the pressure is sustained). The return of pressure indicates that there is a small leak in a casing or through uncemented or poorly cemented intervals that exposes the annulus to a pressured source of gas. It is possible to have pressure in more than one of the annuli.

than well age. Watson and Bachu (2009) found that a higher portion of deviated wells had sustained casing pressure compared to vertical wells. Increased pressures and cyclic stresses (Syed and Cutler, 2010) during hydraulic fracturing and difficulty in cementing horizontal wells (Sabins, 1990) also can lead to increased instances of sustained casing pressure (Muehlenbachs et al., 2012; Rowe and Muehlenbachs, 1999).

Sustained casing pressure can be a concern for several reasons. If the pressures are allowed to build up to above the burst pressure of the exterior casing or the collapse pressure of the interior casing, the casing may fail. Increased pressure can also cause gas or liquid to enter lower-pressured formations that are exposed to the annulus either through leaks or uncemented sections. Laboratory experiments by Harrison (1985) demonstrated that over-pressurized gas in the annulus could cause rapid movement of gas into drinking water resources if a permeable pathway exists between the annulus and the groundwater. Over-pressurization of the annulus is commonly relieved by venting the annulus to the atmosphere; however, this does not address the underlying problem in the well and can result in additional releases of methane to the atmosphere.

One example of an area where sustained casing pressure is common is Alberta, Canada, where 14% of the wells drilled since 1971 experienced serious sustained casing flow. This was defined in a study by Jackson and Dussealt (2014) as more than 10,594 ft^3 (300 m^3)/day at pressures higher than 0.48 psi/ft (11 kPa/m) of depth times the depth of the surface casing. Another study in the same area found gas in nearby drinking water wells had a composition consistent with biogenic methane mixing with methane from nearby coalbed methane and deeper natural gas fields (Tilley and Muehlenbachs, 2012).

In a few cases, sustained casing pressure in wells that have been hydraulically fractured may have been linked to drinking water contamination, although it is challenging to definitively determine the actual cause. In one study in northeastern Pennsylvania, methane to ethane ratios and isotopic signatures were used to investigate stray gas migration into domestic drinking water (U.S. EPA, 2014f). Composition of the gas in the water wells was consistent with that of the gas found in nearby gas wells with sustained casing pressures; other possible sources of the gas could not be ruled out. Several gas wells in the study area were cited by the PA DEP for having elevated sustained casing annulus pressures. One such case included four well pads with two wells drilled on each pad in southeastern Bradford County. The wells, drilled between September 2009 and May 2010, were 6,890 to 7,546 ft (2,100 to 2,300 m) deep and had surface casing to 984 ft (300 m). The casing below the surface casing was uncemented. All four wells experienced sustained casing pressure, with pressures ranging from 483 to 909 psi (3.3 to 6.3 MPa). Methane appeared in three nearby domestic drinking water wells in July 2010. Investigation into the cause of the methane contamination identified the drilled gas wells with sustained casing pressure as the most likely cause. The likely path was over-pressured gas from intermediate zones above the Marcellus Shale entering the uncemented well annulus and traveling up the annulus and along bedding planes which intersected the well annulus.[1] The determination was based on multiple lines of evidence, including: no methane present in a pre-drill sample, increases in methane after the wells had been

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[1] A bedding plane is the surface that separates two layers of stratified rocks.

drilled, similar isotopic composition of the gas in the domestic wells and the gas in the annular space of the gas wells, and the presence of bedding planes which intersected the uncemented portion of the gas wells leading upwards toward the domestic wells (Llewellyn et al., 2015).

Adequate well design, detection (i.e., through annulus pressure monitoring), and repair of sustained casing pressure reduce the potential for fluid movement. (See Chapter 10 for additional discussion of practices that can reduce the frequency or severity of impacts to drinking water quality.) Watson and Bachu (2009) found that regulations requiring monitoring and repair of sustained casing vent flow or sustained casing pressure had a positive effect on lowering leak rates. The authors also found injection wells initially designed for the higher pressures associated with injection (vs. production) experienced sustained casing pressure less often than those that were retrofitted (Watson and Bachu, 2009). As mentioned above, Fleckenstein et al. (2015) found that placing the surface casing below all potential sources of drinking water and cementing intermediate gas zones significantly reduced sustained casing pressure.

Another study in Mamm Creek, Colorado, obtained similar results. The Mamm Creek field is in an area where lost cement and shallow, gas-containing formations are common. All the wells in the formation were hydraulically fractured (S.S. Papadopulos & Associates, 2008). A number of wells in the area have experienced sustained casing pressure, and methane has been found in several drinking water wells along with seeps into local creeks and ponds. In one well, drilled in January 2004, four pressured gas zones were encountered during drilling and there was a lost cement incident, which resulted in the cement top being more than 4,000 ft (1,000 m) lower than originally intended. Due to high bradenhead pressure (661 psi, or 4.6 MPa), cement remediation efforts were implemented (Crescent, 2011; COGCC, 2004).[1] The operator of this well was later cited by the Colorado Oil and Gas Conservation Commission (COGCC) for causing natural gas and benzene to seep into a nearby creek. The proposed route of contamination was contaminants flowing up the well annulus and then along a fault. The proposed contamination route appeared to be validated because, once remedial cementing was performed on the well, methane and benzene levels in the creek began to drop (Science Based Solutions LLC, 2014). In response to the incident, the state instituted requirements to identify and cement above the top of the highest gas-producing formation in the area and to monitor casing pressures after cementing.

A study in the Woodford Shale in Oklahoma examined how various cement design factors affected sustained casing pressure (Landry et al., 2015). The study focused on wells in the Cana-Woodford basin, a very deep basin at 11,000 to 15,000 ft (3,400 to 4,600 m) below ground surface, where the depth, long laterals, fracture gradients, and low permeability of the formations in the basin make cementing a challenge. One operator had seven test wells in the basin, of which six exhibited sustained casing pressure, usually after hydraulic fracturing operations. In early designs, the operator had not been using centralizers on the horizontal sections of the well, because they increased the frequency of stuck pipe. However, improvements in centralizer design allowed the operator to use centralizers more frequently on later well designs, and the operator tried several different techniques to address the sustained casing pressure problems, with varying results:

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[1] Bradenhead pressure is pressure between two casings in an oil and gas well.

- In three of the wells, the operator used three different techniques: a conventional cement job with a water-based drilling mud and single slurry design; oil-based mud with single slurry design; and a foamed cement to cement the vertical portion of the well from the kickoff point up with conventional water-based cement on the lateral. All three of these wells experienced sustained casing pressure after hydraulic fracturing operations.
- In a fourth well, in 2013, the operator used centralizers, with three centralizers per every two casing joints along the lateral and one centralizer per joint in the vertical section. The design also involved an enhanced spacer fluid to remove drilling mud and a self-healing cement in the upper portion of the well. While some channeling was detected in this well, the channels were not connected and did not lead to sustained casing pressure.

The operator constructed an additional 21 wells using the same technique as was performed in the fourth well, and 20 did not show any sustained casing pressure after fracturing. This study shows the importance of cement design factors, such as casing centralization and mud removal, in preventing sustained casing pressure.

Not every well that shows positive pressure in the annulus poses a potential problem. Sustained pressure is only a problem when it exceeds the ability of the wellbore to contain it or when it indicates leaks in the cement or casing (TIPRO, 2012). A variety of management options are available for managing such pressure including venting, remedial cementing, and use of kill fluids in the annulus (TIPRO, 2012).[1] While venting may be a common method to address sustained casing pressure, it does not address the underlying mechanical integrity failure and is only a temporary solution. Furthermore, venting releases fluids at the wellhead which, if gaseous, can contribute to increased atmospheric emissions, or if liquid, potential spills on the surface.

6.3 Fluid Migration Associated with Induced Fractures within Subsurface Formations

This section discusses potential pathways for fluid movement associated with induced fractures and subsurface formations (outside of the well system described in Section 6.2). It examines the potential for fluid migration into drinking water resources by evaluating the development of migration pathways within subsurface formations, the flow of injected and formation fluids, and important factors that affect these processes.

Fluid movement requires both a physical pathway (e.g., via the interconnected pores within a permeable rock matrix or via a fracture in the rock) and a driving force.[2] In subsurface formations, fluid movement is driven by the existence of a hydraulic gradient, which depends on elevation and pressure and is influenced by fluid density, composition, and temperature (Pinder and Celia, 2006).

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[1] A kill fluid is a weighted fluid with a density that is sufficient to overcome the formation pressure and prevent fluids from flowing up the wellbore.

[2] Permeability (i.e., intrinsic or absolute permeability) of formations describes the ability of water to move through the formation matrix, and it depends on the rock's grain size and the connectedness of the void spaces between the grains. Where multiple phases of fluids exist in the pore space, the flow of fluids also depends on relative permeabilities.

In the context of hydraulic fracturing, two key factors govern fluid migration during and after the hydraulic fracturing event:

- Pressure differentials in the reservoir, which are influenced both by initial subsurface conditions and by the pressures created by injection and production regimes. Specific factors that may influence pressure differentials include structural or topographic features, over-pressure in the shale reservoir, or a temporary increase in pressure as a result of fluid injection during hydraulic fracturing (Birdsell et al., 2015a).
- Buoyancy, which is driven by density differences among and between gases and liquids. Fluid migration can occur when these density differences exist in the presence of a pathway (Pinder and Gray, 2008).

During hydraulic fracturing, pressurized fluids leaving the well create fractures within the production zone and then enter the formation through these newly created (induced) fractures. Unintended fluid migration can result from this fracturing process. Migration pathways to drinking water resources could develop as a result of changes in the subsurface flow or pressure regime associated with hydraulic fracturing; via fractures that extend beyond the intended formation or that intersect existing natural faults or fractures; and via fractures that intersect offset wells or other artificial structures (Jackson et al., 2013d). These subsurface pathways may facilitate the migration of fluids by themselves or in conjunction with the well-based pathways described in Section 6.2. Fluids potentially available for migration include both fluids injected into the well (including leakoff) and fluids already present in the formation (including brine or natural gas).[1]

The potential for subsurface fluid migration into drinking water resources can be evaluated during two different time periods (Kim and Moridis, 2015):

1. *Following the initiation of fractures in the reservoir, prior to any oil or gas production.* The injected fluid, pressurizing the formation, flows through the fractures and the fractures grow into the reservoir. Fluid leaks off into the formation, allowing the fractures to close except where they are held open by the proppant (Adachi et al., 2007). Fractures will generally continue to propagate until the fluid lost to leakoff is equal to the fluid injection rate (King and Durham, 2015).
2. *During the production period, after fracturing is completed and pressure in the fractures is reduced.* At this time, fluids (including oil/gas and produced water) flow from the reservoir into the well. As fluids are withdrawn from the formation, pore pressure decreases; as a result, the effective stress applied to fractures increases and (in the absence of proppant) fractures will close (Aybar et al., 2015).

Note that these two time periods vary in duration. As described in Chapter 3, the first period of fracture creation and propagation (i.e., the hydraulic fracturing itself) is a relatively short-term process, typically lasting 2 to 10 days, depending on the number of stages in the fracture treatment

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[1] Leakoff is the fraction of the injected fluid that infiltrates into the formation and is not recovered (i.e., it "leaks off" and does not return through the well to the surface) during production (Economides et al., 2007). Fluids that leak off and are not recovered are sometimes referred to as "lost" fluids.

design. On the other hand, operation of the well for production covers a substantially longer period (depending on many factors such as the amount of hydrocarbons in place and economic considerations), and can be as long as 40 or 60 years in onshore tight gas reservoirs (Ross and King, 2007).

The following discussion of potential subsurface fluid migration into drinking water resources focuses primarily on the physical movement of fluids and the factors affecting this movement. Section 6.3.1 describes the basic principles of subsurface fracture creation, geometry, and propagation, to provide context for the discussion of potential fluid migration pathways in Section 6.3.2. Geochemical and biogeochemical reactions among hydraulic fracturing fluids, formation fluids, subsurface microbes, and rock formations are another important component of subsurface fluid migration and transport. See Chapter 7 for a discussion of the processes that affect pore fluid biogeochemistry and influence the chemical and microbial composition of produced water.

6.3.1 Overview of Subsurface Fracture Growth

Fracture initiation and growth is a highly complex process due to the heterogeneous nature of the subsurface environment. As shown in Figure 6-5, fracture formation is controlled by the three in situ principal compressive stresses: the vertical stress, the maximum horizontal stress, and the minimum horizontal stress. During hydraulic fracturing, pressurized fluid injection creates high pore pressures around the well. Fractures form when this pressure exceeds the local least principal stress and the tensile strength of the rock (Zoback, 2010; Fjaer et al., 2008).

Fractures propagate (increase in length) in the direction of the maximum principal stress; they are tensile fractures that open in the direction of least resistance and then propagate in the plane of the greatest and intermediate stresses (Nolen-Hoeksema, 2013). Deep in the subsurface, the maximum principal stress is generally in the vertical direction, because the overburden (the weight of overlying rock) is the largest single stress. Therefore, in deep formations, fracture orientation is expected to be vertical. This is the scenario illustrated in Figure 6-5. At shallower depths, where the rock is subjected to less pressure from the overburden, more fracture propagation is expected to be in the horizontal direction. Using tiltmeter data from over 10,000 fractures in various North American shale reservoirs, Fisher and Warpinski (2012) found that induced fractures deeper than about 4,000 ft (1,000 m) are primarily vertical (see below for more information on tiltmeters). Between approximately 4,000 and 2,000 ft (1,000 and 600 m), they observed that fracture complexity increases, and fractures shallower than about 2,000 ft (600 m) are primarily (though not entirely) horizontal.[1] However, local geologic conditions can cause fracture orientations to deviate from these general trends (Ryan et al., 2015). Horizontal fracturing can also occur in deeper

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[1] Fracture complexity is the ratio of horizontal-to-vertical fracture volume distribution, as defined by Fisher and Warpinski (2012). Fracture complexity is higher in fractures with a larger horizontal component. For the reasons explained above, this is more likely to occur at shallower depths. However, even in shallow zones, fractures are unlikely to be completely horizontal. As noted by Fisher and Warpinski, “All of the fractures do not necessarily turn horizontal; they might have significant vertical and horizontal components with more of a T-shaped geometry.” In the Fisher and Warpinski data set, the maximum horizontal component of the fractures is approximately 70%.

settings in some less-common reservoir environments where the principal stresses have been altered by salt intrusions or similar types of geologic activity (Jones and Britt, 2009).

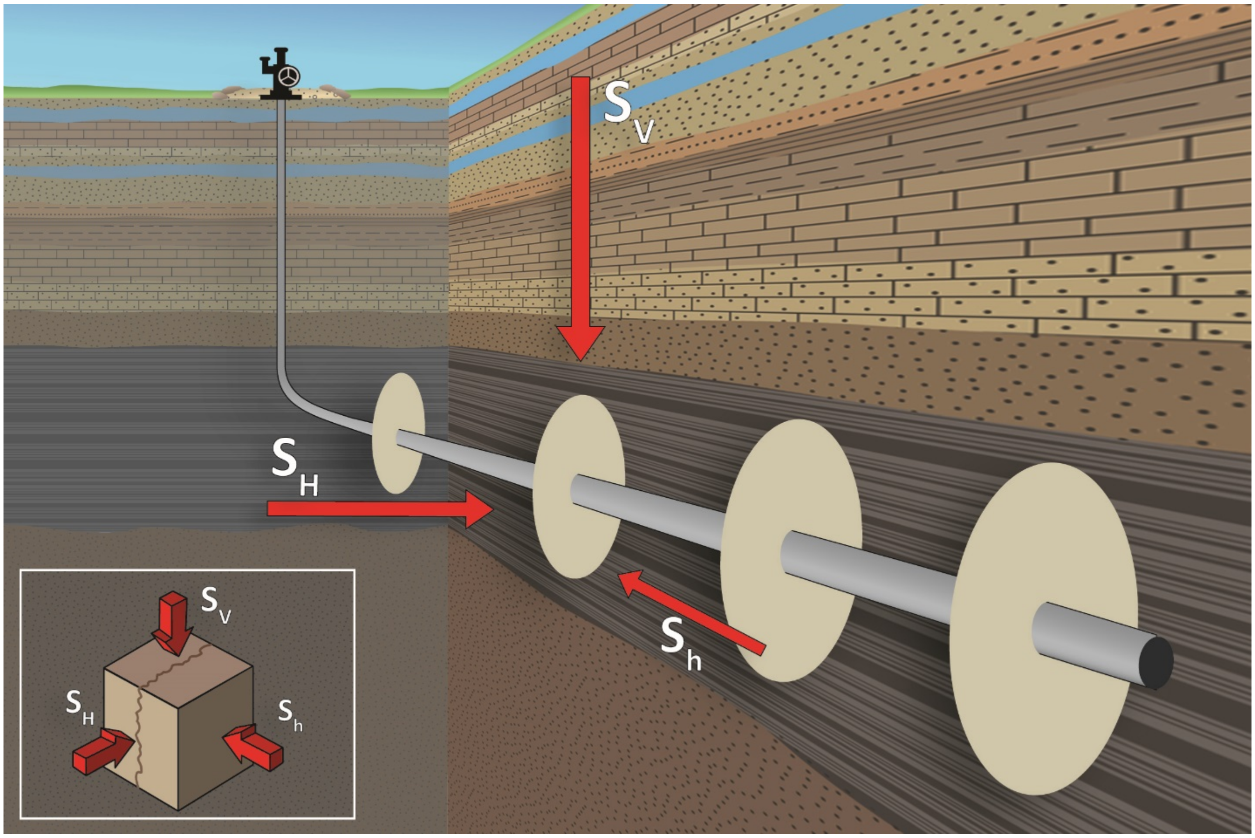

Figure 6-5. Hydraulic fracture planes (represented as ovals), with respect to the principal subsurface compressive stresses: S_V (the vertical stress), S_H (the maximum horizontal stress), and S_h (the minimum horizontal stress).

In addition to the principal subsurface stresses, a variety of factors and processes affect the complex process of fracture creation, propagation, geometry, and containment.[1] Computational modeling techniques have been developed to simulate fracture creation and propagation and to provide a better understanding of this complex process (Kim and Moridis, 2013).[2] Modeling hydraulic fracturing in shale or tight gas reservoirs requires integrating the physics of both flow and geomechanics to account for fluid flow, fracture propagation, and dynamic changes in pore volume and permeability. Some important flow and geomechanical parameters included in these

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[1] Fracture geometry refers to characteristics of the fracture such as height and aperture (width).

[2] There are different kinds of mathematical models. Analytical models have a closed-form solution and therefore are relatively simple to solve. In contrast, computational models (also called numerical models) require more extensive computational resources and are used to study the behavior of complex systems.

types of advanced models are: permeability, porosity, Young's modulus, Poisson's ratio, and tensile strength, as well as heterogeneities associated with these parameters.[1]

Based on modeling and laboratory experiments (e.g., by Khanna and Kotousov, 2016; Li et al., 2016c; Li et al., 2016b; de Pater, 2015; Kim and Moridis, 2015; Lee et al., 2015; Narasimhan et al., 2015; Smith and Montgomery, 2015; Wang and Rahman, 2015; Kim and Moridis, 2013), below are some of the factors that have been noted in the literature as influencing fracture growth:

- Geologic properties of the production zone such as rock type and composition, permeability, thickness, and the presence of pre-existing natural fractures;
- The presence, composition, and properties of the liquids and gases trapped in pore spaces;
- Geomechanical properties, including tensile strength, Young's modulus, and the pressure at which the rock will fracture;
- Characteristics of the interface (boundary) between adjacent rock layers; and
- Operational characteristics, including injection rate and pressure, the properties of the hydraulic fracturing fluids, and fracture spacing.

Some modeling investigations have indicated that the vertical propagation of fractures (due to tensile failure) may be limited by shear failure, which increases the permeability of the formation and allows more fluid to leak off into the rock. These findings demonstrate that elevated pore pressure can cause shear failure, thus further affecting matrix permeability, flow regimes, and leakoff (Daneshy, 2009).

It is important to note that, while computational modeling is a useful tool to understand complex systems, modeling has limitations and associated uncertainties. All models rely on assumptions and simplifications, and there is, as stated by Ryan et al. (2015), "currently no single numerical approach that simultaneously includes the most important thermo-hydromechanical and chemical processes which occur during the migration of gas and fluids along faults and leaky wellbores." Uncertainties in selecting values for input parameters and potentially inadequate field data for model verification limit the reliability of model predictions.

In addition to their use in research applications, analytical and numerical modeling approaches are used to design hydraulic fracturing treatments and predict the extent of fractured areas (Adachi et al., 2007). Specifically, modeling techniques are used to assess the treatment's sensitivity to critical parameters such as injection rate, treatment volumes, fluid viscosity, and leakoff. Existing models range from simpler (typically two-dimensional) theoretical models to computationally more complicated three-dimensional models.

Monitoring of hydraulic fracturing operations can also provide insights into fracture development. Monitoring techniques involve both operational monitoring methods and "external" methods not

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[1] As described in Section 6.2.2.2, Young's modulus, a ratio of stress to strain, is a measure of the rigidity of a material. Poisson's ratio is a ratio of transverse-to-axial (or latitudinal-to-longitudinal) strain, and it characterizes how a material is deformed under pressure. See Zoback (2010) for more information on the geomechanical properties of reservoir rocks.

directly related to the production operation. Operational monitoring refers to the monitoring of pressure and flow rate, along with related parameters such as fluid density and additive concentrations, using surface equipment and/or downhole sensors (Eberhard, 2011). This monitoring is conducted to ensure the operation is proceeding as planned and to determine if operational parameters need to be adjusted. Interpretation of pressure data can be used to better understand fracture behavior (Kim and Wang, 2014). For example, pressure data from previous hydraulic fracturing operations can indicate whether a geologic barrier to fracture growth exists and whether the barrier has been penetrated, or whether fractures have intersected with natural fractures or faults (API, 2015). Anomalies in operational monitoring data can also indicate whether an unexpected event has occurred, such as communication with another well (Section 6.3.2.3).

As described in Chapter 4, the volume of fluid injected is typically monitored and tracked to provide information on the volume and extent of fractures created (Flewelling et al., 2013). However, numerical investigations have found that reservoir gas flows into the fractures immediately after they open from hydraulic fracturing, and injection pressurizes both gas and water within the fracture to induce further fracture propagation (Kim and Moridis, 2015). Therefore, the fracture volume can be larger than the injected fluid volume. As a result, simple estimation of fracture volume based on the amount of injected fluid may underestimate fracture growth, and additional information (e.g., from geophysical monitoring techniques) is needed to accurately predict the extent of induced fractures.

External monitoring technologies can also be used to collect data on fracture characteristics and extent during hydraulic fracturing and/or production. These monitoring methods can be divided into near-wellbore and far-field techniques. Near-wellbore techniques include the use of tracers, temperature logs, video logs, and caliper logs that measure conditions in and immediately around the wellbore (Holditch, 2007). However, near-wellbore techniques and logs only provide information for, at most, a distance of two to three wellbore diameters from the well and are, therefore, not suited for tracking fractures for their entire length (Holditch, 2007).

Far-field methods, such as microseismic monitoring or tiltmeters, are used if the intent is to estimate fracture growth and height across the entire fractured reservoir area. Microseismic monitoring involves placing geophones in a position to detect the very small amounts of seismic energy generated during subsurface fracturing (Warpinski, 2009).[1] Monitoring these microseismic events gives an idea of the location and size of the fracture network, as well as the orientation and complexity of fracturing (Fisher and Warpinski, 2012). Using the results of microseismic monitoring in conjunction with other information, such as time-lapse, multicomponent seismic data (collected with surface surveys), can provide additional information for understanding fracture complexity and the interaction between natural and induced fractures (D'Amico and Davis, 2015). The Well File Review (U.S. EPA, 2016c) found that microseismic monitoring was conducted at 0.5% (100) of the hydraulic fracturing jobs studied.[2] Tiltmeters, which measure extremely small deformations in the earth, can be used to determine the direction and volume of the fractures and,

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[1] Typical microseismic events associated with hydraulic fracturing have a magnitude on the order of -2.5 (negative two and half) (Warpinski, 2009).

[2] 100 jobs (95% confidence interval: 40 – 300 jobs).

within certain distances from the well, to estimate their dimensions (Lecampion et al., 2005). Other monitoring techniques, such as seismic surveys, can also be used to gather information about the subsurface environment. For example, Viñal and Davis (2015) demonstrated the use of time-lapse multi-component seismic surveys to monitor changes in the overburden due to hydraulic fracturing. Chapter 10 provides additional discussion of factors and practices, such as site monitoring, that can reduce the frequency or severity of impacts to drinking water quality.

6.3.2 Migration of Fluids through Pathways Related to Fractures/Formations

As described above, subsurface migration of fluids requires a pathway, induced or natural, with enough permeability to allow fluids to flow, as well as a hydraulic gradient physically driving the movement. The following subsections describe and evaluate potential pathways for the migration of hydraulic fracturing fluids, hydrocarbons, or other fluids from producing formations to drinking water resources. They also present cases where the existence of these pathways has been documented. The potential subsurface migration pathways are categorized as follows: (1) migration out of the production zone through pore space in the rock, (2) migration due to fracture overgrowth out of the production zone, (3) migration via fractures intersecting offset wells or other artificial structures, and (4) migration via fractures intersecting other geologic features, such as permeable faults or pre-existing natural fractures. Although these four potential pathways are discussed separately here, they may act in combination with each other or in combination with pathways along the well (as discussed in Section 6.2) to affect drinking water resources.

The possibility of fluid migration between a hydrocarbon-bearing formation and a drinking water resource can be related to the vertical distance between these formations (Reagan et al., 2015; Jackson et al., 2013d). In general, as the separation distance between the production zone and a drinking water aquifer decreases, the likelihood of upward migration of hydraulic fracturing to drinking water aquifers increases (Birdsell et al., 2015a). The separation distance between hydraulically fractured producing zones and drinking water resources (and these formations' depth from the surface) varies substantially among shale gas plays, coalbed methane plays, and other areas where hydraulic fracturing takes place in the United States (Figure 6-6 and Table 6-3). Many hydraulic fracturing operations target deep shale zones such as the Marcellus or Haynesville/ Bossier, where the vertical distance between the top of the shale formation and the base of drinking water resources may be 1 mi (1.6 km) or greater. This is reflected in the Well File Review, in which approximately half of the wells were estimated to have 5,000 ft (2,000 m) or more of measured distance along the wellbore between the point of the shallowest hydraulic fracturing and the operator-reported base of the protected groundwater resource (U.S. EPA, 2015n).[1] Similarly, in a review of FracFocus data from over 40,000 wells across the United States, Jackson et al. (2015) found that the median depth of wells used for hydraulic fracturing was 8,180 ft (2,490 m) and the mean depth was 8,290 ft (2,530 m).

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[1] In the Well File Review, measured depth represents length along the wellbore, which may be a straight vertical distance below ground or may follow a more complicated path, if the wellbore is not straight and vertical. True vertical separation distances were not reported in the Well File Review. Measured distance along a well is equal to the true vertical distance only in straight, vertical wells. Otherwise, the true vertical distance is less than the measured distance.

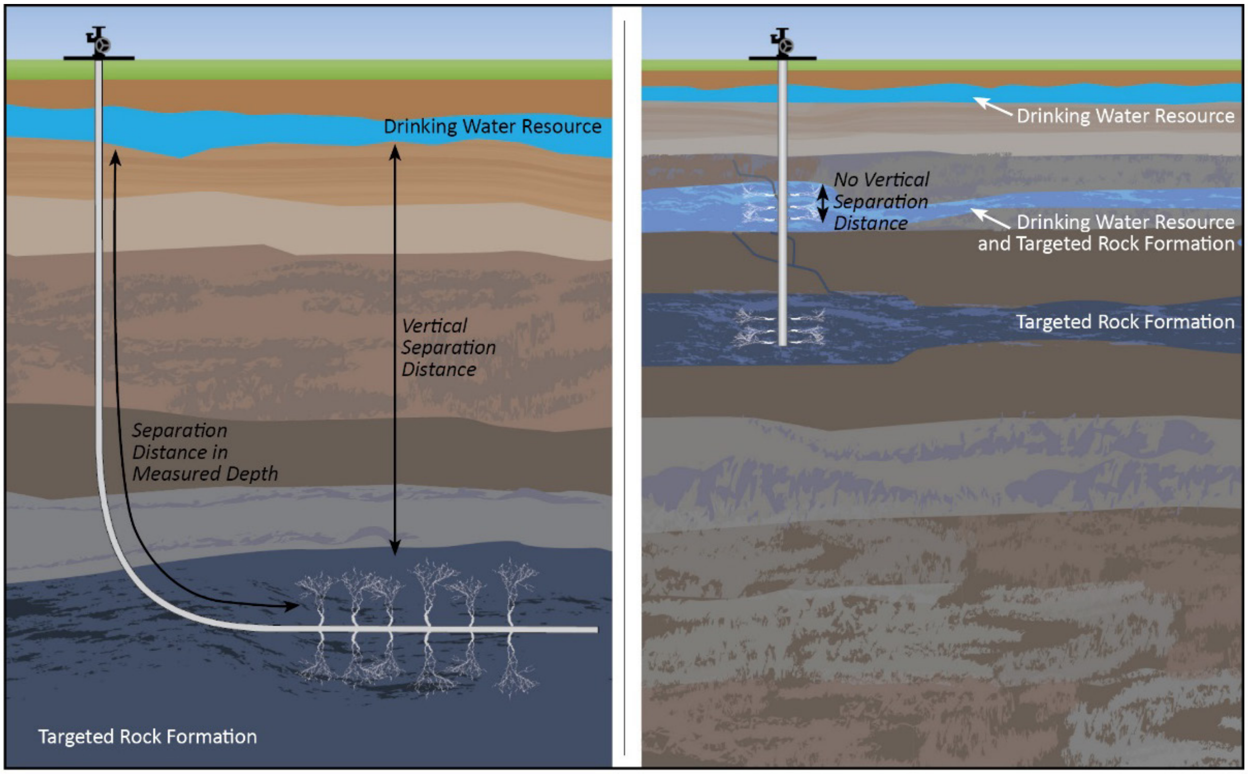

Figure 6-6. Vertical distances in the subsurface separating drinking water resources and hydraulic fracturing depths.

However, as shown in Table 6-3, some hydraulic fracturing operations occur at shallower depths or in closer proximity to drinking water resources. For example, both the Antrim and the New Albany plays are relatively shallow, with distances of 100 to 1,900 ft (31 to 580 m) between the producing formation and the base of drinking water resources. In the Jackson et al. (2015) review of FracFocus data, 16% of wells reviewed were within 1 mi (1.6 km) of the surface and 3% were within 2,000 ft (600 m) of the surface.[1] The distribution of the more shallow hydraulically fractured wells varied nationally but was concentrated in Texas, California, Arkansas, and Wyoming. For example, in California and Arkansas, 88% and 85% of hydraulically fractured wells, respectively, were within about 5,000 ft (2,000 m) of the surface. Overall, the Well File Review found a higher proportion of relatively shallow wells—the data in the Well File Review indicated that 20% of wells used for hydraulic fracturing (an estimated 4,600 wells) had less than 2,000 ft (600 m) between the shallowest point of the fractures and the base of protected groundwater resources (U.S. EPA, 2015n).[2] This is likely because the Well File Review results are more representative of hydraulic fracturing operations across the country; Jackson et al. (2015) acknowledge that their analysis

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[1] Jackson et al. (2015) use true vertical depth data from FracFocus; this represents the depth of the well but not necessarily the depth of the fractures. The depth of the fractures may be shallower than the true vertical depth of the well, though Jackson et al. (2015) note that most states do not require operators to submit information on the true vertical depth to the top of the fractures.

[2] 4,600 wells (95% confidence interval: 900 – 8,300 wells). The Well File Review defines this separation distance as the measured depth of the point of shallowest hydraulic fracturing in the well, minus the depth of the operator-reported protected groundwater resource.

underestimates the occurrence of relatively shallow hydraulic fracturing for states in which FracFocus reporting is not required.

Table 6-3. Comparing the approximate depth and thickness of selected U.S. shale gas plays and coalbed methane basins.

Shale data are reported in GWPC and ALL Consulting (2009) and NETL (2013); coalbed methane data are reported in ALL Consulting (2004) and U.S. EPA (2004a). See Chapter 3 for information on the locations of these basins, plays, and formations.

Basin/play/ formation[a]	**Approx. depth (ft [m] below surface)**	**Approx. net thickness (ft [m])**	**Distance between top of production zone and base of treatable water (ft [m])[b]**
Shale plays			
Antrim	600 to 2,200 [200 to 670]	70 to 120 [20 to 37]	300 to 1,900 [90 to 580]
Barnett	6,500 to 8,500 [2,000 to 2,600]	100 to 600 [30 to 200]	5,300 to 7,300 [1,600 to 2,200]
Eagle Ford	4,000 to 12,000 [1,000 to 3,700]	250 [76]	2,800 to 10,800 [850 to 3,290]
Fayetteville	1,000 to 7,000 [300 to 2,000]	20 to 200 [6 to 60]	500 to 6,500 [200 to 2,000]
Haynesville-Bossier	10,500 to 13,500 [3,200 to 4,120]	200 to 300 [60 to 90]	10,100 to 13,100 [3,080 to 3,990]
Marcellus	4,000 to 8,500 [1,000 to 2,600]	50 to 200 [20 to 60]	2,125 to 7,650 [648 to 2,330]
New Albany	500 to 2,000 [200 to 600]	50 to 100 [20 to 30]	100 to 1,600 [30 to 490]
Woodford	6,000 to 11,000 [2,000 to 3,400]	120 to 220 [37 to 67]	5,600 to 10,600 [1,700 to 3,230]
Coalbed methane basins			
Black Warrior (Upper Pottsville)	0 to 3,500 [0 to 1,100]	< 1 to > 70 [< 1 to > 20]	As little as zero[c]
Powder River (Fort Union)	450 to >6,500 [140 to >2,000]	75 [23]	As little as zero[c]
Raton (Vermejo and Raton)	< 500 to > 4,100 [< 200 to > 1,300]	10 to >140 [3 to >43]	As little as zero[c]
San Juan (Fruitland)	550 to 4,000 [170 to 1,000]	20 to 80 [6 to 20]	As little as zero[c]

[a] For coalbed methane, values are given for the specific coal units noted in parentheses.

[b] The base of treatable water is defined at the state level; the information in the table is based on depth data from state oil and gas agencies and state geological survey data.

[c] Formation fluids in producing formations meet the salinity threshold that is used in some definitions of a drinking water resource in at least some areas of the basin. See the discussion after Text Box 6-5 for more information about this definition.

In coalbed methane plays, which are typically shallower than shale gas plays, vertical separation distances can be even smaller. In the Raton Basin of southern Colorado and northern New Mexico, approximately 10% of coalbed methane wells have less than 675 ft (206 m) of separation between the gas wells' perforated intervals and the depth of local water wells. In certain areas of the basin, this distance is less than 100 ft (31 m) (Watts, 2006). In California, nearly half of the hydraulic fracturing has occurred at depths less than about 900 ft (300 m) (CCST, 2015b), with hundreds of wells in the San Joaquin Valley between 150 ft (46 m) and 2,000 ft (600 m) deep (Jackson et al., 2015).

Some hydraulic fracturing operations are conducted within formations containing drinking water resources (Table 6-3). One example of hydraulic fracturing taking place within a geologic formation that is also used as a drinking water source is in the Wind River Basin in Wyoming (Digiulio and Jackson, 2016; WYOGCC, 2014b; Wright et al., 2012). Vertical gas wells in this area target the lower Wind River Formation and the underlying Fort Union Formation, which consist of interbedded layers of sandstones, siltstones, and mudstones. The Wind River Formation also serves as the principal source of domestic, municipal, and agricultural water in this rural area. There are no laterally continuous confining layers of shale in the basin to prevent upward movement of fluids. While flow in the basin generally tends to be downward, local areas of upward flow have been documented (Digiulio and Jackson, 2016). Assessing the relative depths of drinking water resources and hydraulic fracturing operations near Pavillion, Wyoming, Digiulio and Jackson (2016) found that approximately 50% of fracture jobs were within 1,969 ft (600 m) of the deepest domestic drinking water well in the area, and that 10% were within 820 ft (250 m) (Digiulio and Jackson, 2016). Among the wells evaluated by DiGiulio and Jackson, the shallowest fracturing occurred at 1,057 ft (322 m) below ground surface, which is comparable to depths targeted for drinking water withdrawal in the formation. See Text Box 6-5 for more information on Pavillion, Wyoming.

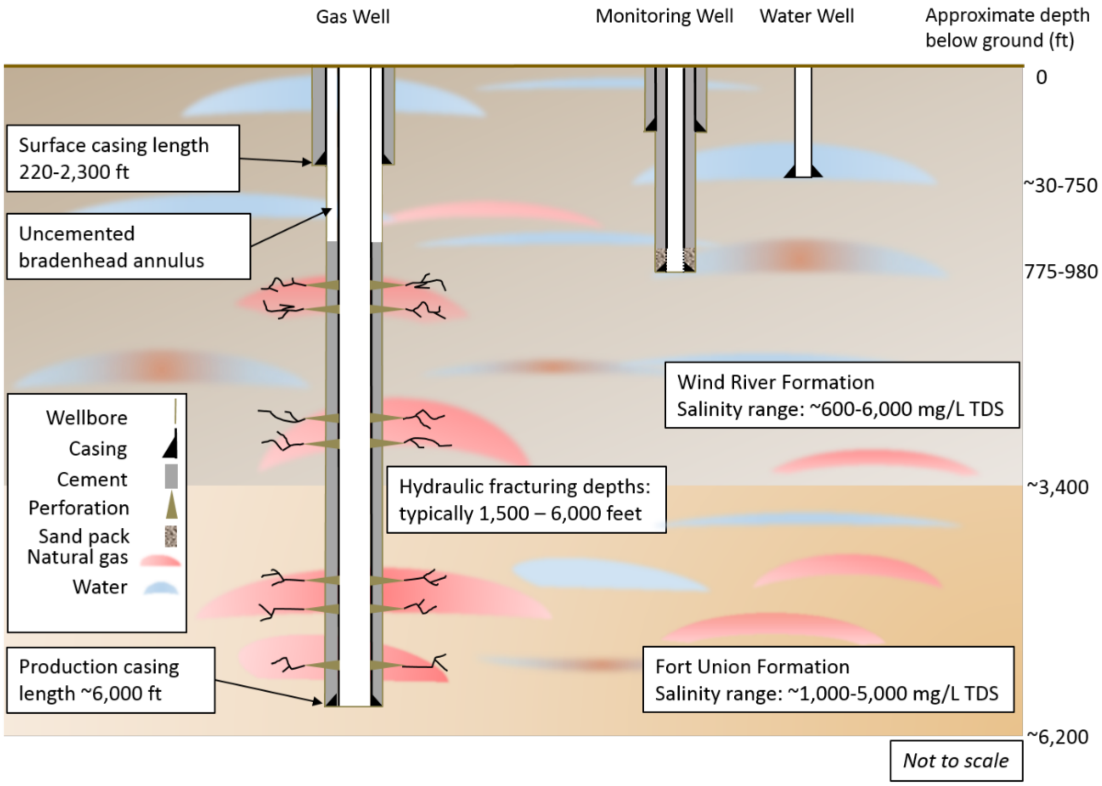
Text Box 6-5. Pavillion, Wyoming.

The Pavillion gas field is located east of the town of Pavillion, Wyoming. In addition to gas production, the field is also home to rural residences that rely on approximately 40 private wells to supply drinking water. The oldest known domestic water well in the field dates to 1934 (AME, 2016). Gas production in the field began in 1960 and, by the 2000s, it had grown to producing from at least 180 wells. Most of these gas wells were drilled since 1990, and approximately 140 to 145 were not plugged as of mid-2016 (AME, 2016; Digiulio and Jackson, 2016).

In the Pavillion gas field the same geologic formation that is used to produce hydrocarbons supplies the area's drinking water (Digiulio and Jackson, 2016). Water wells draw from the Wind River Formation, and gas is extracted from both the Wind River Formation and the underlying Fort Union Formation. The Wind River Formation contains variably permeable strata with lenses of relatively higher permeability rock enriched with natural gas. Water quality is typically freshest nearer the surface, and there is no rock formation acting as a natural barrier to separate the drinking water from hydrocarbons (Digiulio and Jackson, 2016). There is approximately 200 ft (60 m) vertical distance separating the deepest domestic well in the field from the shallowest hydraulic fracturing, although there is approximately 2.5 mi (4 km) lateral distance between them (AME, 2016; Digiulio and Jackson, 2016).

(Text Box 6-5 is continued on the following page.)

Text Box 6-5 (continued). Pavillion, Wyoming.



Following complaints by area residents about changes to their water quality in the mid-2000s, state and federal agencies began a series of investigations, centering on various aspects of the site and supporting differing conclusions about the source and mechanism of the water quality changes (AME, 2016).

Twenty-five pits that were used to dispose of drill cuttings, drilling mud, and spent drilling fluids near some of the water wells were also investigated as a potential source of the groundwater contamination. Based on these evaluations, soil and/or groundwater remediation was performed at approximately six of the pits, no further action was recommended at approximately twelve pits, and the remaining pits are receiving further investigation (AME, 2016).

Samples collected from two monitoring wells at depths between those of the drinking water and active intervals in gas production wells show elevated pH, unexpectedly high potassium values, and several organic constituents, including natural gas, alcohols, phenols, glycols, and benzene, toluene, ethylbenzene, and xylenes (BTEX) (Digiulio and Jackson, 2016). The potential source of chemicals in these two monitoring wells include formation water, contaminants remaining after well construction (AME, 2016) and hydraulic fracturing and other oil and gas activities (Digiulio and Jackson, 2016).

Water samples collected from domestic wells contain dissolved methane and some contain high sodium and sulfate concentrations. Organic chemicals have also been detected in some domestic wells (AME, 2016; Digiulio and Jackson, 2016). These same investigators suspect that pit proximity explains the origin of organic chemicals. In addition, natural gases from intermediate depths not hydraulically fractured are likely moving along some gas wellbores, potentially into zones used for drinking water (AME, 2016).

(Text Box 6-5 is continued on the following page.)

Text Box 6-5 (continued). Pavillion, Wyoming.

Of about 40 production wells at which pressure was measured on the bradenhead annulus between the production and surface casings, about 25% exhibited sustained casing pressure consistent with an ongoing source of gas and/or liquid. Gas samples collected from bradenhead annuli, production tubing and casing, and water wells indicate that the samples have similar gas compositions. This suggests a common origin, which is consistent with long-term migration from a deeper source (AME, 2016; WYOGCC, 2014b).

Production wells may be the source of gas migration, and groundwater immediately around some of the disposal pits has been affected (AME, 2016). However, the investigative reports conclude that identifying the precise source(s) of the water quality issues is challenging due to the lack of comprehensive pre-drilling water quality and other baseline monitoring, the unique hydrogeologic setting, and the difficulty of identifying specific geologic or well pathways.

In other cases, hydraulic fracturing takes place in formations that are not currently being used as sources of drinking water, but that meet the salinity threshold that is used in some definitions of drinking water resources.[1] This occurs in low-salinity coal-bearing formations in the Raton Basin of Colorado (U.S. EPA, 2015k), the San Juan Basin of Colorado and New Mexico (U.S. EPA, 2004a), the Powder River Basin of Montana and Wyoming (as described in Chapter 7), and in several other coalbed methane plays. Hydraulic fracturing in these regions occurs in formations characterized by total dissolved solids (TDS) values substantially lower than the 10,000 mg/L TDS value used in the federal definition of an underground source of drinking water.[2] Across various basins, coalbed methane operations have been reported to occur in formations with 300 to 3,000 mg/L TDS and at depths as shallow as 350 ft (110 m) (U.S. EPA, 2004a). In one field in Alberta, Canada, there is evidence that fracturing in the same formation as a drinking water resource (in combination with mechanical integrity problems; see Section 6.2.2.4) led to gas migration into water wells (Tilley and Muehlenbachs, 2012).

California is another area where hydraulic fracturing occurs in shallow zones with low-salinity groundwater. A study by the California Council on Science and Technology (CCST, 2015b) found that 3% of the hydraulic fracturing in the state occurred within 2,000 ft (600 m) of the surface. In California's San Joaquin Valley, hydraulic fracturing appears to have been conducted in formations with a TDS of less than 1,500 mg/L (CCST, 2014). Another study in California examined the TDS values of water samples taken during oil and gas activities and found that 15% to 19% of the oil and

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[1] For the purposes of this discussion, the federal definition of an underground source of drinking water is used. Pursuant to 40 CFR 144.3, an underground source of drinking water is "an aquifer or its portion which supplies any public water system; or which contains a sufficient quantity of groundwater to supply a public water system; and currently supplies drinking water for human consumption; or contains fewer than 10,000 mg/L TDS; and which is not an exempted aquifer." This definition is used by the EPA's Underground Injection Control Program, which regulates injection wells (but not hydrocarbon production wells).

[2] This salinity threshold is used as a point of comparison only. While the definition of an underground source of drinking water is not exactly the same as the definition of a drinking water resource (and many states have their own definitions of protected drinking water zones), the former provides a useful frame of reference when considering the ability of an aquifer to potentially serve as a source of drinking water.

gas activities in Kern County, California, occurred within zones containing water with less than 3,000 mg/L TDS (Kang and Jackson, 2016).[1]

The overall frequency at which hydraulic fracturing occurs in formations that meet the definition of drinking water resources across the United States is uncertain. Some information, however, that provides insights on the occurrence and geographic distribution of this practice is available. According to the Well File Review, an estimated 0.4% (90) of the 23,200 wells represented in that study had perforations used for hydraulic fracturing that were placed shallower than the base of the protected groundwater resources reported by well operators (U.S. EPA, 2015n).[2] Additional information is available from a database of produced water composition data maintained by the U.S. Geological Survey (USGS). The USGS produced water database contains results from analyses of samples of produced water, including (among other data) samples collected from more than 8,500 oil and gas production wells in unconventional formations (coalbed methane, shale gas, tight gas, and tight oil) within the contiguous United States.[3] Just over 5,000 of these samples, which were obtained from wells located in 37 states, reported TDS concentrations. Because the database does not track whether samples were from wells that were hydraulically fractured, the EPA selected samples from wells that were more likely to have been hydraulically fractured by restricting samples to those collected in 1950 or later and to those that were collected from wells producing from tight gas, tight oil, shale gas, or coalbed methane formations.[4] This yielded 1,650 samples from wells located in Alabama, Colorado, North Dakota, Utah, and Wyoming, with TDS concentrations ranging from approximately 90 mg/L to 300,000 mg/L.[5] Of the 1,650 samples, approximately 1,200 (from wells in Alabama, Colorado, Utah, and Wyoming) reported TDS concentrations at or below 10,000 mg/L, indicating that hydraulic fracturing there may have occurred within formations that meet the salinity threshold that is used in some definitions of a drinking water resource. This analysis, in conjunction with the result from the Well File Review, suggests that the overall frequency of this occurrence is relatively low, but is concentrated in particular areas of the country.

6.3.2.1 Flow of Fluids Out of the Production Zone

One potential pathway for fluid migration out of the production formation into drinking water resources is advective or dispersive flow of injected or displaced fluids through the formation matrix. In this scenario, fluids (such as those “lost” to leakoff, which are not recovered during

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[1] Kern County accounts for 85 percent of the hydraulic fracturing that occurs in California (CCST, 2015b).

[2] 90 wells (95% confidence interval: 10 – 300 wells).

[3] The EPA used the USGS Produced Water Geochemical Database Version 2.1 (USGS database v 2.1) for this analysis (http://energy.cr.usgs.gov/prov/prodwat/). The database is comprised of produced water samples compiled by the USGS from 25 individual databases, publications, or reports.

[4] See Chapter 3, Text Box 3-1, which describes how commercial hydraulic fracturing began in the late 1940s.

[5] For this analysis, the EPA assumed that produced water samples collected in 1950 or later from shale gas, tight oil, and tight gas wells were from wells that had been hydraulically fractured. To estimate which coal bed methane wells had been hydraulically fractured, the EPA matched API numbers from coal bed methane wells in the USGS database v 2.1 to the same API numbers in the commercial database DrillingInfo, in which hydraulically fractured wells had been identified by the EPA using the assumptions described in Section 3.4. Wells with seemingly inaccurate (i.e., less than 12 digit) API numbers were also excluded. Only coalbed methane wells from the USGS database v 2.1 that matched API numbers in the DrillingInfo database were retained for this analysis.

production) would flow through the pore spaces of rock formations, moving from the production zone into other formations. In deep, low-permeability shale and tight gas settings and where induced fractures are contained within the production zone, flow through the production formation has generally been considered an unlikely pathway for migration into drinking water resources (Jackson et al., 2013d).

Leakoff into shale gas formations can be as high as 90% or more of the injected volume (Table 7-2). The actual amount of leakoff depends on multiple factors, including the amount of injected fluid, the concentration of different components in the fracture fluid, the hydraulic properties of the reservoir (e.g., permeability), the composition of the formation matrix, the capillary pressure near the fracture faces, and the period of time the well is shut in following hydraulic fracturing before the start of production (Kim et al., 2014; Byrnes, 2011).[1,2] Researchers generally agree that the subsequent flow of this "lost" leakoff fluid is controlled or limited by processes such as imbibition by capillary forces and adsorption onto clay minerals (Dutta et al., 2014; Dehghanpour et al., 2013; Dehghanpour et al., 2012; Roychaudhuri et al., 2011) and osmotic forces (Zhou, 2016; Wang and Rahman, 2015; Engelder et al., 2014).[3,4] It has been suggested that these processes can sequester the fluids in the producing formations permanently or for geologic time scales (Engelder et al., 2014; Engelder, 2012; Byrnes, 2011). Birdsell et al. (2015b) made quantitative estimates of the amount of fluid that could be imbibed in shale formations. Their results indicate that between 15% and 95% of injected fluid volumes may be imbibed in shale gas systems, while amounts are lower in shale oil systems (3% to 27% of injected volumes). In modeling investigations, O'Malley et al. (2015) found that it is likely that most hydraulic fracturing fluid that does not flow back is stored in rock pore spaces (i.e., having displaced the gas that was present there) and not fractures. The amount that can be stored in fractures is highly dependent on the effective interconnected pore lengths.

If the injected fluid is not sequestered in the immediate vicinity of the fracture network, migration into drinking water resources would likely require a substantial upward hydraulic gradient (e.g., due to the pressures introduced during injection for hydraulic fracturing), particularly for brine that is denser than the groundwater in the overlying formations (Flewelling and Sharma, 2014). In the presence of natural gas, buoyancy of the less dense gas could potentially provide an upward flux (Vengosh et al., 2014). However, Flewelling and Sharma (2014) indicated that pressure

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[1] Relative permeability is a dimensionless property allowing for the comparison of the different abilities of fluids to flow in multiphase settings. If a single fluid is present, its relative permeability is equal to 1, but the presence of multiple fluids generally inhibits flow and decreases the relative permeability (Schlumberger, 2014).

[2] Shutting in the well after fracturing allows fluids to move farther into the formation, resulting in a higher gas relative permeability near the fracture surface and improved gas production (Bertoncello et al., 2014).

[3] Imbibition is the displacement of a nonwetting fluid (i.e., gas) by a wetting fluid (typically water). The terms wetting or nonwetting refer to the preferential attraction of a fluid to the surface. In typical reservoirs, water preferentially wets the surface, and gas is nonwetting. Capillary forces arise from the differential attraction between immiscible fluids and solid surfaces; these are the forces responsible for capillary rise in small-diameter tubes and porous materials. These definitions are adapted from Dake (1978).

[4] The contrast in water activity between brine and fresh water generates very substantial osmotic pressure differences that will drive fluids into the shale matrix. The osmosis process requires a semi-permeable membrane and a concentration gradient to allow the solvent to pass through it. The clay in the shale formation can provide a function similar to a membrane (Zhou, 2016).

perturbations due to hydraulic fracturing operations are localized to the immediate vicinity of the fractures, due to the very low permeabilities of shale formations; this means that hydraulic fracturing operations are unlikely to generate sufficient pressure to drive fluids into shallow drinking water zones. Some natural conditions could also create an upward hydraulic gradient in the absence of any effects from hydraulic fracturing. However, these natural mechanisms have been found to cause very low flow rates over very long distances, yielding extremely small vertical fluxes in sedimentary basins. These translate to some estimated travel times of 100,000 to 100,000,000 years across a 328 ft (100 m) thick layer with about 0.01 nD (1×10^{-23} m^2) permeability (Flewelling and Sharma, 2014). In an area of the Permian Basin with over-pressured source rocks, Engle et al. (2016) concluded that chemical, isotopic, and pressure data suggest that there is little potential for vertical fluid migration to shallow zones in the absence of pathways such as improperly abandoned wells (Section 6.3.2.3).

To account for the combined effect of capillary imbibition, well operation, and buoyancy in upward fluid migration, Birdsell et al. (2015a) conducted a numerical analysis over five phases of activity at a hypothetical Marcellus-like hydraulic fracturing site: a pre-drilling steady state, the injection of fluids, a shut-in period, production, and the continued migration of hydraulic fracturing fluids after the well is plugged and abandoned. They quantified how much hydraulic fracturing fluid flows back up the well after fracturing, how much reaches overlying aquifers, and how much is permanently sequestered by capillary imbibition (which is treated as a sink term). Their results affirmed that, without a pathway such as a permeable fault or leaky wellbore, it is very unlikely that hydraulic fracturing fluid from a deep shale could reach an overlying aquifer. However, the study did indicate that upward migration on the order of 328 ft (100 m) could occur through relatively low-permeability overburden, even if no discrete, permeable pathway exists.

6.3.2.2 Fracture Overgrowth out of the Production Zone

Fractures extending out of the intended production zone into another formation, or into an unintended zone within the same formation, could provide a potential fluid migration pathway into drinking water resources (Jackson et al., 2013d). This migration could occur either through the fractures themselves or in connection with other permeable subsurface features or formations (Figure 6-7). Such “out-of-zone fracturing” is undesirable from a production standpoint and may occur as a result of inadequate reservoir characterization or fracture treatment design (Eisner et al., 2006). Some researchers have noted that fractures growing out of the targeted production zone could potentially contact other formations, such as higher conductivity sandstones or conventional hydrocarbon reservoirs, which may create an additional pathway for migration into a drinking water resource (Reagan et al., 2015). In addition, fractures growing out of the production zone could potentially intercept natural, preexisting fractures (discussed in Section 6.3.2.4) or active or abandoned wells near the well where hydraulic fracturing is performed (discussed in Section 6.3.2.3).

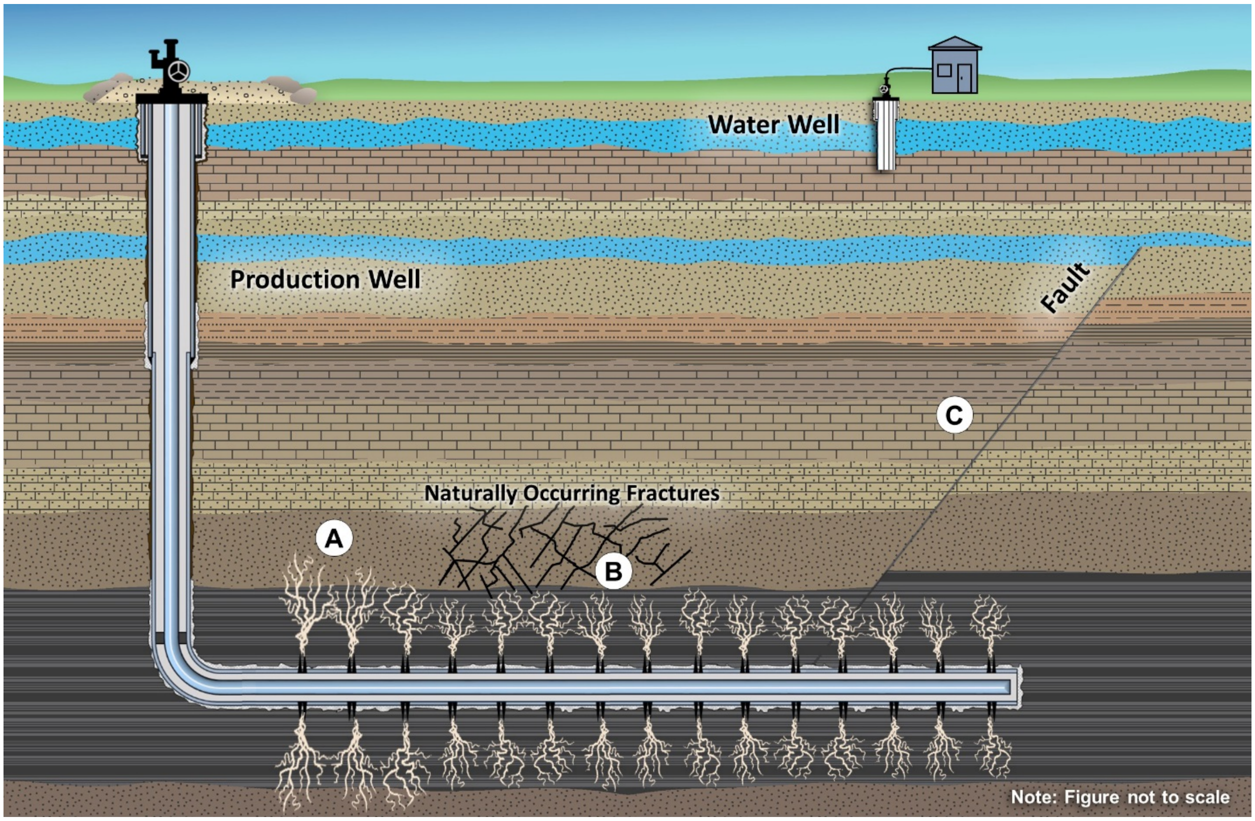

Figure 6-7. Conceptualized depiction of potential pathways for fluid movement out of the production zone: (a) induced fracture overgrowth into over- or underlying formations; (b) induced fractures intersecting natural fractures; and (c) induced fractures intersecting a permeable fault.

The fracture's geometry (Section 6.3.1) affects its potential to extend beyond the intended zone and serve as a pathway to drinking water resources. Vertical heights of fractures created during hydraulic fracturing operations have been measured in several U.S. shale plays, including the Barnett, Woodford, Marcellus, and Eagle Ford, using microseismic monitoring and tiltmeters (Fisher and Warpinski, 2012). These data indicate typical fracture heights extending from tens to hundreds of feet.[1] Davies et al. (2012) analyzed this data set and found that the maximum fracture height was 1,929 ft (588 m) and that 1% of the fractures had a height greater than 1,148 ft (350 m). This may raise some questions about fractures being contained within the producing formation, as some Marcellus fractures were found to extend vertically for at least 1,500 ft (460 m), while the maximum thickness of the formation is generally 350 ft (110 m) or less (MCOR, 2012). However, the majority of fractures within the Marcellus were found to have heights less than 328 ft (100 m), suggesting limited possibilities for fracture overgrowth exceeding the separation between shale reservoirs and shallow aquifers (Davies et al., 2012). This is consistent with modeling results found by Kim and Moridis (2015) and others, as described below. Where the producing formation is not

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[1] As described in Section 6.3.1, microseismic data represent the small amounts of seismic energy generated during subsurface fracturing. The Fisher and Warpinski dataset includes the top and bottom depths of mapped fracture treatments in the four shale plays mentioned, giving the maximum propagation length.

continuous horizontally, the lateral extent of fractures may also become important. For example, in the Fisher and Warpinski (2012) data set, fractures were found to extend to horizontal lengths greater than 1,000 ft (300 m).

Results of National Energy Technology Laboratory (NETL) research in Greene County, Pennsylvania, are generally consistent with those reported in the Fisher and Warpinski (2012) data set. Microseismic monitoring was used at six horizontal Marcellus Shale wells to identify the maximum upward extent of brittle deformation (i.e., rock breakage) caused by hydraulic fracturing (Hammack et al., 2014). At three of the six wells, fractures extending between 1,000 and 1,900 ft (300 and 580 m) above the Marcellus Shale were identified. Overall, approximately 40% of the microseismic events occurred above the Tully Limestone, the formation overlying the Marcellus Shale. The microseismic data suggest that fracture propagation occurs above the Tully Limestone, which is sometimes referred to as an upper barrier to hydraulic fracture growth (Hammack et al., 2014). However, all microseismic events were at least 5,000 ft (2,000 m) below drinking water aquifers, as the Marcellus Shale is one of the deepest shale plays (Table 6-3), and no impacts to drinking water resources or another local gas-producing interval were identified. See Text Box 6-6 for more information on the Greene County site.

Text Box 6-6. Monitoring at the Greene County, Pennsylvania, Hydraulic Fracturing Test Site.

Monitoring performed at the Marcellus Shale test site in Greene County, Pennsylvania, evaluated fracture height growth and zonal isolation during and after hydraulic fracturing operations (Hammack et al., 2014). The site has six horizontally drilled wells and two vertical wells that were completed into the Marcellus Shale. Pre-fracturing studies of the site included a 3D seismic survey to identify faults, pressure measurements, and baseline sampling for isotopes; drilling logs were also run. Hydraulic fracturing occurred April 24 to May 6, 2012, and June 4 to 11, 2012. Monitoring at the site included the following:

- **Microseismic monitoring** was conducted during four of the six hydraulic fracturing jobs on the site, using geophones placed in the two vertical Marcellus Shale wells. These data were used to monitor fracture height growth above the six horizontal Marcellus Shale wells during hydraulic fracturing.
- **Pressure and production data** were collected from a set of existing vertical gas wells completed in Upper Devonian/Lower Mississippian zones 3,800 to 6,100 ft (1,200 to 1,900 m) above the Marcellus. Data were collected during and after the hydraulic fracturing jobs and used to identify any communication between the fractured areas and the Upper Devonian/Lower Mississippian rocks.
- **Chemical and isotopic analyses** were conducted on gas and water produced from the Upper Devonian/Lower Mississippian wells. Samples were analyzed for stable isotope signatures of hydrogen, carbon, and strontium and for the presence of perfluorocarbon tracers used in 10 stages of one of the hydraulic fracturing jobs to identify possible gas or fluid migration to overlying zones (Sharma et al., 2014a; Sharma et al., 2014b).

As of September 2014, no evidence was found of gas or brine migration from the Marcellus Shale (Hammack et al., 2014), although longer-term monitoring is necessary to confirm that no impacts to overlying zones have occurred (Zhang et al., 2014a).

Similarly, in Dunn County, North Dakota, there is evidence suggestive of out-of-zone fracturing in the Bakken Shale (U.S. EPA, 2015i). At the Killdeer site (Section 6.2.2.1), hydraulic fracturing fluids and produced water were released during a rupture of the casing at the Franchuk 44-20 SWH well. Water quality characteristics at two monitoring wells located immediately downgradient of the Franchuk well reflected a mixing of local Killdeer Aquifer water with deep formation brine. Ion and isotope ratios used for brine fingerprinting suggest that Madison Group formations (which directly overlie the Bakken in the Williston Basin) were the source of the brine observed in the Killdeer Aquifer, and the authors concluded that this provides evidence for out-of-zone fracturing (U.S. EPA, 2015i). Industry experience also indicates that out-of-zone fracturing could be fairly common in the Bakken and that produced water from many Bakken wells has Madison Group chemical signatures (Arkadakskiy and Rostron, 2013; Arkadakskiy and Rostron, 2012; Peterman et al., 2012).

Fracture growth from a deep formation to a near-surface aquifer is generally considered to be limited by layered geological environments and other physical constraints (Fisher and Warpinski, 2012; Daneshy, 2009). For example, differences in in-situ stresses in layers above and below the production zone can restrict fracture height growth in sedimentary basins (Fisher and Warpinski, 2012). High-permeability layers near hydrocarbon-producing zones can reduce fracture growth by acting as a “thief zone” into which fluids can migrate, or by inducing a large compressive stress that acts on the fracture (de Pater and Dong, 2009, as cited in Fisher and Warpinski, 2012). Although thief zones may prevent fractures from reaching shallower formations or growing to extreme vertical lengths, they do allow fluids to migrate out of the production zone into receiving formations, which could (depending on site-specific conditions) potentially contain drinking water resources. A volumetric argument has also been used to discuss limits of vertical fracture growth; that is, the volumes of fluid needed to sustain fracture growth beyond a certain height would be unrealistic (Fisher and Warpinski, 2012). However, as described in Section 6.3.1, fracture volume can be greater than the volume of injected fluid due to the effects of pressurized water combined with the effects of gas during injection (Kim and Moridis, 2015). Nevertheless, some numerical investigations suggest that, unless unrealistically high pressures and injection rates are applied to an extremely weak and homogeneous formation that extends up to the near surface, hydraulic fracturing generally induces stable and finite fracture growth in a Marcellus-type environment and fractures are unlikely to extend into drinking water resources (Kim and Moridis, 2015).

Modeling studies have identified other factors that can affect the containment of fractures within the producing formation. As discussed above, additional numerical analysis of fracture propagation during hydraulic fracturing has demonstrated that contrasts in the geomechanical properties of rock formations can affect fracture height containment (Gu and Siebrits, 2008) and that geological layers present within shale gas reservoirs can limit vertical fracture propagation (Kim and Moridis, 2015). In another modeling study, Myshakin et al. (2015) applied a multi-layered geologic model to study whether fracture growth can extend upward through overlying strata and reach drinking water resources in a Marcellus Shale-type environment. Most fractures were predicted either to extend upward to the overlying layer (about 46%) or to remain in the Marcellus Shale (about 34%). About 20% of the fractures were predicted to extend further upward into or above the overlying limestone. These model results are consistent with microseismic events observed above the Tully Limestone in Greene County, Pennsylvania (Hammack et al., 2014), where the fracture heights ranged from 0 to 700 ft (0 to 200 m) and most of the fractures terminated less than 100 ft (31 m) above the top of the Marcellus.

If fractures were to propagate from the production zone to drinking water resources, other factors would need to be in place for fluid migration to occur. Using a numerical simulation, Reagan et al. (2015) investigated potential short-term migration of gas and water between a shale or tight gas formation and a shallower groundwater unit, assuming that a permeable pathway already exists between the two formations. Note that, for the purposes of this study, the pathway was assumed to be pre-existing, and Reagan et al. (2015) did not model the hydraulic fracturing process itself.

The subsurface system evaluated in the Reagan et al. (2015) modeling investigation included a horizontal well used for hydraulic fracturing and gas production, a connecting pathway between the producing formation and the aquifer, and a shallow vertical water well in the aquifer (Figure 6-7). The parameters and scenarios used in the study are shown in Table 6-4; two vertical separation distances between the producing formation and the aquifer were investigated, along with a range of production zone permeabilities and other variables used to describe four production scenarios. The horizontal well was assigned a constant bottomhole pressure of half the initial pressure of the target reservoir, not accounting for any over-pressurization from hydraulic fracturing. (As noted in Section 6.3.2.1, over-pressurization during hydraulic fracturing can create an additional driving force for upward migration.) In the simulation, migration was assessed immediately after hydraulic fracturing and for up to a 2-year simulation period representing the production stage.

Results of this modeling investigation indicate a generally downward water flow within the connecting fracture (i.e., flow from the aquifer through the connecting fracture into the hydraulically induced fractures in the production zone) with some upward migration of gas (Reagan et al., 2015). In certain simulated cases, gas breakthrough (the appearance of gas at the base of the drinking water aquifer) was also observed. The key parameter affecting migration of gas into the aquifer was the production regime, particularly whether gas production (which drives migration toward the production well) was occurring in the reservoir. Simulations that included a producing gas well showed only a few instances of breakthrough, while simulations without gas production (i.e., that assumed the well was shut-in) tended to result in breakthrough. When gas breakthrough did occur, the breakthrough times ranged from minutes to 20 days. However, in all cases, the gas escape was limited in duration and scope, because the amount of gas available for immediate migration toward the shallow aquifer was limited to that initially stored in the hydraulically induced fractures after the stimulation process and prior to production. These simulations indicate that the target reservoir may not be able to replenish the gas that was available for migration prior to production.

Based on the results of the Reagan et al. (2015) modeling study, gas production from the reservoir appears likely to mitigate gas migration, both by reducing the amount of available gas and depressurizing the induced fractures (which counters the buoyancy of any gas that may escape from the production zone into the connecting fracture). Production at the gas well also creates pressure gradients that drive a downward flow of water from the aquifer via the fracture into the producing formation, increasing the amount of water produced at the gas well. Furthermore, the effective permeability of the connecting feature is reduced during water (downward) and gas (upward) counter-flow within the fracture, further retarding the upward movement of gas or allowing gas to dissolve into the downward flow. However, Reagan et al. (2015) did find an increased potential for gas release from the producing formation in cases where there is no gas production following hydraulic fracturing. The potential for gas migration during shut-in periods following hydraulic fracturing and prior to production may be more significant, especially when out-of-zone fractures are formed. Without the effects of production, gas can rise via buoyancy, with any downward-flowing water from the aquifer displacing the upward-flowing gas.

Reagan et al. (2015) also found that the permeability of a connecting fault or fracture may be an important factor affecting the potential upward migration of gas (although not as significant as the production regime). For the cases where gas escaped from the production zone, the maximum volume of migrating gas depended upon the permeability of the connecting feature: the higher the permeability, the larger the volume. The modeling results also showed that lower permeabilities delay the downward flow of water from the aquifer, allowing the trace amount of gas that entered into the fracture early in the modeled period to reach the aquifer, which was otherwise predicted to dissolve in the water flowing downward in the feature. Similarly, the permeabilities of the target reservoir, fracture volume, and the separation distance were found to affect gas migration, because they affected the initial amount of gas stored in the hydraulically induced fractures. In contrast, the permeability of the drinking water aquifer was not found to be a significant factor in the assessment.

Table 6-4. Modeling parameters and scenarios investigated by Reagan et al. (2015).

This table illustrates the range of parameters included in the Reagan et al. (2015) modeling study. See Figure 6-7, Figure 6-8, and Figure 6-9 for conceptualized illustrations of these scenarios.

Model parameter or variable	Values investigated in model scenarios
All scenarios	
Lateral distance from connecting feature to water well	328 ft (100 m)
Vertical separation distance between producing formation and drinking water aquifer	656 ft (200 m); 2,625 ft (800 m)
Producing formation permeability range	1 nD (1 x 10^{-21} m^2); 100 nD (1 x 10^{-19} m^2); 1 μD (1 x 10^{-18} m^2)
Drinking water aquifer permeability	0.1 D (1 x 10^{-13} m^2); 1 D (1 x 10^{-12} m^2)
Initial conditions	Hydrostatic
Production well bottom hole pressure	Half of the initial pressure of the producing formation (not accounting for over-pressurization from hydraulic fracturing)
Production regime	Production at both the water well and the gas well; Production at only the water well; Production at only the gas well; No production

Model parameter or variable	Values investigated in model scenarios
Fracture pathway scenarios	
Connecting feature permeability	1 D (1 x 10^{-12} m^2); 10 D (1 x 10^{-11} m^2); 1,000 D (1 x 10^{-9} m^2)
Offset well pathway scenarios	
Lateral distance from production well to offset well	33 ft (10 m)
Cement permeability of offset well	1 µD (1 x 10^{-18} m^2); 1 mD (1 x 10^{-15} m^2); 1 D (1 x 10^{-12} m^2); 1,000 D (1 x 10^{-9} m^2)

6.3.2.3 Migration via Fractures Intersecting with Offset Wells and Other Artificial Structures

Another potential pathway for fluid migration is one in which hydraulic fracturing fluids or displaced subsurface fluids move through newly created fractures into an offset well or its fracture network, resulting in a process called well communication (Jackson et al., 2013d). The offset well can be an abandoned (i.e., plugged), inactive, or actively producing well. In addition, if the offset well has also been used for hydraulic fracturing, the fracture networks of the two wells might intersect. The situation where hydraulic fractures propagate to (and inject fluid into and/or cause pressure increases in) other existing wells or hydraulic fractures is referred to as a "frac hit" and is known to occur in areas with a high density of wells (Jackson et al., 2013a).

Frac hits can be more common in unconventional production settings compared to conventional production settings, due to the closer/denser well spacing (King and Valencia, 2016). Figure 6-8 provides a schematic to illustrate fractures that intercept an offset well, and Figure 6-9 depicts (in a simplified illustration) how the fracture networks of two such wells might intersect. This can be a particular concern in shallower formations, where the local least principal stress is vertical (resulting in more horizontal fracture propagation), and in situations where there are drinking water wells in the same formation as wells used for hydraulic fracturing.

Instances of well communication have been known to occur and are described in well records and the oil and gas literature. For example, an analysis of operator data collected by the New Mexico Oil Conservation Division (NM OCD) in 2013−2014 identified 120 instances of well communication in the San Juan Basin between 2007 and 2013 (Vaidyanathan, 2014). In some cases, well communication incidents have led to documented production and/or environmental problems. A study in the Barnett Shale noted two cases of well communication, one with a well 1,100 ft (340 m) away and the other with a well 2,500 ft (760 m) away from the initiating well; ultimately, one of the offset wells had to be re-fractured because the well communication halted production (Craig et al., 2012). In some cases, the fluids that intersect the offset well flow up the wellbore and spill onto the surface. In its report *Review of State and Industry Spill Data: Characterization of Hydraulic Fracturing-Related Spills*, the EPA (2015m) recorded 10 incidents in which fluid spills were attributed to well communication events (see Text Box 5-10 for more information on this effort).[1] The Well File Review (U.S. EPA, 2016c) reports that 1% of the wells (an estimated 280 wells) represented in the study reported a frac hit, where the hydraulic fracturing operation documented in the Well File Review led to communication with a nearby well.[2] (It was not possible to determine whether fluids reached protected groundwater resources during these frac hits based on information in the well files.) While the subsurface effects of frac hits have not been extensively studied, these cases demonstrate the possibility of fluid migration via communication with other wells and/or their fracture networks. More generally, well communication events can indicate fracture behavior that was not intended by the treatment design.

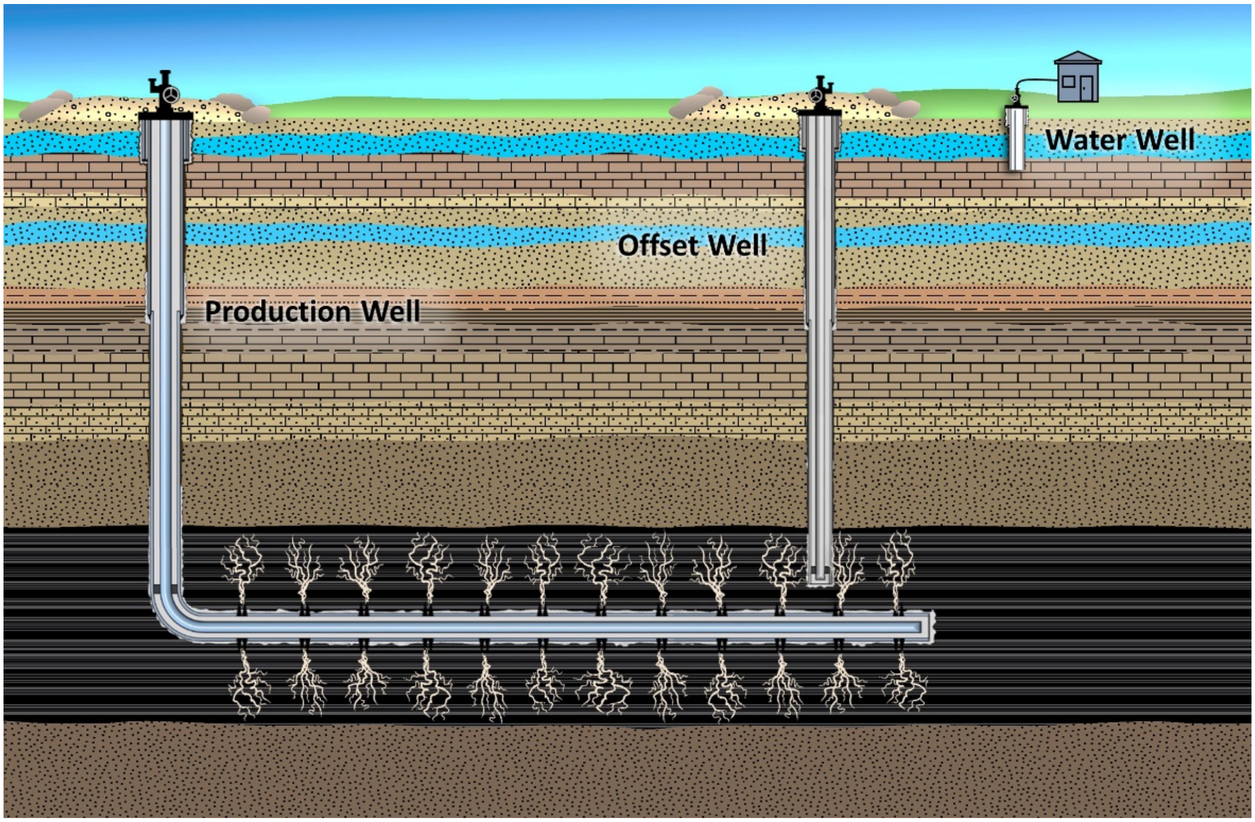

Figure 6-8. Induced fractures intersecting an offset well (in a production zone, as shown, or in overlying formations into which fracture growth may have occurred).

This image shows a conceptualized depiction of potential pathways for fluid movement out of the production zone (not to scale).

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[1] These spills are represented by line numbers 163, 236, 265, 271, 286, 287, 375, 376, 377, and 380 in Appendix B of U.S. EPA (2015m).

[2] 280 wells (95% confidence interval: 240 – 320 wells).

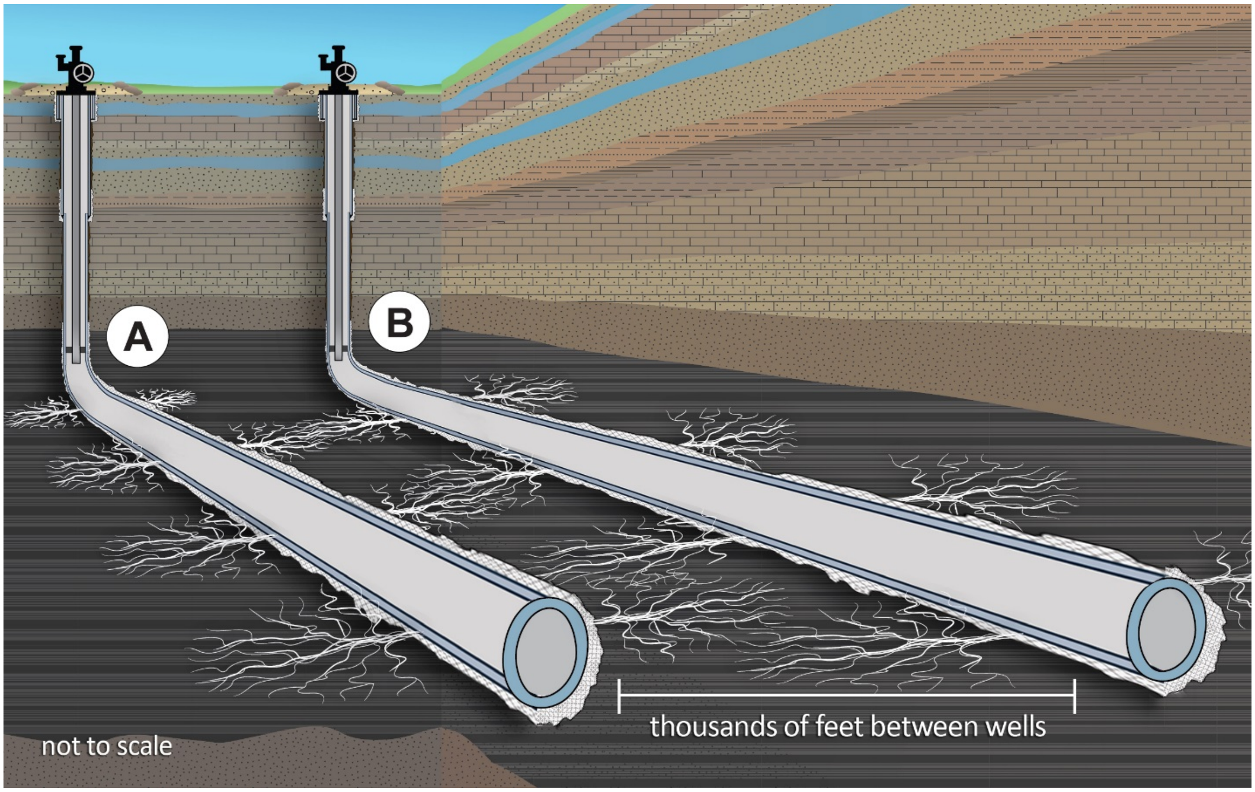

Figure 6-9. Well communication (a frac hit).
This image shows a conceptualized depiction of the fractures of a newly fractured well (Well A) intersecting the existing fracture network created during a previous hydraulic fracturing operation in an offset well (Well B). Evidence of this interaction may be observed in the offset well as a pressure change, lost production, and/or introduction of new fluids. Depending on the condition of the offset well, this can result in fluid being spilled onto the surface, rupturing of cement and/or casing and hydraulic fracturing fluid leaking into subsurface formations, and/or fluid flowing out through existing flaws in the casing and/or cement. (Figure is not to scale.)

A well communication event is usually observed at the offset well as a pressure spike, due to the elevated pressure from the originating well, or as an unexpected drop in the production rate (Lawal et al., 2014; Jackson et al., 2013a). Ajani and Kelkar (2012) performed an analysis of frac hits in the Woodford Shale in Oklahoma, studying 179 wells over a 5-year period. The authors used fracturing records from the newly completed wells and compared them to production records from surrounding wells. The authors assumed that sudden changes in production of gas or water coinciding with fracturing at a nearby well were caused by communication between the two wells, and increased water production at the surrounding wells was assumed to be caused by hydraulic fracturing fluid flowing into these offset wells. The results of the Oklahoma study showed that 24 wells had decreased gas production or increased water production within 60 days of the initial gas production at the nearby fractured well. A total of 38 wells experienced decreased gas or increased water production up to a distance of 7,920 ft (2,410 m), which the study authors defined as the distance between the midpoints of the laterals; 10 wells saw increased water production from as far away as 8,422 ft (2,567 m). In addition, one well showed a slight increase in gas production rather than a decrease.[1]

Other studies of well communication events have relied on similar information. In the NM OCD operator data set, the typical means of detecting a well communication event was through pressure changes at the offset well, production lost at the offset well, and/or fluids found in the offset well. In some instances, well operators determined that a well was producing fluid from two different formations, while in one instance, the operator identified a potential well communication event due to an increase in production from the offset well (Vaidyanathan, 2014). In another study, Jackson et al. (2013a) found that the decrease in production due to well communication events was much greater in lower permeability reservoirs. The authors note an example where two wells 1,000 ft (300 m) apart communicated, reducing production in the offset well by 64%. These results indicate that the subsurface interactions of well networks or complex hydraulics driven by each well at a densely populated (with respect to wells) area are important factors to consider for the design of hydraulic fracturing treatments and other aspects of oil and gas production.

The key factor affecting the likelihood of a well communication event and the impact of a frac hit is the location of the offset well relative to the well where hydraulic fracturing was conducted (Ajani and Kelkar, 2012). In the Ajani and Kelkar (2012) analysis, the likelihood of a communication event was less than 10% in wells more than 4,000 ft (1,000 m) apart, but rose to nearly 50% in wells less than 1,000 ft (300 m) apart. Well communication was also much more likely with wells drilled from the same pad. The affected wells were found to be in the direction of maximum horizontal stress in the field, which correlates with the expected direction of fracture propagation. Modeling work by Myshakin et al. (2015) is generally consistent with these results, indicating that the risk of fluid movement through pre-existing wellbores or open faults is negligible unless hydraulic fractures are located very close to these features.[2]

Statistical modeling by Montague and Pinder (2015) investigated the probability that a hypothetical new well used for hydraulic fracturing within the area of New York underlain by the Marcellus Shale would intersect an existing wellbore. The results indicated that this probability would be from 0 to 3.45%. The model incorporated the depth of the hypothetical new well, the vertical growth of induced fractures, and the depth and locations of existing nearby wells. The model also assumed that the existing wells are vertical and fracture growth is not impacted by nearby wells or existing fractures. However, the authors concluded that the inclusion of horizontal wells within the data set could increase the chance of intersection with induced fractures.

Well communication may be more likely to occur where there is less resistance to fracture growth. Such conditions may be related to existing production operations (e.g., where previous hydrocarbon extraction has reduced the pore pressure, changed stress fields, or affected existing fracture networks) or the existence of high-permeability rock units (Jackson et al., 2013a). As Ajani and Kelkar (2012) found in the Woodford Shale, one of the deepest major shale plays (Table 6-3), induced fractures tend to enter portions of the reservoir that have already been fractured as

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[1] The numbers of wells cited in the study reflect separate analyses, and the numbers cited are not additive.

[2] In the Myshakin et al. (2015) paper, the authors do not quantify or explain what is meant by "very close."

opposed to entering previously unfractured rocks, ultimately causing interference in offset wells. Mukherjee et al. (2000) described this tendency for asymmetric fracture growth toward depleted areas in low-permeability gas reservoirs due to pore pressure depletion from production at offset wells. The authors note that pore pressure gradients in depleted zones would affect the subsurface stresses. Therefore, depending on the location of the new well with respect to depleted zone(s) and the orientation of the existing induced fractures, the newly created fracture can be asymmetric, with only one wing of the fracture extending into the depleted area and developing significant length and conductivity (Mukherjee et al., 2000). The extent to which the depleted area affects fracturing depends on factors such as cumulative production, pore volume, hydrocarbon saturation, effective permeability, and the original reservoir or pore pressure (Mukherjee et al., 2000). Similarly, high-permeability rock types acting as thief zones may also cause preferential fracturing due to a higher leakoff rate into these layers (Jackson et al., 2013a).

In addition to location, the potential for impact on a drinking water resource also depends on the condition of the offset well. (See Section 6.2 for information on the mechanical integrity of well components.) In their analysis, Ajani and Kelkar (2012) found a correlation between well communication and well age: older wells were more likely to be affected. If the cement in the annulus between the casing and the formation is intact and the well components can withstand the stress exerted by the pressure of the fluid, nothing more than an increase in pressure and extra production of fluids would occur during a well communication event. However, if the offset well is not able to withstand the pressure of the hydraulic fracturing fluid, well components could fail (Figure 6-4), allowing fluid to migrate out of the well.

The highest pressures most hydraulic fracturing wells will face during their life spans occur during the process of fracturing (Section 3.3). In some cases, temporary equipment is installed in wells during fracturing to protect the well against the increased pressure. Therefore, many producing wells may not be designed to withstand pressures typical of hydraulic fracturing (Enform, 2013) and can experience problems when fracturing occurs in nearby wells. Depending on the location of the weakest point in the offset well, this could result in fluid being spilled onto the surface; rupturing of cement and/or casing and hydraulic fracturing fluid leaking into subsurface formations; and/or fluid flowing out through existing flaws in the casing and/or cement. (See Chapters 5 and 7 for additional information on how such spills can affect drinking water resources.) For example, a documented well communication event near Innisfail, Alberta, Canada (Text Box 6-7) occurred when several well components failed, because they were not rated to handle the increased pressure caused by the well communication (ERCB, 2012). In addition, if the fractures were to intersect an uncemented portion of the wellbore, the fluids could potentially migrate into formations that are uncemented along the wellbore.

In older wells near a hydraulic fracturing operation, plugs and cement can degrade over time; in some cases, abandoned wells may never have been plugged properly. Before the 1950s, most well plugging efforts were focused on preventing water from the surface from entering oil fields. As a result, many wells from that period were abandoned with little or no cement (NPC, 2011b). This can be a significant issue in areas with legacy (i.e., historic) oil and gas exploration and when wells are re-entered and hydraulically fractured (or re-fractured) to increase production in a reservoir. In one study, 18 of 29 plugged and abandoned wells in Quebec were found to show signs of leakage (Council of Canadian Academies, 2014). Similarly, a PA DEP report cited three cases where migration of natural gas had been caused by well communication events with old, abandoned wells, including one case where private drinking water wells were affected (PA DEP, 2009c). In Tioga County, Pennsylvania, following hydraulic fracturing of a shale gas well, an abandoned well nearby produced a 30 ft (9 m) geyser of brine and gas for more than a week (Dilmore et al., 2015).

Text Box 6-7. Well Communication at a Horizontal Well near Innisfail, Alberta, Canada.

In most cases, well communication during fracturing results in a pressure surge accompanied by a drop in gas production and additional flow of produced water or hydraulic fracturing fluid at an offset well. However, if the offset well is not capable of withstanding the high pressures of fracturing, more significant damage can occur.

In January 2012, fracturing at a horizontal well near Innisfail in Alberta, Canada, caused a surface spill of fracturing and formation fluids at a nearby operating vertical oil well. According to the investigation report by the Alberta Energy Resources Conservation Board (ERCB, 2012), pressure began rising at the vertical well less than two hours after fracturing ended at the horizontal well.

Several components of the vertical well facility—including surface piping, discharge hoses, fuel gas lines, and the pressure relief valve associated with compression at the well—were not rated to handle the increased pressure and failed. Ultimately, the spill released, in addition to gas, an estimated 19,816 gal (75,012 L^3) of hydraulic fracturing fluid, brine, and oil covering an area of approximately 656 ft by 738 ft (200 m by 225 m).

The ERCB determined that the lateral of the horizontal well passed within 423 ft (129 m) of the vertical well at a depth of approximately 6,070 ft (1,850 m) below the surface in the same formation. The operating company had estimated a fracture half-length of 262 to 295 ft (80 to 90 m) based on a general fracture model for the field.[1] While there were no regulatory requirements for spacing hydraulic fracturing operations in place at the time, the 423 ft (129 m) distance was out of compliance with the company's internal policy to space fractures from adjacent wells at least 1.5 times the predicted half-length. The company also did not notify the operators of the vertical well of the hydraulic fracturing operations. The incident prompted the ERCB to issue *Bulletin 2012-02—Hydraulic Fracturing: Interwellbore Communication between Energy Wells*, which outlines expectations for avoiding well communication events and preventing adverse effects on offset wells.

Various studies estimate the number of abandoned wells in the United States to be significant. The Interstate Oil and Gas Compact Commission (IOGCC, 2008) estimates that over one million wells were drilled in the United States prior to the enactment of state oil and gas regulations, and the status and location of many of these wells are unknown. A recent estimate of wells completed before the adoption of statewide well abandonment criteria in 1957 in Pennsylvania placed the range at 305,000 to 390,000 wells in the state, with more than 176,000 of those wells likely abandoned pre-1957 (Dilmore et al., 2015). As of 2000, PA DEP's well plugging program reported that it had documented 44,700 wells that had been plugged and 8,000 that were in need of plugging, and approximately 184,000 additional wells with an unknown location and status (PA

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[1] The fracture half-length is the radial distance from a wellbore to the outer tip of a fracture propagated from that well (Schlumberger, 2014).

DEP, 2000). A similar evaluation from New York State found that the number of unplugged wells was growing in the state despite an active well plugging program (Bishop, 2013). In the Midwest, Sminchak et al. (2014) examined two areas of historical oil and gas exploration as part of an investigation of potential carbon dioxide sequestration sites. They found that a 4.3 mi by 4.3 mi (6.9 km by 6.9 km) square area in Michigan contained 22 abandoned oil and gas wells and a 9.3 mi by 9.3 mi (15.0 km by 15.0 km) square area in Ohio contained 359 abandoned oil and gas wells.

Various state programs exist to plug identified orphaned wells, but they face the challenge of identifying and addressing a large number of wells.[1] In some cases, remote sensing technologies can be used to identify wells for which no records exist. For example, an NETL study in Pennsylvania found that helicopter-based high-resolution magnetic surveys can be used to accurately locate wells with steel casing; wells with no steel casing exhibit weak or no magnetic anomaly and are not detected by such surveys (Veloski et al., 2015). Chapter 10 includes a discussion of factors and practices, including those related to active and abandoned wells near hydraulic fracturing operations, that can reduce the frequency of impacts to drinking water quality.

The Reagan et al. (2015) numerical modeling study included an assessment of migration via an offset well as part of its investigation of potential fluid migration from a producing formation into a shallower groundwater unit (Section 6.3.2.2). For the offset well pathway, it was assumed that the hydraulically induced fractures intercepted an older offset well with deteriorated components. (This assessment can also be applicable to cases where potential migration may occur via the production well-related pathways discussed in Section 6.2) The highest permeability value tested for the connecting feature represented a case with an open wellbore. A key assumption for this investigation was that the offset well was already directly connected to a permeable feature in the reservoir or within the overburden.

Similar to the cases for permeable faults or fractures discussed in Section 6.3.2.2, the study investigated the effect of multiple well- and formation-related variables on potential fluid migration (Table 6-4). Based on the simulation results, an offset well pathway can have a greater potential for gas release from the production zone into a shallower groundwater unit than the fracture pathway discussed in Section 6.3.2.2 (Reagan et al., 2015). This difference is primarily due to the total pore volume of the connecting pathway within the offset well; if the offset well pathway has a significantly lower pore volume compared to the fracture pathway, this would reduce possible gas storage in the connecting feature and increase the speed of buoyancy-dependent migration. However, as with the fracture scenario, the gas available for migration in this case is still limited to the gas that is initially stored in the hydraulically induced fractures. Accordingly, any incidents of gas breakthrough in the model results were limited in both duration and magnitude.

In their modeling study, Reagan et al. (2015) found that production at the gas well (the well used for hydraulic fracturing) also affects the potential upward migration of gas and its arrival times at the drinking water formation due to its effect on the driving forces (e.g., pressure gradient). Similar to the fracture cases described in Section 6.3.2.2, production in the target reservoir appears to mitigate upward gas migration, both by reducing the amount of gas that might otherwise be

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[1] An orphaned well is an inactive oil or gas well with no known (or financially solvent) owner.

available for upward migration and by creating a pressure gradient toward the production well. Only scenarios without the mitigating feature of gas production result in upward migration into the aquifer. This assessment also found a generally downward water flow within the connecting well pathway, which is more pronounced when the production well is operating and there is de-pressurization within the fractures. The producing formation and aquifer permeabilities appear not to be significant factors for upward gas migration via this pathway. Instead, Reagan et al. (2015) found the permeability of the connecting well to be the key factor affecting the migration of gas to the aquifer and the water well. Very low permeabilities (less than 1 mD, or 1×10^{-15} m^2) for the connecting well lead to no migration of gas into the aquifer regardless of the vertical separation distance, whereas larger permeabilities presented a greater potential for gas breakthrough.

Brownlow et al. (2016) also modeled communication with an abandoned well. The modeling exercise was based on operator data from the Eagle Ford Shale. Two types of cases were modeled: cases with an open (unplugged) abandoned well (which the authors note are known to occur in Texas) and cases with an abandoned well that was converted into a water well after the lower portion of the well had been filled with drilling mud (a practice allowed in Texas until 1967). The modeling results indicated that fluid could potentially migrate up both types of abandoned wells, with relatively greater flow rates in open abandoned wells and in abandoned wells closer to the well used for hydraulic fracturing. Similar to the Reagan et al. (2015) study, the production regime was also a key factor; when production and flowback were included in the simulation, they were found to inhibit upward migration. Modeled flow rates through the mud-filled well were comparable to those found by Reagan et al. (2015) with higher flows predicted through the open well.

A similar study was conducted by Nowamooz et al. (2015), who modeled a hypothetical well in the Utica Shale in Quebec. They assumed a 7.9 in (200 mm) wellbore with an approximately 2 in (51 mm) annulus space filled with intact cement. The researchers varied the permeability of the cement from 1 μD (1×10^{-19} m^2) to 1 mD (1×10^{-15} m^2). The results indicated that, at the highest permeability of 1 mD, a flow of methane of 1.02×10^{-2} ft^3/day (2.9×10^{-4} m^3/d) was possible. This was two orders of magnitude higher than the flow when the cement permeability was 1 μD (1×10^{-19} m^2). The wellbore permeabilities used by Nowamooz et al. (2015) appear to be consistent with actual permeabilities observed in the field, which can vary widely. For example, a study of 31 abandoned oil and gas wells in Pennsylvania found effective permeability values along the wellbores in the range of 10^{-6} to 10^2 mD (1×10^{-21} to 1×10^{-13} m^2) (Kang et al., 2015).

In the same way that fractures can propagate to intersect offset wells, they can also potentially intersect other artificial subsurface structures including mine shafts or solution mining sites. No known incidents of this type of migration have been documented. However, the Bureau of Land Management (BLM) has identified over 48,000 abandoned mines in the United States and is adding new mines to its inventory every year (BLM, 2015). In addition, the Well File Review identified an estimated 800 cases where wells used for hydraulic fracturing were drilled through mining voids, and an additional 90 cases of drilling through gas storage zones or wastewater disposal zones (U.S.

EPA, 2015n).[1,2] The analysis suggests emplacing cement within such zones can be challenging, which, in turn, could lead to a loss of zonal isolation (as described in Section 6.2) and create a pathway for fluid migration.

6.3.2.4 Migration via Fractures Intersecting Geologic Features

Potential fluid migration via natural, permeable fault or fracture zones in conjunction with hydraulic fracturing has been recognized as a potential contamination hazard for several decades (Harrison, 1983). Natural fracture systems have a strong influence on the success of a fracture treatment, and the topic has been studied extensively from the perspective of optimizing treatment design (e.g., Dahi Taleghani and Olson, 2011; Weng et al., 2011; Vulgamore et al., 2007). While porous flow in unfractured shale or tight sand formations is assumed to be negligible due to very low formation permeabilities (as discussed in Section 6.3.2.1), the presence of small natural fractures known as "microfractures" within tight sand or shale formations is widely recognized, and these fractures affect fluid flow and production strategies. Naturally occurring permeable faults and larger-scale fractures within or between formations can potentially allow for more significant flow pathways out of the production zone (Jackson et al., 2013d). Figure 6-7 illustrates the concept of induced fractures intersecting with permeable faults or fractures extending out of the target reservoir.[3]

The specific effects of natural fractures on fluid migration, and the mechanisms by which these effects occur, are not completely understood. While naturally occurring microfractures can impact the growth of induced fractures (e.g., by affecting the tensile strength of a shale layer), studies based on modeling and monitoring data generally do not indicate that they contribute to fracture growth in a way that could affect the frequency or severity of impacts. Microfractures could affect fluid flow patterns near the induced fractures by increasing the effective contact area. Conversely, these microfractures could act as capillary traps for the hydraulic fracturing fluid during treatment (contributing to fluid leakoff) and potentially hinder hydrocarbon flow due to lower gas relative permeabilities (Dahi Taleghani et al., 2013). Ryan et al. (2015) suggested that some natural fracture processes/patterns (such as the presence of two subvertical fracture sets) can contribute to upward gas migration, while others (such as small fracture sets with low connectivity that are confined to individual geologic layers) can preclude it.

In some areas, larger-scale geologic features may affect potential fluid flow pathways. As discussed in Text Box 6-3, baseline measurements taken before shale gas development show evidence of thermogenic methane in some shallow aquifers, suggesting that, in some cases, natural subsurface pathways exist and might allow for naturally occurring migration of gas over geologic time (Robertson et al., 2012). There is also evidence demonstrating that gas undergoes mixing in

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[1] 800 wells (95% confidence interval: 10 – 1,900 wells).

[2] 90 wells (95% confidence interval: 50 – 100 wells).

[3] Faults and fractures can exhibit a range of permeabilities. For example, permeable (also referred to as "transmissive" or "conductive") faults or fault segments have enough permeability to allow fluids to flow along or across them, while others are relatively impermeable and can serve as barriers to flow. These differences in permeability are associated with geologic conditions such as rock type, depth, and stress regime. Generally, when researchers refer to the potential for migration via natural geologic features, it is assumed that these features are sufficiently permeable to serve as a pathway.

subsurface pathways (Baldassare et al., 2014; Molofsky et al., 2013; Fountain and Jacobi, 2000). Warner et al. (2012) compared recent sampling results to data published in the 1980s and found geochemical evidence for migration of fluids through natural pathways between deep underlying formations and shallow aquifers—pathways that the authors suggest could lead to contamination from hydraulic fracturing activities. In northeastern Pennsylvania, there is evidence that brine from deep saline formations has migrated into shallow aquifers over geologic time, preferentially following certain geologic structures (Llewellyn, 2014). However, this depends on local geologic characteristics and does not appear to happen in all locations; for example, in the Monongahela River Basin in West Virginia, shallow groundwater samples did not show evidence of mixing with deep brines (Boothroyd et al., 2016). As described in Chapter 7, karst features (created by the dissolution of soluble rock) can also serve as a potential pathway of fluid movement on a faster time scale.

Monitoring data show that the presence of natural faults and fractures can affect both the height and width of induced hydraulic fractures. When faults are present, relatively larger microseismic responses are seen and larger fracture growth can occur, as described below. Rutledge and Phillips (2003) suggested that, for a hydraulic fracturing operation in East Texas, pressurizing existing fractures (rather than creating new hydraulic fractures) was the primary process that controlled enhanced permeability and fracture network conductivity at the site. Salehi and Ciezobka (2013) used microseismic data to investigate the effects of natural fractures in the Marcellus Shale and concluded that fracture treatments are more efficient in areas with clusters or “swarms” of small natural fractures, while areas without these fracture swarms require more thorough stimulation. These microseismic data show that swarms of natural fractures within a shale formation can result in a fracture network with a larger width-to-height ratio (i.e., a shorter and wider network) than would be expected in a zone with a low degree of natural fracturing.

A few studies have used monitoring data to specifically investigate the effect of natural faults and fractures on the vertical extent of induced fractures. A statistical analysis of microseismic data by Shapiro et al. (2011) found that fault rupture (movement along a fault) from hydraulic fracturing is limited by the extent of the stimulated rock volume and is unlikely to extend beyond the fracture network. However, as demonstrated by microseismic data presented by Vulgamore et al. (2007), in some settings, the fracture network—and, in this case, the possibility of fault rupture—could extend laterally for thousands of feet. In the Fisher and Warpinski (2012) data set (Section 6.3.2.2), the greatest fracture heights occurred when the hydraulic fractures intersected pre-existing faults. Similarly, Hammack et al. (2014) reported that fracture growth seen above the Marcellus Shale is consistent with the inferred extent of pre-existing faults at the Greene County, Pennsylvania, research site (Section 6.3.2.2 and Text Box 6-6). The authors suggested that clusters of microseismic events may have occurred where preexisting small faults or natural fractures were present above the Marcellus Shale. Viñal (2015) used time-lapse multi-component seismic monitoring to monitor the overburden of the Montney Shale during a hydraulic fracturing operation in Alberta, Canada. The researchers found increases in the anisotropy in the overburden, which they interpreted as fractures being propagated along natural faults out of the shale and into the overburden. At a site in Ohio, Skoumal et al. (2015) found that hydraulic fracturing induced a rupture along a pre-existing fault approximately 0.6 mi (1 km) from the hydraulic fracturing operation. Using a new monitoring method known as tomographic fracturing imaging, Lacazette and Geiser (2013) also found vertical hydraulic fracturing fluid movement from a production well into a natural fracture network for distances of up to 0.6 mi (1.0 km). However, Davies et al. (2013) questioned whether this technique actually measures hydraulic fracturing fluid movement.

Modeling studies have also investigated whether hydraulic fracturing operations are likely to reactivate faults and create a potential fluid migration pathway into shallow aquifers. Results from one study suggest that, under specific circumstances, interaction with a permeable fault could result in fluid migration to the surface but only on relatively long (ca. 1,000 year) time scales (Gassiat et al., 2013). These findings have been disputed in the literature due to certain suggested limitations of the study, including the model setup, assumptions, and calibration; unrealistic fault representation; lack of constraints on fluid overpressure; and exclusion of the capillary imbibition effect (Birdsell et al., 2015b; Flewelling and Sharma, 2015). In response to these critiques, the authors stated that their work was a parametric study in which the model geometry, parameter, and boundary conditions were defined based on data collected from multiple shale gas basins, and the objective of the study was not to calibrate results to a specific site (Lefebvre et al., 2015). Other researchers reject the notion that open, permeable faults coexist with hydrocarbon accumulation (Flewelling et al., 2013). However, it is unclear whether the existence of faults in low permeability reservoirs affects the accumulation of hydrocarbons because, under natural conditions, the flow of gas may be limited due to capillary tension.

Like the other pathways discussed in this section, other conditions in addition to the physical presence of a permeable fault or fracture would need to exist for fluid migration to a drinking water resource to occur. The modeling study conducted by Reagan et al. (2015) and discussed in Section 6.3.2.2 indicates that, if such a permeable feature exists, the transport of gas and fluid flow would strongly depend upon the production regime and, to a lesser degree, the features' permeability and the separation between the reservoir and the aquifer. In addition, the pressure distribution within the reservoir (e.g., over-pressurized vs. hydrostatic conditions) will affect the fluid flow through fractures/faults. As a result, the presence of multiple geologic and well-related factors can increase the potential for fluid migration into drinking water resources. For example, in the Mamm Creek area of Colorado (Section 6.2.2.4), mechanical integrity and drilling-related problems likely acted in concert with natural fracture systems to result in a gas seep into surface water and shallow groundwater (Crescent, 2011). A similar situation occurred in southeastern Bradford County, Pennsylvania (discussed in Section 6.2), where natural fractures intersected an uncemented casing annulus and allowed gas to flow from the annulus into nearby domestic wells and a stream (Llewellyn et al., 2015).

Other modeling studies investigating the potential of fluid migration related to existing faults and fractures have given mixed results. Pfunt et al. (2016) performed modeling based on conditions in the North German Basin, i.e., deep geological settings where undisturbed cap rocks are present between the fractured formation and shallow aquifers. Their modeling indicated that the hydraulic fracturing fluid did not reach the near-surface area either during hydraulic fracturing operations or in the long-term in the presence of highly permeable pathways (fault zones, fractures). Like previous modeling studies, the authors found that the injection pressure and permeability of the connecting fault are two important factors that control upward fluid migration.

Rutqvist et al. (2013) found that, while somewhat larger microseismic events are possible in the presence of faults, repeated events and a seismic slip would amount to a total rupture length of 164 ft (50 m) or less along a fault, not far enough to allow fluid migration between a deep gas reservoir (approximately 6,562 ft or 2,000 m deep) and a shallow aquifer. A follow-up study using more sophisticated three-dimensional modeling techniques also found that deep hydraulic fracturing is unlikely to create a direct flow path into a shallow aquifer, even when hydraulic fracturing fluid is injected directly into a fault (Rutqvist et al., 2015). Similarly, a modeling study that investigated potential fluid migration from hydraulic fracturing in Germany found potential vertical fluid migration up to 164 ft (50 m) in a scenario with high fault zone permeability, although the authors note this is likely an overestimate because their goal was to "assess an upper margin of the risk" associated with fluid transport (Lange et al., 2013). More generally, results from Rutqvist et al. (2013) indicate that fracturing along an initially impermeable fault (as is expected in a shale gas formation) would result in numerous small microseismic events that act to prevent larger events from occurring (and, therefore, prevent the creation of more extensive potential pathways).

Schwartz (2015) modeled methane flow through a hypothetical permeable fault at a well in Germany. Methane flow was modeled through a permeable leakage zone that was 0.1 ft by 13 ft (0.03 m by 4 m) with an assumed permeability in the range of approximately 100 D to of 10,000 D (1×10^{-10} m^2 to 1×10^{-8} m^2). The model indicated that methane could reach a drinking water aquifer approximately 2,953 ft (900 m) above the gas zone in about a half a day and reach a maximum flow after two days. According to the model results, methane entering the aquifer led to an increase in pH, the release of negatively charged constituents such as chromium, and the adsorption of positively charged ions such as arsenic. Decreasing the permeability of the leakage zone by a factor of 100 increased the travel time by a factor of four. In another study, Myshakin et al. (2015) modeled brine migration through a natural and induced fracture network. Their results indicated that the main pathway for vertical migration of hydraulic fracturing fluid to overlying layers is through the induced fractures, and not the natural fractures. The location of hydraulic fractures relative to each other affects the extent of brine migration into overburden layers; compared to single fractures separated by large distances, closely spaced fractures were associated with higher pressures in—and, consequently, more brine migration into—overlying layers.

6.4 Synthesis

In the injection stage of the hydraulic fracturing water cycle, operators inject hydraulic fracturing fluids into a well under pressure that is high enough to fracture the production zone. These fluids flow through the well and then out into the surrounding formation, where they create fractures in the rock, allowing hydrocarbons to flow through the fractures, to the well, and then up the production string.

The production well and the surrounding geologic features function as a system that is often designed with multiple elements that can isolate hydrocarbon-bearing zones and water-bearing zones, including groundwater resources, from each other. This physical isolation optimizes oil and gas production and can protect drinking water resources via isolation within the well (by the casing and cement) and/or through the presence of multiple layers of subsurface rock between the target formations where hydraulic fracturing occurs and drinking water aquifers.

6.4.1 Summary of Findings

In this chapter, we consider impacts to drinking water resources to occur if hydraulic fracturing fluids or other subsurface fluids affected by hydraulic fracturing enter and adversely impact the quality of groundwater resources. Potential pathways for fluid movement to drinking water resources may be linked to one or more components of the well and/or features of the subsurface geologic system. If present, these potential pathways can, in combination with the high pressures under which fluids are injected and pressure changes within the subsurface due to hydraulic fracturing, result in the subsurface movement of fluids to drinking water resources.

The potential for these pathways to exist or form has been investigated through modeling studies that simulate subsurface responses to hydraulic fracturing, and demonstrated via case studies and other monitoring efforts. In addition, the development of some of these pathways—and fluid movement along them—has been documented. It is important to note that, if multiple barriers afforded by the well design and the presence of subsurface rock formations are present, the development of a pathway within this system does not necessarily result in an impact on a drinking water resource.

6.4.1.1 Fluid Movement via the Well

A production well undergoing hydraulic fracturing is subject to higher stresses during the relatively brief hydraulic fracturing phase than during any other period of activity in the life of the well. If the well cannot withstand the stresses experienced during hydraulic fracturing operations, pathways associated with the casing and cement can form that can result in the unintended movement of fluids into the surrounding environment (Section 6.2).

Multiple barriers within the well, including casing, cement, and a completion assembly can, if present, isolate hydrocarbon-bearing formations from drinking water resources located at a different depth. However, inadequate construction, defects in or degradation of the casing or cement, and/or the absence of redundancies such as multiple layers of casing and proper emplacement of cement can allow fluid movement into drinking water resources. Various studies of wells in the Marcellus Shale showed failure rates between 3 and 10%, depending on the type of failure studied (contamination of drinking water resources may or may not have occurred at these wells). The EPA's Well File Review found that 3% of all hydraulic fracturing jobs involved a downhole mechanical integrity failure, which generally resulted in hydraulic fracturing fluid entering the annular space between the casing and formation or between two casing strings.

Ensuring proper well design and mechanical integrity—particularly proper cement placement and quality—are important actions for preventing unintended fluid migration along the wellbore. While not all of the mechanical integrity failures described above resulted in fluid movement to—or contamination of—a drinking water resource, aspects of well design that lead to increased failure rates have the potential to increase the frequency or severity of impacts to drinking water quality associated with hydraulic fracturing operations.

6.4.1.2 Fluid Movement within Subsurface Geologic Formations

Potential subsurface pathways for fluid migration to drinking water resources include flow of fluids out of the production zone into formations above or below it, fractures extending out of the production zone or into other induced fracture networks, intersections of fractures with abandoned or active wells, and hydraulically induced fractures intersecting with faults or natural fractures (Section 6.3).

Vertical separation between the zone where hydraulic fracturing operations occur and drinking water resources reduces the potential for fluid migration to impact the quality of drinking water resources. However, not all hydraulic fracturing operations are characterized by large vertical distances between the production zone and drinking water resources. In coalbed methane plays, which are typically shallower than shale gas plays, these separation distances can be smaller than in other types of formations. Also, in certain areas, hydraulic fracturing is known to take place in formations containing water that meets the salinity threshold that is used in some definitions of a drinking water resource.

Lateral separation between wells undergoing hydraulic fracturing and other wells (including active and abandoned wells) also reduces the potential for fluid migration to impact drinking water resources. While some operators design fracturing treatments to communicate with the fractures of another well and optimize oil and gas production, unintended communication between two wells or their fracture systems can lead to spills in an offset well, which is an indicator of hydraulic fracturing treatments extending beyond their planned design. These well communication incidents, or “frac hits,” have been reported in New Mexico, Oklahoma, and a few other locations. Surface spills from well communication incidents have also been documented. Based on the available information, frac hits most commonly occur on multi-well pads and when wells are spaced less than 1,100 ft (340 m) apart, but they have been observed at wells up to 8,422 ft (2,567 m) away from a well undergoing hydraulic fracturing.

6.4.1.3 Impacts to Drinking Water Resources

We identified some example cases in the literature where the pathways associated with hydraulic fracturing resulted in an impact on the quality of drinking water resources.

One of these cases took place in Bainbridge Township, Ohio, in 2007. Failure to cement over-pressured formations through which a production well passed—and proceeding with the hydraulic fracturing operation without adequate cement and an extended period during which the well was shut in—led to a buildup of natural gas within the well annulus and high pressures within the well. This ultimately resulted in movement of gas from the production zone into local drinking water aquifers (Section 6.2.2.2). Twenty-six domestic drinking water wells were taken off-line and the houses were connected to a public water system after the incident due to elevated methane levels.

Casings at a production well near Killdeer, North Dakota, ruptured in 2010 following a pressure spike during hydraulic fracturing, allowing fluids to escape to the surface. Brine and tert-butyl alcohol were detected in two nearby monitoring wells. Following an analysis of potential sources, the only source consistent with the conditions observed in the two impacted water wells was the well that ruptured during hydraulic fracturing. There is also evidence that out-of-zone fracturing occurred at the well (Sections 6.2.2.1 and 6.3.2.2).

There are other cases where contamination of or changes to the quality of drinking water resources near hydraulic fracturing operations were identified. Hydraulic fracturing remains a potential contributing cause in these cases. For example:

- Migration of stray gas into drinking water resources involves many potential routes, including poorly constructed casing and naturally existing or induced fractures in subsurface formations. Multiple pathways for fluid movement may have worked in concert in northeastern Pennsylvania (possibly due to cement issues or sustained casing pressure), the Raton Basin in Colorado (where fluid migration may have occurred along natural rock features or faulty well seals), and the Wattenberg field in Colorado (where the surface casing depth and the presence of uncemented gas zones are major factors in determining the likelihood of mechanical integrity failures and contamination). While the sources of methane identified in drinking water wells in each study area could be determined with varying degrees of certainty, attempts to definitively identify the pathways of migration have generally been inconclusive (Text Box 6-3).
- At the East Mamm Creek drilling area in Colorado, inadequate placement of cement allowed the migration of methane through natural faults and fractures in the area. This case illustrates how construction issues, sustained casing pressure, and the presence of natural faults and fractures, in conjunction with elevated pressures associated with hydraulic fracturing, can work together to create a pathway for fluids to migrate toward drinking water resources (Sections 6.2.2.2 and 6.3.2.4).

Additionally, there are places in the subsurface where oil and gas resources and drinking water resources co-exist in the same formation. Evidence we examined indicates that some hydraulic fracturing for oil and gas occurs within formations where the groundwater has a salinity of less than 10,000 mg/L TDS. By definition, this results in the introduction of hydraulic fracturing fluids into formations that meet both the Safe Drinking Water Act's salinity-based definition of an underground source of drinking water and the broader definition of a drinking water resource developed for this assessment. According to the data we examined, these formations are generally in the western United States, e.g., near Pavillion, Wyoming. Hydraulic fracturing in a drinking water resource may be of concern in the short-term (where people are currently using these zones as a drinking water supply) or the long-term (if drought or other conditions necessitate the future use of these zones for drinking water).

There are other cases in which production wells associated with hydraulic fracturing are alleged to have caused contamination of drinking water resources. Data limitations in most of those cases (including the unavailability of information in litigation settlements resulting in sealed documents) make it difficult to assess whether or not hydraulic fracturing was a cause of the contamination.

6.4.2 Factors Affecting Frequency or Severity of Impacts

The multiple barriers within the hydraulic fracturing well and the presence of subsurface low-permeability geologic formations between the production zone and drinking water resources isolate fluids from drinking water resources. Because of this, any factors that affect the integrity of the system comprised of the well and the surrounding geology have the potential to affect the frequency or severity of impacts on drinking water quality. The primary factors that can affect the frequency or severity of impacts are: (1) the construction and condition of the well that is being hydraulically fractured, (2) the amount of vertical separation between the production zone and formations that contain drinking water resources, and (3) the location, depth, and condition of nearby wells or natural faults or fractures.

The presence and condition of the well's casing and cement are key factors that affect the frequency or severity of impacts to drinking water resources. Even in wells where there is substantial vertical separation (e.g., thousands of feet), defects in the well can, in theory, allow fluid movement over significant vertical distance. For example, fully cemented surface casing that extends through the base of drinking water resources is a key protective component of the well. Risk evaluation studies of a limited number of injection wells show that, if the surface casing is not set deeper than the bottom of the drinking water resource, the risk of aquifer contamination increases a thousand-fold. A review of wells that were hydraulically fractured in the Wattenberg field in Colorado showed that wells with fewer casing and cementing barriers across gas-bearing zones exhibited higher rates of failures. Most, but not all, wells used in hydraulic fracturing operations have fully cemented surface casing.

The absence of or defects in casing or cement can be the result of inadequate design or construction, including fewer layers of protective casing or when cement is incomplete (i.e., not present across all oil-gas- or water-bearing formations), of inadequate quality, or improperly emplaced. Wells that were constructed pursuant to older, less stringent requirements have a greater likelihood of exhibiting mechanical integrity problems associated with inadequate design and/or construction.

Deviated and horizontal wells may exhibit more casing and cement problems compared to vertical wells. Some (but not all) studies have shown that sustained casing pressure—a buildup of pressure within the well annulus that can indicate the presence of leaks—occurs more frequently in deviated and horizontal wells compared to vertical wells. Cement integrity problems can arise as a result of challenges in centering the casing and placing the cement in these wells. Absent efforts to ensure the emplacement of sufficient cement that is of adequate integrity, the increased use of these wells in hydraulic fracturing operations has the potential to increase the frequency at which associated cementing problems occur. This, in turn, has the potential to increase the frequency of impacts to the quality of drinking water resources.

Even in optimally designed wells, degradation of the casing and cement as they age or due to the cumulative effects of formation or operational stresses exerted on the well over time (e.g., cyclic stresses in multi-stage fractures) can impact the mechanical integrity of the well and affect the frequency of impacts to drinking water quality. Older wells exhibit more mechanical integrity problems compared to newer wells when hydraulically fractured or re-fractured. If mechanical integrity issues exist but are not detected and subsequently addressed, hydraulic fracturing fluids or other fluids can move into drinking water resources and the concentrations of contaminants in those drinking water resources—and therefore the severity of the impact—can increase.

In areas where there is little or no vertical separation between the production zone and drinking water resources, there is a greater potential to increase the frequency or severity of impacts to drinking water quality. For example, when the vertical separation is relatively small and other subsurface pathways (e.g., artificial penetrations) are present, the potential for these pathways to provide a more direct link between the production zone and a drinking water resource is greater than if there is a large separation. As described above, there are places where hydraulic fracturing operations occur in formations meeting the salinity threshold that is used in some definitions of a drinking water resource. The practice of injecting hydraulic fracturing fluids into a formation that also contains a drinking water resource can affect the quality of that water, because it is likely some of that fluid remains in the formation following hydraulic fracturing. The properties (e.g., chemical composition, toxicity, etc.) of hydraulic fracturing fluids or naturally occurring fluids that migrate to drinking water resources can affect the severity of the impact on the quality of those resources (see Chapter 9 for more information on the chemicals used in hydraulic fracturing fluids).

Where the separation between the production zone and drinking water resources is small, and where natural or induced fractures that transect the layers between these formations are present, there is a potential for increased frequency of impacts to drinking water quality via induced or natural fractures or faults. (Impacts via well-related pathways can also be a concern in these situations, as described above.)

Research shows that fractures created during hydraulic fracturing can extend out of the production zone, and that the vertical component of fracture growth is generally greater in deeper formations than shallow formations. Out-of-zone fracturing could be a concern in deeper formations if there is little vertical separation between the production zone and a deep drinking water resource and fractures propagate to unintended vertical heights. If out-of-zone fracturing is not detected (e.g., via monitoring) and subsequently addressed, the impacts to the quality of drinking water resources associated with fluid movement via these induced fractures have the potential to become more severe.

Regardless of the extent of the vertical separation between the production zone and drinking water resources, the presence of active or abandoned wells near hydraulic fracturing operations can increase the potential for hydraulic fracturing fluids to move to drinking water resources. For example, a deficiency in the construction of a nearby well (or degradation of the well's components), can provide a pathway for movement of hydraulic fracturing fluids, methane, or brines that might affect drinking water quality. If the fractures intersect an uncemented portion of a nearby wellbore, the fluids can potentially migrate along that wellbore into any formations where the well is not cemented.

The frequency of impacts to the quality of drinking water resources may increase where wells are densely spaced (particularly in shallow hydraulic fracturing operations where more fracture propagation is expected to be in the horizontal direction). The frequency of impacts may also be higher in mature oil and gas fields that pre-date the use of construction/plugging methods that can withstand the stresses associated with hydraulic fracturing operations. In these mature fields, wells tend to be older so degradation is a concern, and the location or condition of abandoned wells may not be documented. Based on the information presented in this chapter, the increased use of hydraulic fracturing in horizontal wells and in multiple wells on a single pad can increase the likelihood that these pathways could develop. This, in turn, could increase the frequency at which impacts on drinking water quality occur.

See Chapter 10 for a discussion of factors and practices that can reduce the frequency or severity of impacts to drinking water quality.

6.4.3 Uncertainties

Generally, less is known about the occurrence of (or potential for) impacts of injection-related pathways in the subsurface than for other components of the hydraulic fracturing water cycle, which tend to be easier to observe and measure. Furthermore, while there is a large amount of information available on production wells in general, there is little information that is both specific to hydraulic fracturing operations and readily accessible across the states to form a national picture.

6.4.3.1 Limited Availability of Information Specific to Hydraulic Fracturing Operations

There is extensive information available on the design goals for hydraulically fractured oil and gas wells (i.e., to address the stresses imposed by high-pressure, high-volume injection), including from industry-developed best practices documents. Additionally, many studies have documented how production wells have historically been constructed, how they perform, and the rates at which they experience problems that can lead to pathways for fluid movement. However, because of possible differences in well construction and operational practices, it is unknown how historical well performance studies apply to wells used in hydraulic fracturing operations.

Because wells that have been hydraulically fractured must withstand many of the same downhole stresses as other production wells, we consider studies of the pathways for impacts to drinking water quality in production wells to be relevant to identifying the potential pathways relevant to hydraulic fracturing operations. However, without specific data on the as-built construction of wells used in hydraulic fracturing operations, we cannot definitively state whether these wells are consistently constructed to withstand the stresses they may encounter.

There is also, in general, very limited information available on the monitoring and performance of wells used in hydraulic fracturing operations. Published information is sparse regarding mechanical integrity tests (MITs) performed during and after hydraulic fracturing, the frequency at which mechanical integrity issues arise in wells used for hydraulic fracturing, and the degree and speed with which identified issues are addressed. There is also little information available regarding MIT results for the original hydraulic fracturing event in wells built for that purpose, for wells that are later re-fractured, or for existing, older wells not initially constructed for hydraulic fracturing but repurposed for that use.

These limitations on hydraulic fracturing-specific information make it difficult to provide definitive estimates of the rate at which wells used in hydraulic fracturing operations experience the types of mechanical integrity problems that can contribute to the movement of hydraulic fracturing fluids or other fluids to drinking water resources.

There is also a limited number of peer-reviewed published studies based on groundwater sampling that provide evidence to assess whether formation brines, hydraulic fracturing fluids, or gas move in unintended ways through the subsurface during and after hydraulic fracturing. Subsurface monitoring data (i.e., data that characterize the presence, migration, or transformation of fluids within subsurface formations related to hydraulic fracturing operations) are scarce relative to the tens of thousands of oil and gas wells that are estimated to be hydraulically fractured across the country each year (see Chapter 3 for more information on the occurrence of hydraulic fracturing in the United States).

Information on fluid movement within the subsurface and the extent of fractures that develop during hydraulic fracturing operations is also limited. For example, limited information is available in the published literature on how flow regimes or other subsurface processes change at sites where hydraulic fracturing is conducted. Instead, much of the available research, and therefore the literature, addresses how hydraulic fracturing and other production technologies perform to optimize hydrocarbon production. In addition, much of the published data on fracture propagation are for shale formations, and no large-scale data sets on fracture growth in other unconventional formations exist or are publicly available.

These limitations on hydraulic fracturing-specific information make it difficult to provide definitive estimates of the rate at which wells used in hydraulic fracturing operations experience the types of mechanical integrity problems that can contribute to unintended fluid movement.

6.4.3.2 Limited Systematic, Accessible Data on Well Performance or Subsurface Movement

While the oil and gas industry generates a large amount of information on well performance as part of operations, most of this is proprietary, or otherwise not readily available to the public in a compiled or summary manner. Therefore, no national or readily accessible way exists to evaluate the design and performance of individual wells or wells in a region, particularly in the context of local geology or the presence of other wells and/or hydraulic fracturing operations. Many states have large amounts of operator-submitted data, but information about construction practices or the performance of individual wells is typically not in a searchable or aggregated form that would enable assessments of well performance under varying settings, conditions, or timeframes. Although it is collected in some cases, there is no collection, reporting, or publishing of baseline (pre-drilling and/or pre-fracturing) and post-fracturing monitoring data on a national basis that could indicate the presence or absence of hydraulic fracturing-related fluids in shallow zones and whether or not migration of those fluids has occurred. (See Chapter 10 for additional discussion of data limitations.) Ideally, data from groundwater monitoring are needed to complement theories and modeling on potential pathways and fluid migration.

While some of the types of impacts described above can occur quickly (i.e., on the scale of days or weeks, as with mechanical integrity problems or well communication events), other impacts (e.g., in slow-moving, deep groundwater) may be detectable only on much longer timescales. Without comprehensive collection and review of information about how hydraulic fracturing operations perform, fluid movement could occur without early detection, which could, in turn, increase the severity of any resultant impacts to drinking water quality. For example, testing the mechanical integrity of wells, monitoring the extent of the fractures that form, and conducting pre- and post-hydraulic fracturing water quality monitoring can detect fluid movement (or the potential for fluid movement) and provide opportunities to mitigate or minimize the severity of impacts associated with unforeseen events.

The limited amount of available information also hinders our ability to evaluate how frequently drinking water impacts are occurring, the probability that these impacts occur, or to what extent they are tied to specific well construction, operation, and maintenance practices. This also significantly limits our ability to evaluate the aggregate potential for hydraulic fracturing operations to affect drinking water resources or to identify the potential cause of drinking water contamination in areas where hydraulic fracturing occurs. The absence of this information greatly limits the ability to make quantitative statements about the frequency or severity of these impacts.

6.4.4 Conclusions

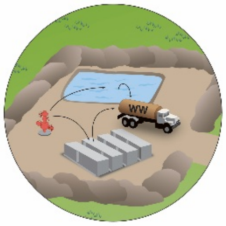
The production well and the surrounding geologic features function as a system that provides multiple barriers that can isolate hydrocarbon-bearing zones and water-bearing zones, including drinking water resources. Because of this, factors affecting the integrity of any of these barriers have the potential to adversely affect the quality of drinking water resources.

We have identified a number of pathways by which hydraulic fracturing fluids can reach and affect the quality of drinking water resources. These pathways include migration via inadequate casing and/or cement in the hydraulic fracturing well, fluid movement in the subsurface via fractures extending out of the target zone, or vertical fluid movement via other natural or artificial structures.

The primary factors affecting the frequency or severity of impacts to drinking water quality associated with hydraulic fracturing operations include the condition of the casing and cement of the production well and their placement relative to drinking water resources, the extent of the vertical separation between the production zone and drinking water resources, and the presence and condition of offset wells or natural faults or fractures near the hydraulic fracturing operation.

There is evidence that, in some cases highlighted in the literature, these pathways have formed and the quality of drinking water resources has been impacted. We do not know the frequency of such impacts associated with the injection stage of the hydraulic fracturing water cycle, however. This is related to the following: the subsurface environment is geologically complex, the relevant production processes cannot be directly observed, and publicly available data that can support an evaluation of the impacts of hydraulic fracturing on the quality of drinking water resources is, in general, very limited.

Chapter 7. Produced Water Handling



Abstract

Produced water is a byproduct of hydrocarbon production and flows to the surface through the production well, along with oil and gas. Operators must store and dispose of (or in some cases treat) large amounts of non-potable produced water, either on site or off site, and spills or releases of produced water have the potential to impact drinking water resources. Unlike produced water from conventional oil and gas production, produced water generated following hydraulic fracturing initially contains returned hydraulic fracturing fluids. Much of the hydraulic fracturing fluid remains below ground; the median amount of fluid returned to the surface is 30% or less. Up to several million gallons of water can be produced from each well, with production generally decreasing with time.

Produced water contains several classes of constituents: salts, metals, radioactive materials, dissolved organic compounds, and hydraulic fracturing chemicals and their transformation products (the result of reactions of these chemicals in the subsurface). The concentrations of these constituents change with time, as the initially returning hydraulic fracturing fluid blends with formation water. Typically, this means that the produced water becomes more saline with time. Produced water composition and volume vary from well to well, both among different formations and within formations. A large number of organic compounds have been identified in produced water, many of which are naturally occurring petroleum hydrocarbons; some are known hydraulic fracturing chemicals. Only a few transformation products have been identified, and they include chlorinated organics.

Spills and releases of produced water with a variety of causes have been documented at different steps in the production process. The causes include human error, equipment or container failure (for instance, pipeline, tank or storage pit leaks), accidents, and storms. Unauthorized discharges may account for some releases as well. An estimated half of the spills are less than 1,000 gal (3,800 L). A small number of much larger spills has been documented, including a spill of 2.9 million gal (11 million L). Both short- and long-term impacts to soil, groundwater, and surface from spills have occurred. For many spills, however, the impacts are unknown. The potential of spills of produced water to affect drinking water resources depends upon the release volume, duration, and composition, as well as watershed and water body characteristics.

Data are lacking to characterize the severity and frequency of impacts on a nationwide scale. Suspected local-scale impacts often require an extensive multiple lines-of-evidence investigation to determine their cause. Further, when investigations do take place, the lack of baseline water quality data can make it difficult to determine the cause and severity of the impact. In such cases, additional data are necessary to determine the full extent of the impact of releases of produced water.

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7. Produced Water Handling

7.1 Introduction

Water is a byproduct of oil and gas production. After the hydraulic fracturing of the formation is completed, the injection pressure is reduced, and a possible inactive period where the well is "shut in" is completed, water is allowed to flow back from the well to prepare for oil or gas production.[1] This return-flow water may contain chemicals injected as part of the hydraulic fracturing fluid, chemicals naturally occurring in the formation, or the products of reactions that take place in the formation. Initially this water, sometimes called flowback, is mostly hydraulic fracturing fluid, but as time goes on, water chemistry becomes more similar to water associated with the formation. For formations containing saline water (brine), the salinity of the returned water increases as time passes as the result of increased contact time between the hydraulic fracturing fluid and the formation and inclusion of an increased portion of formation water. For this assessment, and consistent with industry practice, the term produced water is used to refer to any water flowing from the oil or gas well.

Produced water is piped directly to an injection well or stored and accumulated at the surface for eventual management by injection into disposal wells, transport to wastewater treatment plants, reuse, or in some cases, placement in evaporation pits or permitted direct discharge. See Text Box ES-11 and Section 8.4 for discussion of these management practices.

Produced water spills and releases can occur due to several causes, including events associated with pipelines, transportation, blowouts, and storage. Impacts to drinking water resources can occur if this released water enters surface water bodies or reaches groundwater. Such impacts may result in the water becoming unfit for consumption, either through obvious taste and odor considerations or the constituents in the water exceeding hazard levels (Chapter 9). Once released to the environment, transport of chemical constituents depends on the characteristics of the:

- Spill (volume, duration, concentration);
- Fluid (density as influenced by salinity);
- Chemicals (volatility, sorption, solubility); and
- Site-specific environmental characteristics (surface topography and location of surface water bodies, the type of the soil and aquifer materials, layering and heterogeneity of rocks, and the presence of dissolved oxygen and other factors needed to support biodegradation, and the presence of inorganic species that affect metal transport).

This chapter provides characterization of produced water and also provides background information for the coverage of wastewater disposal and reuse in Chapter 8. Chapter 7 addresses the characteristics of produced water including per-well generation of produced water. Chapter 8 considers management of this water, now called wastewater, at an aggregate level, and thus

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[1] There can be no shut-in period at all or it can last several weeks (Stepan et al., 2010).

discusses state, regional, and national estimates of treatment volumes. While Chapter 7 considers impacts from several types of unintentional releases, Chapter 8 focuses on impacts that are associated with wastewater management practices. One specific issue, leakage from pits and impoundments, is introduced in Chapter 7 as one of several avenues for accidental releases, with a more detailed exploration of the use of pits in wastewater management presented in Chapter 8.

Chapter 7 begins with a review of definitions for flowback and produced water in Section 7.1.1. Definitions are followed by a discussion in Section 7.2 of water volumes per well, first presenting data on the volume and percent of hydraulic fracturing fluid returned to the surface and then presenting data on the volume of water returned during production. These data all represent the response of individual wells. Because of the need to have aggregated volumes for estimating wastewater treatment loadings, estimates of total volumes are given in Section 8.2.

Chapter 7 continues with discussion of the chemical composition of produced water (Section 7.3). Because the composition of produced water is only known through analysis of samples, laboratory methods and their limitations are described in Section 7.3.1. Time-dependent changes in composition are discussed via three specific examples in Section 7.3.3, followed by discussion of five types of constituents: salts, metals, radioactive materials, organics, and known hydraulic fracturing additives in Section 7.3.4. The chemical and geological processes controlling the chemical composition of produced water are described in Appendix E. Spatial and temporal trends in the composition of produced water are illustrated with examples from the literature and data compiled for this report (Section 7.3.5).

The potential for impacts on drinking water resources of produced water releases and spills are described based on reported spill incidents (Section 7.4), and examples of spills from specific sources and data compilation studies are given in Section 7.4.2. The potential for impacts is described using contaminant transport principles in Section 7.6. The chapter concludes with a discussion of uncertainties and knowledge gaps, factors that influence the severity of impacts, and major findings (Section 7.7).

7.1.1 Definitions

Multiple definitions exist for the terms flowback and produced water. Appendix Section E.1 gives examples of definitions used by different organizations. These differing definitions reflect differing usage of the terms among various groups and that produced water reflects the continuously varying mixture between returning injection fluid and formation water. The majority of produced water definitions are fundamentally similar. The following definition is used in this report for produced water: any type of water that flows from the subsurface through oil and gas wells to the surface as a by-product of oil and gas production. Thus produced water can variously refer to returned hydraulic fracturing fluid, formation water alone, or a mixture of the two.

The term flowback has two major meanings. First is the process used to prepare the well for production by allowing excess liquids and proppant to return to the surface. The second use of the term is to refer to fluids predominantly containing hydraulic fracturing fluid that return to the surface. Because formation water can contact and mix with injection fluids, the distinction between returning hydraulic fracturing fluid and formation water is not clear. Definitions of flowback are operational in the sense that they include some characteristic of the oil and gas operation (i.e., fluids returning within 30 days). These reflect that during the early phases of operation, a higher concentration of chemical additives is expected and later, water is characteristic of the formation. Because we use existing literature in our review, we do not introduce a preferred definition of flowback, and describe all water flowing from the well as produced water.

7.2 Volume of Hydraulic Fracturing Flowback and Produced Water

Veil (2015) estimated that, in 2012, all types (i.e., from conventional and unconventional reservoirs) of U.S. onshore and offshore oil and gas production generated 8.90 x 10^{11} gal (3.37 x 10^{12} L) of produced water. More details and state-level estimates are given in Section 8.2. This section presents information on flowback and produced water volume over various time scales, and where possible, on a per-well and per-formation basis, because characteristics and volume of flowback and produced water vary by well, formation, and time.

The amount of produced water from a well varies and depends on several factors, including production, formation, and operational factors. Production factors include the amount of fluid injected, the type of hydrocarbon produced (gas or liquid), and the location within the formation. Formation factors include the formation pressure, the interaction between the formation and injected fluid (capillary forces), and reactions within the reservoir. Operational factors include the volume of the fractured production zone that includes the length of well segments and the height and width of the fractures. Certain types of problems also influence water production, including possible loss of mechanical integrity and subsurface communication between wells, both of which can result in an unexpected increase in water production (U.S. GAO, 2012; Byrnes, 2011; DOE, 2011a; GWPC and ALL Consulting, 2009; Reynolds and Kiker, 2003).

The processes that allow gas and liquids to flow are related to the conditions along the faces of fractures. Byrnes (2011) conceptualized fluid flow across the fracture face as being composed of three phases. The first is characterized by forced imbibition of fluid into the reservoir and occurs during and immediately following fracture stimulation.[1] Second is fluid redistribution within the reservoir rock, due to capillary forces. Estimates have shown that 50% or more of fracturing fluid could be captured within the Marcellus shale if imbibition drives water 2 to 6 in (5 to 15 cm) into the formation (Engelder, 2012; Byrnes, 2011; He, 2011). In the last phase, water flows out of the formation when the well is opened and pressure is reduced in the wellbore and fractures. The purpose of this phase is to recover as much of the injected fluid as possible (Byrnes, 2011) to allow higher oil or gas flow rates. The length of the last phase and, consequently, the amount of water removed, depends on factors such as the amount of injected fluid, the permeability and relative permeability of the reservoir, capillary pressure properties of the reservoir rock, and the pressure near the fracture faces.[2] The well can be shut in for varying time periods depending on operator scheduling, surface facility construction and connection thereto, or other reasons.

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[1] The displacement of a non-wet fluid (i.e., gas) by a wet fluid (typically water). Adapted from Dake (1978).

[2] When multiple fluids (water, oil, gas) occupy portions of the pore space, the permeability to each fluid depends on the fraction of the pore space occupied by the fluid and the fluid's properties. As defined by Dake (1978), when this effective permeability is normalized by the absolute permeability, the resulting relationship is known as the relative permeability.

7.2.1 Flowback of Injected Hydraulic Fracturing Fluid

The amount of water produced by wells within the first few days following fracturing varies from formation to formation. Wells in the Mississippi Lime and Permian Basin can produce 1 million gal (3.8 million L) in the first 10 days of production. Wells in the Barnett, Eagle Ford, Granite Wash, Cleveland/Tonkawa Sand, Niobrara, Marcellus, and Utica Shales can produce 300,000 to 1 million gal (1.14 to 3.78 million L) within the first 10 days. Haynesville wells produce less, about 250,000 gal (950,000 L) (Mantell, 2013). Data show that the rate of water produced during the flowback period decreases as time passes (Ziemkiewicz et al., 2014; Hansen et al., 2013; Hayes, 2009).

It is not possible to specify precisely the amount of injected fluids that return in the flowback, because there is not a clear distinction between flowback and produced water, and the indicators (e.g., salinity and radioactivity, to name two) are not routinely monitored (GWPC and ALL Consulting, 2009). Rather, flowback estimates usually relate the amount of produced water measured at a given time after fracturing as a percentage of the total amount of injected fluid. Estimates of the fraction of injected hydraulic fracturing fluid that returns as flowback are highly variable (U.S. EPA, 2016d; Vengosh et al., 2014; Mantell, 2013; Vidic et al., 2013; Minnich, 2011; Xu et al., 2011). The maxima are less than 85% in all but one of the examples given in Table 7-1, Table 7-2, and Table 7-3, and most of the median values are less than 30%. In some cases, the amount of flowback is greater than the amount of injected hydraulic fracturing fluid, and the additional water comes from the formation (Nicot et al., 2014) or from a conductive pathway from an adjacent formation (Arkadakskiy and Rostron, 2013). See Appendix Section E.2.1 for more details.

Table 7-1. Data from one company's operations indicating approximate total water use and approximate produced water volumes within 10 days after completion of wells.
From Mantell (2013).

Formation	Approx. total average water use per well (million gal)	Produced water (flowback) within the first 10 days after completion		Produced water as a percentage of average water use per well	
		Low estimate (million gal)	High or only estimate (million gal)	Low estimate (% of total water use)	High or only estimate (% of total water use)
Gas shale plays (primarily dry gas)					
Barnett[a]	3.4	0.3	1.0	9%	29%
Marcellus[a]	4.5	0.3	1.0	7%	22%
Haynesville	5.4	--	0.25	--	5%
Liquid plays (gas, oil, condensate)					
Mississippi Lime	2.1	--	1.0	--	48%

Formation	Approx. total average water use per well (million gal)	Produced water (flowback) within the first 10 days after completion		Produced water as a percentage of average water use per well	
		Low estimate (million gal)	High or only estimate (million gal)	Low estimate (% of total water use)	High or only estimate (% of total water use)
Cleveland/ Tonkawa	2.7	0.3	1.0	11%	37%
Niobrara	3.7	0.3	1.0	8%	27%
Utica	3.8	0.3	1.0	8%	26%
Granite Wash	4.8	0.3	1.0	6%	21%
Eagle Ford	4.9	0.3	1.0	6%	20%

[a] Mantell (2011) reported produced water for the first 10 days at 500,000 to 600,000 gal for the Barnett, Fayetteville and Marcellus Shales.

Table 7-2. Additional short-, medium-, and long-term produced water estimates.

Location–formation	Produced water as percentage of injected fluid	Reference	Comment
Estimates without reference to a specific data set			
Unspecified Shale	5% – 35%	Hayes (2011)	
Marcellus Shale	10% – 25%	Minnich (2011)	Initial flowback
ND–Bakken	25%	EERC (2013)	
Estimates with reference to specific data evaluation			
Short duration			
Marcellus Shale	10%	Clark et al. (2013)	0 – 10 days
TX—Barnett	20%	Clark et al. (2013)	0 – 10 days
TX—Haynesville	5%	Clark et al. (2013)	0 – 10 days
AR—Fayetteville	10%	Clark et al. (2013)	0 – 10 days
Medium duration			
WV—Marcellus	8%	Hansen et al. (2013)	30 days
Marcellus Shale	24%	Hayes (2011, 2009)	Average from 19 wells, 90 days

Location–formation	Produced water as percentage of injected fluid	Reference	Comment
Long duration			
TX—Barnett	~100%[a]	Nicot et al. (2014)	72 months
WV—Marcellus	10% – 30%	Ziemkiewicz et al. (2014)	Up to 115 months
TX—Eagle Ford	<20%	Nicot and Scanlon (2012)	Lifetime
Unspecified duration			
PA—Marcellus	6%	Hansen et al. (2013)	

[a] Approximate median with large variability: 5th percentile of 20% and 90th percentile of 350%.

Table 7-3. Flowback water characteristics for wells in unconventional reservoirs.

Source: U.S. EPA (2016d). The formation-level data used to develop Tables 7-3 and 7-4 appear in Appendix Table E-1.

Resource type	Well type	Fracturing fluid (million gal)			Flowback (percent of fracturing fluid returned)		
		Weighted average	Range	Data points	Weighted average	Range	Data points
Shale	Horizontal	4.2	0.091–24	80,388	7%	0%–580%	7,377
	Directional	1.4	0.037–20	340	33%	1%–57%	36
	Vertical	1.1	0.015–19	5,197	96%	2%–581%	57
Tight	Horizontal	3.4	0.069–12	7,301	12%	0%–60%	75
	Directional	0.05	0.046–4	3,581	10%	0%–60%	342
	Vertical	1	0.016–4	10,852	4%	0%–60%	130

7.2.2 Produced Water Volumes

Mantell (2013, 2011) described the amount of produced water over the long term as high, moderate, or low for several formations. Wells in the Barnett Shale, Cleveland/Tonkawa Sand, Mississippi Lime, and the Permian Basin can produce more than 1,000 gal (3,800 L) of water per million cubic feet (MMCF) of gas. The most water-productive of these can be as high as 5,000 gal (19,000 L) per MMCF of gas. As a specific example, a high water producing formation in the western United States was described as producing 4,200 gal (16,000 L) per MMCF of gas for the life of the well (McElreath, 2011). The well was fractured and stimulated with about 4 million gal (15 million L) of water and returned 60,000 gal (230,000 L) per day in the first 10 days, followed by 8,400 gal (32,000 L) per day in the remainder of the first year. The Niobrara, Granite Wash, Eagle Ford, Haynesville, and Fayetteville Shales are relatively dry formations (with small amounts of naturally occurring formation water) and produce between 500 and 2,000 gal (1,900 to 7,600 L) of produced water per MMCF of gas (Mantell, 2013). The Utica and Marcellus Shales are viewed as drier still and produce less than 200 gal (760 L) per MMCF of gas.

Wells producing in various formation show high produced water volume variability, including the Barnett Shale, which was attributed by Nicot et al. (2014) to a few wells with exceptionally high water production. Some of these wells produced more than the amount of injected fracturing fluid.

Wells in conventional and unconventional reservoirs produce differing amounts of water. Individual hydraulically fractured wells producing gas from the Marcellus Shale produced more water than hydraulically fractured wells in conventional wells in Pennsylvania (Lutz et al., 2013). However, on a per-unit of gas produced basis, wells producing from the Marcellus Shale generate less water (35%), than those in the conventional formations.

The EPA (2016d) reported characteristics of long-term produced water for hydraulically fractured shale and tight formations (Table 7-4). For shale, horizontal wells produced more water (1,100 gal/day; 4,200 L/day) than vertical wells (500 gal/day; 1,900 L/day). Typically, this would be attributed to the longer length of the production zone in horizontal laterals than in vertical wells.

Table 7-4. Long-term produced water generation rates (gal/day per well) for wells in unconventional reservoirs.

Source: U.S. EPA (2016d). The formation-level data used to develop Tables 7-3 and 7-4 appear in Appendix Table E-1.

		Long-Term Produced Water Generation Rates (gal per day per well)		
Resource type	**Well type**	**Weighted average**	**Range**	**Data points**
Shale	Horizontal	1,100	0–29,000	43,893
	Directional	820	0.83–12,000	1,493
	Vertical	500	4.8–51,000	12,551
Tight	Horizontal	980	10–120,000	4,692
	Directional	390	15–8,200	10,784
	Vertical	650	0.71–2100	34,624

In an example from the Pennsylvania Marcellus Shale, the EPA determined that, for vertical wells in unconventional reservoirs, 6% of water came from drilling, 35% from flowback, and 59% from long-term produced water; for horizontal wells, the corresponding numbers were 9%, 33%, and 58% (U.S. EPA, 2016d). This result agrees with the U.S. Department of Energy (DOE, 2011a) who concluded that the characteristic small amount of produced water from the Marcellus Shale was due either to its low water saturation or low relative permeability to water (see Section 6.3.2.1). For these dry formations, low shale permeability and high capillarity cause water to imbibe into the formation, where some is retained permanently.

7.2.2.1 Time Trends

High rates of water production (flowback) typically occur in the first few months after hydraulic fracturing, followed by rates reduced by an order of magnitude (e.g., Nicot et al., 2014). In many cases half of the total produced water from a well is generated in the first year. Similarly, the EPA (2016d) reported a general rule of thumb that, for unconventional reservoirs, the volume of flowback (which occurs over a short period of time) is roughly equal to the volume of long-term produced water. These trends in produced water volumes occur within the timeline of hydraulic fracturing activities (Section 3.3), and show that the large, initial return volumes of flowback last for several weeks, whereas the lower-rate produced water phase can last for years (Figure 7-1).

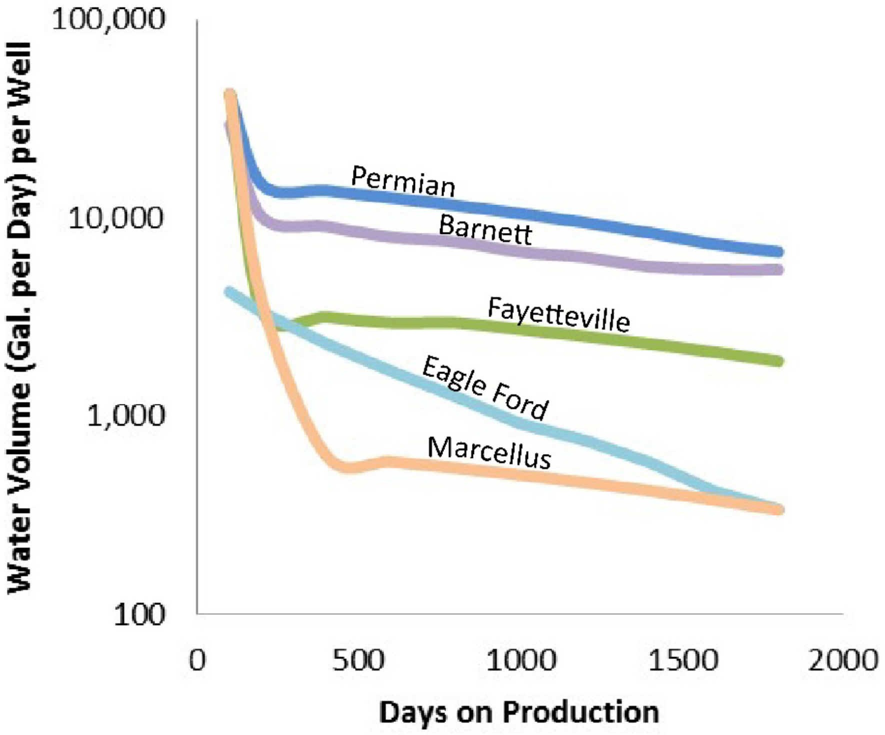

Figure 7-1. Generalized examples of produced water flow from five formations.
Actual produced water flows vary by location, play, basin, and amount of water used for hydraulic fracturing (EWI, 2015). Figure used with permission.

7.2.2.2 Coalbed Methane

Water is pumped from coal seams to reduce pressure so that gas adsorbed to the surface of the coal can flow to the production well (Guerra et al., 2011). Consequently, CBM tends to produce large volumes of water early on: more than conventional gas-bearing formations (U.S. GAO, 2012) (Figure 7-2). Within producing CBM formations, water production can vary for unknown reasons (U.S. GAO, 2012). As an example, data show that CBM production in the Powder River Basin produces 16 times more water than that in the San Juan Basin (U.S. GAO, 2012).

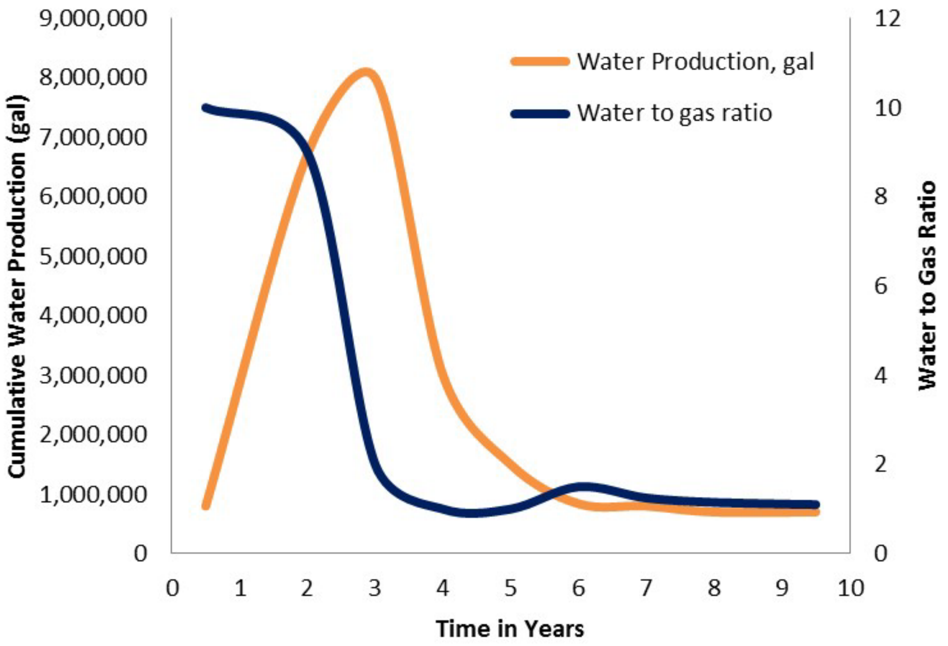

Figure 7-2. Typical produced water volume for a coal bed methane well in the western United States.
Source: Guerra et al. (2011).

7.3 Chemical Composition of Produced Water

For hydraulically fractured wells, the chemical composition of produced water changes from being similar to the injected hydraulic fracturing fluid to reflecting a mixture of hydraulic fracturing fluids, naturally occurring hydrocarbons, transformation products, and formation water. Initial produced water data show continuous changes in chemical composition and reflect processes occurring in the formation (Section 7.3.3). The data presented on longer-term produced water represent water that is primarily associated with the formation, rather than the hydraulic fracturing fluid (Section 7.3.4). Unlike the hydraulic fracturing fluid, the composition of which may be disclosed, compositional data on produced water comes from laboratory analysis of samples. Because of this reliance, we first discuss sampling and analysis of produced water, and especially note the limitations of existing analytical methods for organic chemicals and radionuclides.[1] It is important to note that the analytical methods can differ depending on the purpose of the analysis. Specifically, advanced laboratory methods have been used to identify unknown organic constituents of produced water (Section 7.3.1), routine methods are used for pre-drilling sampling, and a combination of methods may be needed for assessing environmental impacts (Section 7.4.2.5).

7.3.1 Determination of Produced Water Composition

Recent advances in analytical methods for produced water have allowed detection and quantification of a broad range of organic compounds, including those associated with hydraulic

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[1] Chemical components of produced water are described below.

fracturing fluid (Section 7.3.4.7 and Appendix E.3.5.). These studies make clear that standard analytical methods are not adequate for detecting and quantifying the numerous organic chemicals, both naturally occurring and anthropogenic, that are now known to occur in produced water (Lester et al., 2015; Maguire-Boyle and Barron, 2014; Thurman et al., 2014). Similarly, methods commonly applied for the analysis of radionuclides in drinking water may suffer from analytical interferences that result in poor data quality (Maxwell et al., 2016; Ying et al., 2015; Zhang et al., 2015b; Nelson et al., 2014; U.S. EPA, 2014i, 2004b). In these instances, alternative methods that have been developed to support the nuclear materials production and waste industry provide more reliable approaches to ensure adequate detection limits and avoid sample matrix interferences that are anticipated for the high salinity and concentrations of organic constituents that may be present in produced water samples.[1] Development of advanced or non-routine methods for both organics and inorganics (especially radium) suggests that data generated from earlier methods may be less reliable that those developed by the new methods (Nelson et al., 2014), and that advanced analytical techniques are needed to detect or quantify some analytes.

The compositional data that follow in this chapter and Appendix E rely on the analytical procedures used in measurement and were summarized as noted from numerous produced water studies or compilations, such as the U.S. Geological Survey (USGS) produced water database (Blondes et al., 2014).

7.3.2 Factors Influencing Produced Water Composition

Several interacting factors influence the chemical composition of produced water: (1) the composition of injected hydraulic fracturing fluids, (2) the targeted geological formation and associated hydrocarbon products, (3) the stratigraphic environment, and (4) subsurface processes and residence time (Barbot et al., 2013; Chapman et al., 2012; Dahm et al., 2011; Blauch et al., 2009).

The mineralogy and structure of a formation are determined initially by deposition, when rock grains settle out of their transporting medium (Marshak, 2004). Generally, shale forms from clays that were deposited in deep, oxygen-poor marine environments, and sandstone can form from sand deposited in shallow marine environments (Ali et al., 2010; U.S. EPA, 2004a). Coal forms when carbon-rich plant matter collects in shallow peat swamps. In the United States, coal formed in both freshwater (northern Rocky Mountains) and marginal-marine environments (Alabama's Black Warrior formation) (NRC, 2010; Horsey, 1981). Consequently, shale and sandstone produced water are expected to be saline, and CBM water may be much less so.

7.3.3 Produced Water Composition During the Flowback Period

The chemistry of produced water changes over time, especially during the first days or weeks after hydraulic fracturing. Generally, produced water concentrations of cations, anions, metals, naturally occurring radioactive material (NORM), and organics increase as time goes on (Barbot et al., 2013; Haluszczak et al., 2013; Chapman et al., 2012; Davis et al., 2012; Gregory et al., 2011; Blauch et al.,

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[1] For guidance in planning, implementing, and assessing projects that require laboratory analysis of radionuclides, see U.S. EPA (2004b).

2009). The causes include precipitation and dissolution of salts, carbonates, sulfates, and silicates; pyrite oxidation; leaching and biotransformation of organic compounds; and mobilization of NORM and trace elements. Concurrent precipitation of sulfates (e.g., $BaSO_4$) and carbonates (e.g., $CaCO_3$) alongside decreases in pH, alkalinity, dissolved carbon, and microbial abundance and diversity occur over time after hydraulic fracturing (Orem et al., 2014; Barbot et al., 2013; Murali Mohan et al., 2013; Davis et al., 2012; Blauch et al., 2009; Brinck and Frost, 2007). Leaching of organics appears to be a result of injected and formation fluids associating with shale and coal strata (Orem et al., 2014). Concentrations of organics in CBM produced water decrease with time, possibly due to the depletion of coal-associated water through formation pumping (Orem et al., 2007).

7.3.3.1 Total Dissolved Solids

Produced water total dissolved solids concentrations (TDS) increase by varying degrees because of the formation's geological origin. As an example, TDS concentrations increased to upper bound values in samples from four Marcellus Shale gas wells (Chapman et al., 2012) (Figure 7-3). The increased TDS was composed of increased sodium, calcium, and chloride (Chapman et al., 2012; Blauch et al., 2009). Similarly, TDS in flowback from the Westmoreland County wells started low and exceeded that of typical seawater (35,000 mg/L) within three days (Chapman et al., 2012). In a similar study, wells with hydraulic fracturing fluid containing less than 1,000 mg/L saw TDS concentrations increase above a median value of 200,000 mg/L within 90 days (Hayes, 2009).

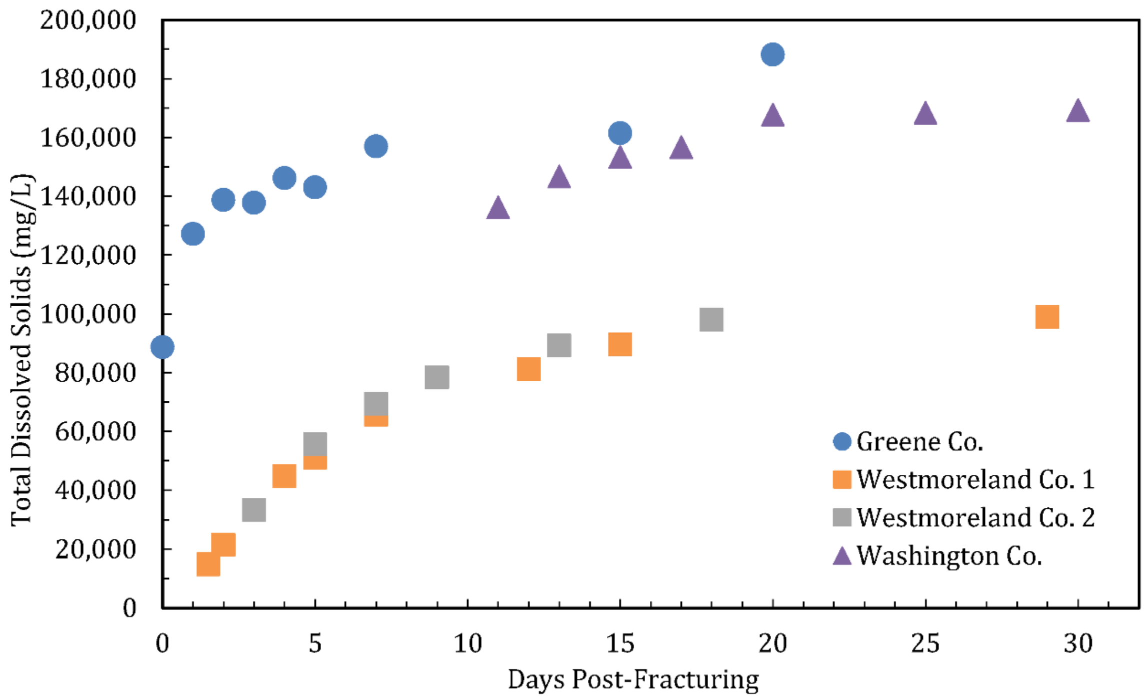

Figure 7-3. TDS concentrations measured through time for injected fluid (at 0 days), and produced water samples from four Marcellus Shale gas wells in three southwest Pennsylvania counties.

Data from Chapman et al. (2012).

7.3.3.2 Radionuclides

Shales and sandstones naturally contain various radionuclides (Sturchio et al., 2001).[1] Radium in pore waters or adsorbed onto clay particles and grain coatings can dissolve and return in produced water (Langmuir and Riese, 1985). Available data indicate that radium and TDS concentrations in produced water are positively correlated (Rowan et al., 2011; Fisher, 1998), likely because radium remains adsorbed to mineral surfaces when salinity is low, and then desorbs into solution with increased salinity (Sturchio et al., 2001). As an example, over the course of 20 days, radium concentration in flowback from a Marcellus Shale gas well increased by almost a factor of four (Chapman et al., 2012; Rowan et al., 2011) (Figure 7-4).

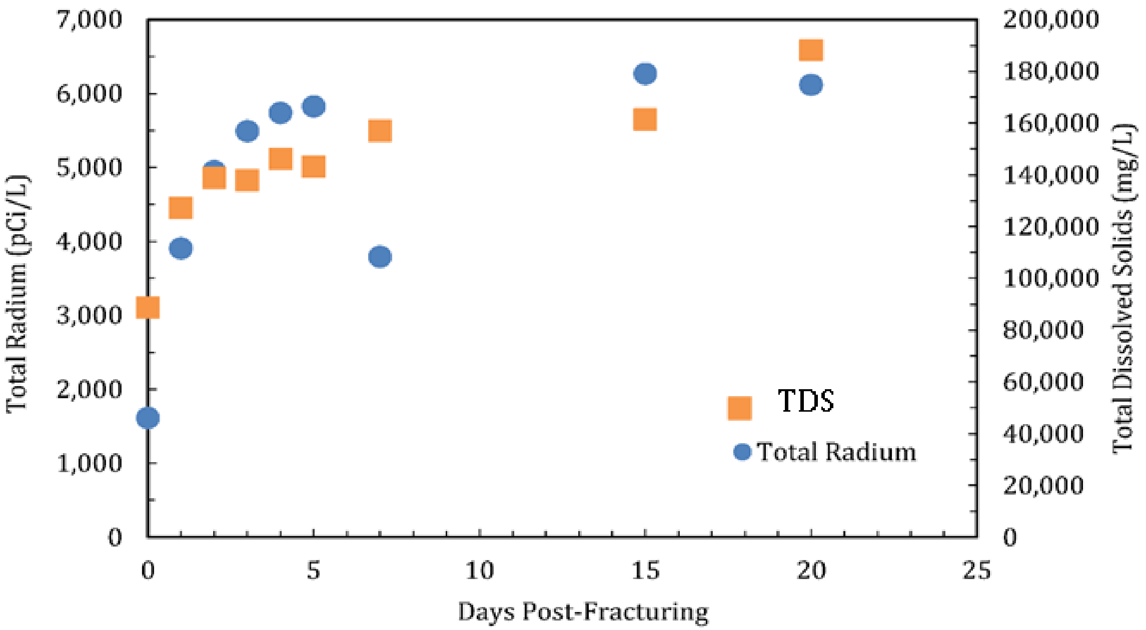

Figure 7-4. Total radium and TDS concentrations measured through time for injected (day 0), and produced water samples Greene County, PA, Marcellus Shale gas wells.
Data from Rowan et al. (2011) and Chapman et al. (2012).

7.3.3.3 Dissolved Organic Carbon

Dissolved organic carbon (DOC) concentrations decrease from initial levels in shales and coalbeds (Murali Mohan et al., 2013; Orem et al., 2007). This occurs while TDS and chloride concentrations are increasing (Barbot et al., 2013; Chapman et al., 2012). DOC sorption, dilution with injected or formation water, biochemical reactions, and microbial transformation may all cause decreased concentrations of DOC during flowback. Injected organics can include gel polymer formulations, namely guar gum; petroleum distillates; and ethyl and ether glycol formulations, which can serve as food sources for microbes. (Wuchter et al., 2013; Arthur et al., 2009b; Hayes, 2009). In coalbeds,

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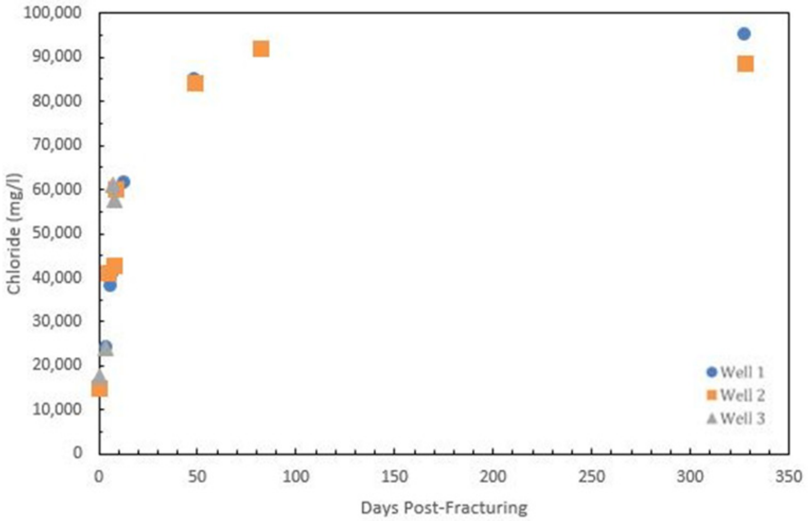
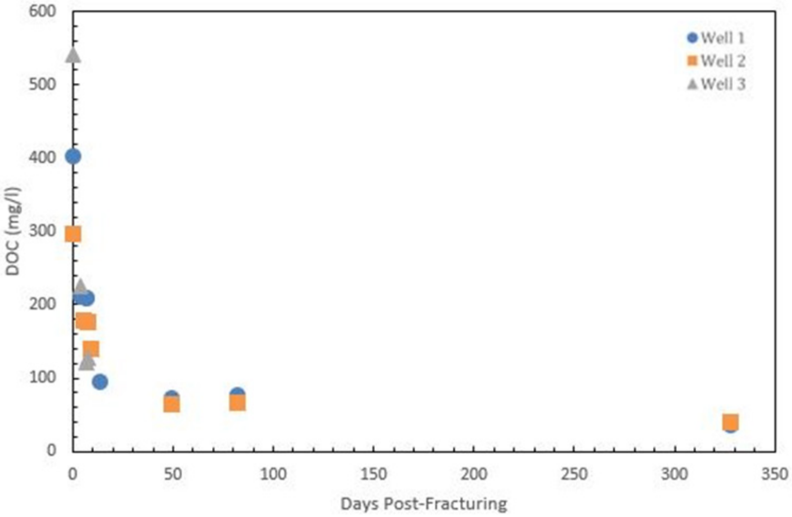
[1] Hydraulic fracturing fluids typically do not contain radioactive material (Rowan et al., 2011). However, reusing produced water can introduce radioactive material into hydraulic fracturing fluid. See Section 7.3.4.6 and PA DEP (2015b).

water contacting the coal may become depleted in DOC to the degree that when outside water of lower DOC is produced, the resulting DOC concentrations in the produced water are reduced (Orem et al., 2014).



(a)



(b)

Figure 7-5. (a) Increasing chloride (Cl) and (b) decreasing DOC concentrations measured through time for samples from three Marcellus Shale gas wells on a single well pad in Greene County, PA.

Data from Cluff et al. (2014). Reprinted with permission from Cluff, M; Hartsock, A; Macrae, J; Carter, K; Mouser, PJ. (2014). Temporal changes in microbial ecology and geochemistry in produced water from hydraulically fractured Marcellus Shale Gas Wells. Environ Sci Technol 48: 6508-6517. Copyright 2014 American Chemical Society.

As an example, produced water DOC concentrations decreased from their initial levels twofold from the hydraulic fracturing fluid and initial samples (Figure 7-5b) followed by a decrease of 11-fold over nearly 11 months. The DOC leveled off several months after hydraulic fracturing, presumably as a result of in situ attenuation processes (Cluff et al., 2014). As DOC was decreasing, chloride concentrations increased five- to six-fold. These chloride concentrations increased linearly during the first two weeks (Cluff et al., 2014) and then later approached higher levels (Figure 7-5a). The pattern in the DOC and chloride levels reflected the changing composition of the produced water—initially high in DOC from hydraulic fracturing additives and low in salinity, then higher in salinity and lower in DOC reflecting the chemistry of formation water. The changing composition of produced water suggests that the potential concern for produced water spills also changes: initially the produced water may contain more hydraulic fracturing chemicals, and later the concern may shift to the impact of high salinity water.

7.3.4 Produced Water Composition

The chemical composition of produced water continues to change after the initial flowback period. Produced water may contain a range of constituents, but in widely varying amounts. Generally, these can include:

- Salts, including those composed from chloride, bromide, sulfate, sodium, magnesium and calcium;
- Metals including barium, manganese, iron, and strontium;
- Radioactive materials including radium (radium-226 and radium-228);
- Oil and grease, and dissolved organics (including BTEX);[1]
- Hydraulic fracturing chemicals, including tracers and their transformation products; and
- Produced water treatment chemicals.[2]

We discuss these groups of chemicals and then conclude by discussing variability within formation types and within production zones.

7.3.4.1 Similarity of Produced Water from Conventional and Unconventional Reservoirs

Produced water generated from unconventional reservoirs is reported to be similar to produced water from conventional reservoirs in terms of TDS, pH, alkalinity, oil and grease, TOC, and other organics and inorganics (Wilson, 2014; Haluszczak et al., 2013; Alley et al., 2011; Hayes, 2009; Sirivedhin and Dallbauman, 2004). Although produced water salinity varies within and among shales and tight formations, produced water is typically characterized as saline (Lee and Neff, 2011; Blauch et al., 2009). Produced water from coalbeds may have low TDS if the coal source bed was formed in freshwater. Saline produced water is also enriched in major anions (e.g., chloride, bicarbonate, sulfate); cations (e.g., sodium, calcium, magnesium); metals (e.g., barium, strontium);

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[1] BTEX is an acronym representing benzene, toluene, ethylbenzene, and xylenes.

[2] Some chemicals are added to produced water for the purpose of oil/water separation, improved pipeline flow, or equipment maintenance, including prevention of corrosion and scaling in equipment (Cal/EPA, 2016). Generally the chemicals serve as clarifiers, emulsifiers, emulsion breakers, floating agents, and oxygen scavengers. Among proprietary formulations, a few specific chemicals have been disclosed including low concentrations of benzene, toluene, and inorganics (acetic acid, ammonium chloride, cupric sulfate, sodium hypochlorite).

naturally occurring radionuclides (e.g., radium-226, radium-228) (Chapman et al., 2012; Rowan et al., 2011); and organics (e.g., hydrocarbons) (Orem et al., 2007; Sirivedhin and Dallbauman, 2004).

7.3.4.2 Variability in Produced Water Composition Among Unconventional Reservoirs

Alley et al. (2011) compared geochemical parameters of shale gas, tight gas, and CBM produced water. This comparison aggregated data on produced water from original analyses, peer-reviewed literature, and public and confidential government and industry sources and determined the statistical significance of the results.

As shown in Table 7-5, Alley et al. (2011) found that of the constituents of interest common to all three types of produced water from unconventional reservoirs (calcium, chloride, potassium, magnesium, manganese, sodium, and zinc):

1. Shale gas produced water had significantly different concentrations from those of CBM;
2. Shale gas produced water constituent concentrations were significantly similar to those of tight gas, except for potassium and magnesium; and
3. Five tight gas produced water constituent concentrations (calcium, chloride, potassium, magnesium, and sodium) were significantly similar to those of CBM (Alley et al., 2011).

The degree of variability between produced waters of these three resource types is consistent with the degree of mineralogical and geochemical similarity between shale and sandstone formations, and the lack of the same between shale and coalbed formations (Marshak, 2004). Compared to the others, shale gas produced water tends to be more acidic, as well as enriched in strontium, barium, and bromide. CBM produced water is alkaline, and it contains relatively low concentrations of TDS (one to two orders of magnitude lower than in shale and sandstone). It also contains lower levels of sulfate, calcium, magnesium, DOC, sodium, bicarbonate, and oil and grease than typically observed in shale and sandstone produced waters (Alley et al., 2011; Dahm et al., 2011; Benko and Drewes, 2008; Van Voast, 2003).[1]

Table 7-5. Compiled minimum and maximum concentrations for various geochemical constituents in produced water from shale gas, tight gas, and CBM produced water.
Source: Alley et al. (2011).

Parameter	Unit	Shale gas[a]	Tight Gas Sands[b]	CBM[c]
Alkalinity	mg/L	160–188	1,424	54.9–9,450
Ammonium-N	mg/L	-	2.74	1.05–59
Bicarbonate	mg/L	ND–4,000	10–4,040	-
Conductivity	µS/cm	-	24,400	94.8–145,000
Nitrate	mg/L	ND–2,670	-	0.002–18.7

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[1] Several regions had low representation in the Alley et al. (2011) data set, including the Appalachian Basin (western New York and western Pennsylvania), West Virginia, eastern Kentucky, eastern Tennessee, and northeastern Alabama.

Parameter	Unit	Shale gas[a]	Tight Gas Sands[b]	CBM[c]
Oil and grease	mg/L	-	42	-
pH	SU[d]	1.21–8.36	5–8.6	6.56–9.87
Phosphate	mg/L	ND–5.3	-	0.05–1.5
Sulfate	mg/L	ND–3,663	12–48	0.01–5,590
Radium-226	pCi/g	0.65–1.031	-	-
Aluminum	mg/L	ND–5,290	-	0.5–5,290
Arsenic	mg/L	-	0.17	0.0001–0.06
Boron	mg/L	0.12–24	-	0.002–2.4
Barium	mg/L	ND–4,370	-	0.01–190
Bromide	mg/L	ND–10,600	-	0.002–300
Calcium	mg/L	0.65–83,950	3–74,185	0.8–5,870
Cadmium	mg/L	-	0.37	0.0001–0.01
Chloride	mg/L	48.9–212,700	52–216,000	0.7–70,100
Chromium	mg/L	-	0.265	0.001–0.053
Copper	mg/L	ND–15	0.539	ND–0.06
Fluorine	mg/L	ND–33	-	0.05–15.22
Iron	mg/L	ND–2,838	0.015	0.002–220
Lithium	mg/L	ND–611	-	0.0002–6.88
Magnesium	mg/L	1.08–25,340	2–8,750	0.2–1,830
Manganese	mg/L	ND–96.5	0.525	0.002–5.4
Mercury	mg/L	-	-	0.0001–0.0004
Nickel	mg/L	-	0.123	0.0003–0.20
Potassium	mg/L	0.21–5,490	5–2,500	0.3–186
Sodium	mg/L	10.04–204,302	648–80,000	8.8–34,100
Strontium	mg/L	0.03–1,310	-	0.032–565
Uranium	mg/L	-	-	0.002–0.012
Zinc	mg/L	ND–20	0.076	0.00002–0.59

-, No value available; ND, non-detect. If no range, but a singular concentration is given, this is the maximum concentration.

[a] *n* = 541. Alley et al. (2011) compiled data from USGS (2006); McIntosh and Walter (2005); McIntosh et al. (2002) and confidential industry documents.

[b] *n* = 137. Alley et al. (2011) compiled data from USGS (2006) and produced water samples presented in Alley et al. (2011).

[c] Alley et al. (2011) compiled data from Montana GWIC (2009); Thordsen et al. (2007); ESN Rocky Mountain (2003); Rice et al. (2000); Rice (1999); Hunter and Moser (1990).

[d] SU = standard units.

7.3.4.3 General Water Quality Parameters

Data characterizing the content of produced water from unconventional reservoirs in 12 shale and tight formations and CBM basins were evaluated for this assessment. These reservoirs and basins include parts of 18 states, but the data do not allow for comparison of trends over time.

For most reservoirs, the amount of available general water quality parameter data is variable (see Appendix Table E-2 for an example). Average pH levels range from 5.87 to 8.19, with typically lower values for shales. Larger variations in average specific conductivity are seen among unconventional reservoirs and range from 213 microsiemens (µS)/cm in the Bakken Shale to 184,800 µS/cm in Devonian sandstones (Appendix Table E-2). Shale and tight formation produced waters are enriched in suspended solids, as reported concentrations for total suspended solids and turbidity exceed those of coalbeds by one to two orders of magnitude.

The average dissolved oxygen (DO) concentrations of CBM produced water range from 0.39-1.07 mg/L (Appendix Table E-3). By comparison, well-oxygenated surface water can contain up to 10 mg/L DO at 59 °F (15 °C) (U.S. EPA, 2012a). Thus, coalbed produced water is either hypoxic (less than 2 mg/L DO) or anoxic (less than 0.5 mg/L DO) and, if released to surface waters, could contribute to aquatic organism stress (USGS, 2010; NSTC, 2000).

7.3.4.4 Salinity and Inorganics

The TDS profile of produced water from unconventional reservoirs is dominated by sodium and chloride, with large contributions to the profile from mono- and divalent cations (Sun et al., 2013; Guerra et al., 2011). Shale and sandstone produced waters tend to be characterized as sodium-chloride-calcium water types, whereas CBM produced water tends to be characterized as sodium chloride or sodium bicarbonate water types (Dahm et al., 2011). Elevated levels of bromide, sulfate, and bicarbonate are also present (Sun et al., 2013). Elevated strontium and barium levels are characteristic of Marcellus Shale produced water (Barbot et al., 2013; Haluszczak et al., 2013; Chapman et al., 2012). Data representing shales and tight formations are presented in Appendix Table E-4.

Marcellus Shale produced water salinities range from less than 1,500 mg/L to over 300,000 mg/L, as shown by Rowan et al. (2011). By comparison, the average salinity concentration for seawater is 35,000 mg/L.

Of the CBM data presented in Appendix Table E-5, differences are evident between the Black Warrior and the three western formations (Powder River, Raton, and San Juan). The Black Warrior is higher in average chloride, specific conductivity, TDS, TOC, and total suspended solids, and lower in alkalinity and bicarbonate than the other three. These differences are due to the saline or brackish conditions during deposition in the Black Warrior, and its older geologic age that contrasts with the freshwater conditions for the younger western basins. The TDS concentration of CBM produced water can range from 170 mg/L to nearly 43,000 mg/L (range composited from Dahm et al. (2011) and Benko and Drewes (2008); see also Van Voast (2003)).[1]

7.3.4.5 Metals

The metals content of produced water from unconventional reservoirs varies by well and site lithology. Levels of iron, magnesium, and boron were within ranges known for conventional produced water (Hayes, 2009). Produced water from unconventional reservoirs may also contain low levels of heavy metals (e.g., chromium, copper, nickel, zinc, cadmium, lead, arsenic, and mercury as found by Hayes). Data illustrating metal concentrations in produced water appear in Appendix Tables E-6 and E-7.

7.3.4.6 Naturally Occurring Radioactive Material (NORM) and Technologically Enhanced Naturally Occurring Radioactive Material (TENORM)

Geologic environments contain naturally occurring radioactive material (NORM). Radioactive materials commonly present in shale and sandstone sedimentary environments include uranium, thorium, radium, and their decay products. Elevated formation uranium levels have been used to identify potential areas of natural gas production for decades (Fertl and Chilingar, 1988). Shales that contain significant levels of uranium include the Barnett in Texas, the Woodford in Oklahoma, the New Albany in the Illinois Basin, the Chattanooga Shale in the southeastern United States, and a group of black shales in Kansas and Oklahoma (Swanson, 1955).[2] When exposed to the environment in produced water, NORM is called *technologically enhanced* naturally occurring radioactive material (TENORM).[3] Water soluble forms of TENORM are present in most produced water from unconventional reservoirs, but particularly so in Marcellus Shale produced water (Rowan et al., 2011; Fisher, 1998).

Due to insolubility under prevailing reducing conditions encountered within shale formations, only low levels of uranium and thorium are found in produced water, typically in the concentrated form of mineral phases or organic matter (Nelson et al., 2014; Sturchio et al., 2001). Conversely, radium, a decay product of uranium and thorium, is known to be relatively soluble within the redox range encountered in subsurface environments (Sturchio et al., 2001; Langmuir and Riese, 1985). As noted in Section 7.3.3.2, radium and TDS produced water concentrations are positively correlated (Rowan et al., 2011; Fisher, 1998); therefore, in formations containing radium, increasing TDS concentration indicates likely increasing radium concentration.

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[1] From a similar dataset, Dahm et al. (2011) report TDS concentrations from a composite CBM produced water database (n = 3,255) for western basins that often are less than 5,000 mg/L (85% of samples).

[2] Marine black shales are estimated to contain an average of 15−60 ppm uranium depending on depositional conditions (Fertl and Chilingar, 1988).

[3] The U.S. EPA Office of Air and Radiation's website (https://www.epa.gov/radiation/technologically-enhanced-naturally-occurring-radioactive-materials-tenorm) states that TENORM is produced when activities such as uranium mining or sewage sludge treatment concentrate or expose radioactive materials that occur naturally in ores, soils, water, or other natural materials. Formation water containing radioactive materials contains NORM, because it is not exposed; produced water contains TENORM, because it has been exposed to the environment.

Median values of total radium in the Marcellus Shale ranged from about 1,000 pCi/L to less than 6,000 pCi/L, which are values far exceeding the industrial discharge limit of 60 pCi/L (Rowan et al., 2011) (Figure 7-6). In the Marcellus Shale, TENORM levels in produced water from unconventional reservoirs exceeded levels from conventional reservoirs levels by factors of 4 to 26 (PA DEP, 2015b) (Appendix Table E-8). The individual median concentrations in produced water from unconventional reservoirs of 11,300 pCi/L gross alpha, 3,445 pCi/L gross beta, and total radium of 7,180 pCi/L (Appendix Table E-8). TENORM has been identified in hydraulic fracturing fluid, presumably due to the reuse of produced water at levels from 2 to 4.5 times lower than produced water from unconventional reservoirs (PA DEP, 2015b) (Appendix Table E-8).

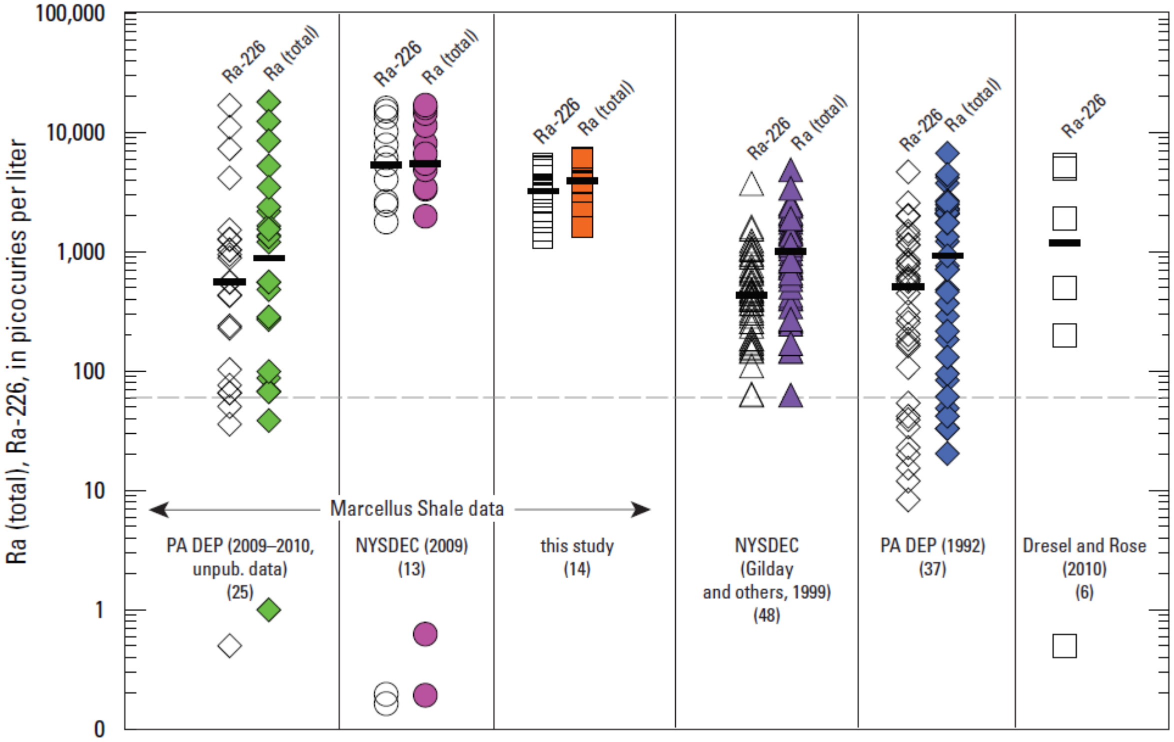

Figure 7-6. Data on radium 226 (open symbols) and total radium (filled symbols) for Marcellus Shale wells (leftmost three columns) and other formations (rightmost three columns).

Source: Rowan et al. (2011). The dashed line represents the industrial effluent discharge limit of 60 pCi/L set by the Nuclear Regulatory Commission. The black lines indicate the median concentrations, and the number of points in each dataset are shown in parentheses. Citations within the figure are provided in Rowan et al. (2011).

7.3.4.7 Organics

The organic content of produced water varies by well and lithology, but consists of naturally occurring and injected organic compounds (Lee and Neff, 2011). Of the organics detected by either routine or advanced analytical methods (Section 7.3.1), the majority are naturally occurring constituents of petroleum (Appendix Tables H-4 and H-5). These organics may be dissolved in water or, in the case of oil production, in the form of a separate or emulsified phase. Several classes of organic chemicals have been found in shale gas and CBM produced water, including aromatics, polyaromatic hydrocarbons, heterocyclic compounds, aromatic amines, phenols, phthalates, aliphatic alcohols, fatty acids, and nonaromatic compounds (list from Orem et al. (2014), see also: Hayes (2009), Benko and Drewes (2008), Orem et al. (2007), and Sirivedhin and Dallbauman (2004)). Compounds found in CBM waters included pyrene, phenanthrenone, alkyl phthalates, C_{12} through C_{18} fatty acids, and others. Similarly, compounds found in shale gas produced water included pyrene and perylene, ethylene glycol, diethylene glycol monododecyl ether, 2-(2-butoxyethoxy) ethanol, and others (Orem et al., 2014). Biomarkers—organic molecules characteristically produced by life forms, and unique to shale formations—have recently been suggested to fingerprint produced water (Hoelzer et al., 2016). More representative examples from five coal bed and two shale gas formations with reported concentrations are given in Appendix Tables E-9, E-11, and E-12, and the complete list of chemicals with CAS registry numbers identified by the EPA for this assessment appears in Appendix H. (See Appendix Table H-4 for chemicals with EPA-identified CAS numbers and Appendix Table H-5 for chemicals without.) Appendix Table E-13 lists concentrations of organic chemicals that were identified in three specific studies (Khan et al., 2016; Lester et al., 2015; Orem et al., 2007).

7.3.4.8 Hydraulic Fracturing Fluid Additives

Several chemicals used in hydraulic fracturing fluids have been identified in produced water. (Examples are shown in Table 7-6, Appendix Table E-10, and Appendix Tables H-4 and H-5.) Many of these chemicals were identified through advanced analytical procedures and equipment, and would not be expected to be found by routine analyses. Of note is that phthalates do not occur naturally. Their presence in produced water is due to either their use in hydraulic fracturing fluids; polyvinyl chloride (PVC) in well adhesives, valves, or fittings; or coatings on laboratory sample bottles (Orem et al., 2007).[1] Phthalates can also be used in drilling fluids, as breaker additives, or as plasticizers (Maguire-Boyle and Barron, 2014; Hayes and Severin, 2012a).[2] One of the produced water phthalates has been identified as a component of hydraulic fracturing fluid (di(2-ethylhexyl) phthalate) (Appendix Table H-2), while others have not, and those may originate from laboratory or field equipment.

Table 7-6. Examples of compounds identified in produced water that can be components of hydraulic fracturing fluid.

Appendix Tables H-4 and H-5 list chemicals identified in produced water and indicates those also identified as constituents of hydraulic fracturing fluid. Chemical or class designation in this table is taken directly from the text of the cited references except where noted, and may or may not reflect the chemical names from the Distributed Structure-Searchable Toxicity Database (DSSTox) show in Appendix Table H-4 or other chemicals listed in Appendix Table H-5.

Chemical or class	Use	Reference
2-Butanone	Solvent; microbial degradation product	Lester et al. (2015)

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[1] Examples include di(2-ethylhexyl) phthalate, diisodecyl phthalate, and diisononyl phthalate (Orem et al., 2007).

[2] Specifically fatty acid phthalate esters (Maguire-Boyle and Barron, 2014).

Chemical or class	Use	Reference
2-Butoxyethanol	Acid dispersant, solvent, non-emulsifier	Thacker et al. (2015)
Acetone	Solvent; microbial degradation product	Lester et al. (2015)
Cocamidopropyl dimethylamine (C-7)	Foaming and lubrication enhancer	Lester et al. (2015)
Di(2-ethylhexyl) phthalate[a]	Derivative of polyvinyl chloride used in adhesives, valves, fittings or coatings of sample bottles	Orem et al. (2007)
Diethylene glycol monododecyl ether	Antifreeze, scale inhibitor, friction reducer	Orem et al. (2014)
Dioctadecyl ester of phosphate phosphoric acid	Common lubricant	Maguire-Boyle and Barron (2014)
Ethylene glycol	Antifreeze, scale inhibitor, friction reducer	Orem et al. (2014)
Fatty acid phthalate esters	(Related to) use in drilling fluids and breakers	Maguire-Boyle and Barron (2014)
Fluorocarbons	Tracers	Maguire-Boyle and Barron (2014)
Hexahydro-1,3,5-trimethyl-1,3,5-triazine-2-thione	Biocide	Orem et al. (2014)
Linear alkyl ethoxylates (C-4 to C-8, C-11 to C-14)	Enhancer of surfactant properties	Lester et al. (2015); Thurman et al. (2014)
Polyethylene glycol carboxylates (PEG-C-EO2 to PEG-C-EO10)	Friction reducer, clay stabilizer, surfactants	Thurman et al. (2016)
Polyethylene glycols (PEG-EO4 to PEG-EO10)	Friction reducer, clay stabilizer, surfactants	Thurman et al. (2016)
Polypropylene glycols (PPG-PO2 to PPG PO10)	Friction reducer, clay stabilizer, surfactants	Thurman et al. (2016)
Toluene	Solvent, scale inhibitor	Thacker et al. (2015)
Triethylene glycol monododecyl ether	Antifreeze, scale inhibitor, friction reducer	Orem et al. (2014)
Xylenes	Solvent, scale inhibitor	Thacker et al. (2015)

[a] Di(2-ethylhexyl) phthalate was named di-2-ethyl hexyl phthalate in Maguire-Boyle and Barron (2014).

7.3.4.9 Reactions within Formations

The introduction of hydraulic fracturing fluids into the target formation induces a number of changes to formation solids and fluids that influence the chemical evolution and composition of produced water. These changes can result from physical processes (e.g., rock fracturing and fluid mixing); geochemical processes (e.g., introducing oxygenated fluids of composition unlike that of the formation); and down hole conditions (elevated temperature, salinity, and pressure) that mobilize trace or major constituents into solution.

The creation of fractures exposes new formation surfaces to interactions involving hydraulic fracturing fluids and existing formation fluids. Formations in unconventional reservoirs targeted for development are composed of detrital, cement, and organic fractions. For example, elements potentially available for mobilization when exposed via fracturing include calcium, magnesium, manganese, and strontium in cement fractions, and silver, chromium, copper, molybdenum, niobium, vanadium, and zinc in organic fractions.

From organic compounds identified in five flowback samples and one produced water sample from the Fayetteville Shale, three possible types of reactions were identified by Hoelzer et al. (2016): hydrolysis of delayed acids, oxidant-caused halogenation reactions, and transformation of disclosed additives. First, delayed acids are used to “break” gel structures and would be intentionally introduced for their ability to cause in-formation reactions. Second, strong oxidants or other compounds introduced as breakers, along with elevated temperature and salinity, can trigger reactions between halogens (chloride, bromide, and iodide) and methane, acetone and pyrane resulting in halomethane compounds. A similar suggestion was made by Maguire-Boyle and Barron (2014). Low pH was found to promote oxidation of additives (Tasker et al., 2016). Third, known additives may react to form byproducts. Hoelzer et al. (2016) postulate examples from several types of compounds, two of these are the formation of benzyl alcohol from the hydraulic fracturing additive benzyl chloride, and abiotic and biotic reactions of phenols. In a study that used synthetic fracturing fluid, Tasker et al. (2016) reported that surfactants were recalcitrant to degradation under high pressure and temperature, which may explain the presence of the surfactant glycols in produced water as reported by Thurman et al. (2016) (Table 7-6), and the oxidation of other additives (gelling and some friction reducers (Table 5-1)) may explain their absence.

7.3.5 Spatial Trends in Produced Water Composition

As was reported for the volume of produced water (Section 7.2.2), the composition of produced water varies spatially on a regional to local scale according to the geographic and stratigraphic locations of each well within a hydraulically fractured production zone (Bibby et al., 2013; Lee and Neff, 2011). Spatial variability of produced water content occurs: (1) between plays of different rock sources (e.g., coal vs. sandstone); (2) between plays of the same rock type (e.g., Barnett Shale vs. Bakken Shale); and (3) within formations of the same source rock (e.g., northeastern vs. southwestern Marcellus Shale) (Barbot et al., 2013; Alley et al., 2011; Breit, 2002).

Geographic variability in produced water content has been established at a regional scale for conventional produced water. As an example, Benko and Drewes (2008) demonstrate TDS variability in conventional produced water among fourteen western geologic basins (e.g., Williston, San Juan, and Permian Basins). Median TDS in these basins range from as low as 4,900 mg/L in the Big Horn Basin to as high as 132,400 mg/L in the Williston Basin based on over 133,000 produced water samples from fourteen basins (Benko and Drewes, 2008).[1]

Average or median TDS of more than 100,000 mg/L has been reported for the Bakken (North Dakota, Montana) and Marcellus (Pennsylvania) formations; between 50,000 mg/L and 100,000 mg/L for the Barnett (Texas), and less than 50,000 mg/L for the Fayetteville (Arkansas) shale formations.[2] In tight formations, the average TDS was above 100,000 mg/L for the Devonian Sandstone (Pennsylvania) and Cotton Valley Group (Louisiana, Texas), between 50,000 mg/L and 100,000 mg/L for the Oswego (Oklahoma), and less than 50,000 mg/L for the Mesaverde Formation (Colorado, New Mexico, Utah, Wyoming). Maximum concentrations above 200,000 mg/L have been reported for the Marcellus, Bakken, Cotton Valley Group and Devonian Sandstone (Appendix Table E-2).

CBM produced waters had average TDS of less than 5,000 mg/L in the Powder River (Montana, Wyoming), Raton (Colorado, New Mexico), and San Juan (Arizona, Colorado, New Mexico, Utah) basins; while above 10,000 mg/L in the Black Warrior Basin (Alabama, Mississippi), which as noted above are due to the depositional history of these basins (Appendix Table E-3, Section 7.3.2).

Data further illustrating variability within both shale and tight gas reservoirs, as well as coalbed methane fields, at both the formation and local scales are presented and discussed in Appendix Section E.3.

7.4 Spill and Release Impacts on Drinking Water Resources

Surface spills of produced water from oil and gas production have occurred across the country and, in some cases, have caused impacts to drinking water resources. Released fluids can flow into nearby surface waters, if not contained on-site, or infiltrate into groundwater via soil. In this section, we first briefly describe the potential for spills from produced water handling equipment. Next, we address individually reported spill events. These have originated from pipeline leaks, well blowouts, well communication events, and leaking pits and impoundments. We then summarize several studies of aggregated spill data, which are based on state agency spill reports.

7.4.1 Produced Water Handling and Spill Potential

Throughout the production phase at oil and certain wet gas production facilities, produced water is stored in containers and pits that can contain free phase, dissolved phase, and emulsified crude oil. Since the crude oil is not efficiently separated out by the flow-through process vessels (such as

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[1] Data were drawn from the USGS National Produced Water Geochemical Database v2.0. Published updates made in October 2014 to the database (v2.1) are not reflected in this document.

[2] Because publications we are comparing may report either average or median values (but not uniformly both), we combine average and medians in this paragraph.

three-phase separators, heater treaters, or gun barrels), this crude oil can remain present in the produced water container or pit.

Produced water can be transferred to surface pits for long-term storage and evaporation. Surface pits are typically uncovered, earthen pits that may or may not be lined.[1] Unlined pits can lead to contamination of groundwater, especially shallow alluvial systems. Recovered fluids can overflow or leak from surface pits due to improper pit design and weather events.

Produced water that is to be treated or disposed of off-site is typically stored in storage tanks or pits until it can be loaded into transport trucks for removal (Gilmore et al., 2013). Tank storage systems are typically closed loop systems in which produced water is transported from the wellhead to aboveground storage tanks through interconnecting pipelines (GWPC and IOGCC, 2014). Failure of connections and lines during the transfer process or the failure of a storage tank can result in a surface release of fluids.

Depending on its characteristics, produced water can be recycled and reused on-site. It can be directly reused without treatment (after blending with freshwater), or it can be treated on-site prior to reuse (Boschee, 2014). As with other produced water management options, these systems also can spill during transfer of fluids.

7.4.2 Spills of Produced Water

7.4.2.1 Pipeline Leaks

Produced water is typically transported from the wellhead through a series of pipes or flowlines to on-site storage or treatment units (GWPC and IOGCC, 2014), or nearby injection wells. Faulty connections at either end of the transfer process or leaks or ruptures in the lines carrying the fluid can result in surface spills. A field report from PA DEP (2009b) described a leak from a 90-degree bend in an overland pipe carrying a mixture of produced water and freshwater between two pits. The impact included a “dull sheen” on the water and measured chloride concentration of 11,000 mg/L. The leak impacted a 0.4 mi (0.6 km) length of a stream, and fish and salamanders were killed. Beyond a confluence at 0.4 mi (0.6 km) with a creek, no additional dead fish were found. The release was estimated at 11,000 gal (42,000 L). In response to the incident, the pipeline was shut off, a dam was constructed for recovering the water, water was vacuumed from the stream, and the stream was flushed with fresh water (PA DEP, 2009b).

Another example of a pipeline release occurred in January 2015, when 70,000 bbls (2,940,000 gal or 11,130,000 L) of produced water containing petroleum hydrocarbons (North Dakota Department of Health, 2015) were released from a broken pipeline that crosses Blacktail Creek in Williams County, ND. The response included placing absorbent booms in the creek, excavating contaminated soil, removing oil-coated ice, and removing produced water from the creek. The electrical conductivity and chloride concentration in the water along the creek, the Little Muddy River, and Missouri River were found to be elevated above background levels, as were samples

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[1] The use of the terms “impoundments” and “pits” varies and is described in Chapter 8. For the purposes of this section, the term “pits” will be generally used to cover all below-grade storage (but not above ground closed or open tanks).

taken from groundwater recovery trenches. Remediation work on this site continues as of the date of this writing (August, 2016).

7.4.2.2 Well Blowouts

Spills of produced water have occurred as a result of well blowouts. Fingerprinting of water from two monitoring wells in Killdeer, ND, was used to determine that brine contamination in the two wells resulted from a well blowout during a hydraulic fracturing operation. See the discussion in Section 6.2.2.1 for more information.

Another example of a well blowout associated with a hydraulic fracturing operation occurred in Clearfield County, PA. The well blew out, resulting in an uncontrolled flow of approximately 35,000 gal (132,000 L) of brine and fracturing fluid; some of the liquids reportedly reached a nearby stream (Barnes, 2010). The blowout occurred during drilling of plugs that were used to isolate fracture stages from each other. An independent investigation found that the primary cause of the incident was that the sole blowout preventer on the well had not been properly tested. In addition, the company did not have certified well control experts on hand or a written pressure control procedure (Vittitow, 2010).

In North Dakota, a blowout preventer failed, causing a release of between 50 and 70 bbls per day (2,100 gal/day or 7,900 L/day and 2,940 gal/day or 11,100 L/day) of produced water and oil (Reuters, 2014). Frozen droplets of oil and water sprayed on a nearby frozen creek. Liquid flowing from the well was collected and trucked offsite. A 3-ft (0.9-m) berm was placed around the well for containment. Multiple well communication events have also led to produced water spills ranging from around 700 to 35,000 gal (2,600 L to 130,000 L) (Vaidyanathan, 2013a). Well communication is described in Section 6.3.2.3.

The Chesapeake Energy ATGAS 2H well, located in Leroy Township, Bradford County, PA, experienced a wellhead flange failure on April 19, 2011, during hydraulic fracturing operations. Approximately 10,000 gal (38,000 L) of produced water spilled into an unnamed tributary of Towanda Creek, a state-designated trout stock fishery and a tributary of the Susquehanna River (USGS, 2013b; SAIC and GES, 2011). Chesapeake conducted post-spill surface water and groundwater monitoring (SAIC and GES, 2011).

Chesapeake concluded that there were short-term impacts to surface waters of a farm pond within the vicinity of the well pad, the unnamed tributary, and Towanda Creek following the event (SAIC and GES, 2011). The lower 500 ft (200 m) of the unnamed tributary exhibited elevated chloride, TDS, and specific conductance, which returned to background levels in less than a week. Towanda Creek experienced these same elevations in concentration, but only at its confluence with the unnamed tributary; elevated chloride, TDS, and specific conductance returned to background levels the day after the blowout (SAIC and GES, 2011).

7.4.2.3 Leaks from Pits and Impoundments

Leaks of produced water from on-site pits have caused releases as large as 57,000 gal (220,000 L) and have caused surface water and groundwater impacts (Vaidyanathan, 2013b; Levis, 2011; 2010c; PADEP, 2010). VOCs have been measured in groundwater near the Duncan Oil Field in New Mexico downgradient of an unlined pit storing produced water. More example releases from pits are described in Section 8.4.5.

Two of EPA's retrospective case studies evaluated potential impacts from produced water pits. The EPA retrospective case studies were designed to determine whether multiple lines of evidence might be found that could specifically link constituent(s) found in drinking water to hydraulic fracturing activities using the tiered assessment framework presented in Appendix Section E.6. A multiple-lines-of-evidence approach was used to evaluate potential cause-and-effect relationships between hydraulic fracturing activities and contaminant presence in groundwater. Such an approach is needed, because the presence of a constituent in groundwater that is also found in hydraulic fracturing fluids or produced water does not necessarily implicate hydraulic fracturing activities as the cause. This is because some constituents of hydraulic fracturing fluids or produced water are ubiquitous in society (i.e., BTEX), and some constituents of produced water can be present in groundwater as background constituents (i.e., methane, iron, and manganese).

Elements of the assessment framework include gathering background information, including pre-drilling sample results; developing a conceptual model of the site; and assessing multiple analytes to develop lines of evidence. Development of these requires adherence to sampling and quality assurance protocols to generate defensible data. Among many other quality assurance requirements, proper well purging and analyses of field and laboratory blanks are needed (Appendix Table E-17 and Figure E-15).

In the EPA's *Retrospective Case Study in Southwestern Pennsylvania: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (U.S. EPA, 2015j), elevated chloride concentrations and their timing relative to historical data suggested a recent groundwater impact on a private water well occurred near a pit. The water quality trends suggested that the chloride anomaly was related to the pit, but site-specific data were not available to provide a definitive assessment of the cause(s) and the longevity of the impact. Evaluation of other water quality parameters did not provide clear evidence of produced water impacts.

In the EPA's *Retrospective Case Study in Wise County, Texas: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (U.S. EPA, 2015l), impacts to two water wells were attributed to brine, but the data collected for the study were not sufficient to distinguish among multiple possible brine sources, including reserve pits, migration from underlying formations along wellbores, migration from underlying formation along natural fractures and a nearby brine injection well.

To aid in assessing impacts, a number of geochemical indicators and isotopic tracers for identifying oil and gas produced water have been identified. These include (Lauer et al., 2016; Warner et al., 2014a, b):

- Common ion ratios, including bromide/chloride and lithium/chloride;
- Isotope ratios, especially Strontium isotope ratios ($^{87}Sr/^{86}Sr$); and

- Enrichment of certain isotopes: δ^{18}O, δ^{2}H, δ^{7}Li, δ^{13}C-DIC, δ^{11}B.[1]

For the case study, twelve geochemical indicators, including the bromine/chlorine (Br/Cl) and strontium isotope ratios, were considered for the well-water samples.[2] The results were used to assess whether the likelihood that the observed values originated with produced water (the aforementioned sources of brine), sea water, road salt, landfill leachate, sewage/septic tank leachate, and animal waste. In each sample evaluated, it was found that the water could have originated with one or more of the six sources. Thus these lines of evidence did not allow identification of neither a specific source nor a hydraulic fracturing source (Appendix Table E-18). A third well experienced similar impacts, and a landfill leachate source could not be ruled out in that case.

The case studies illustrate how multiple lines of evidence were needed to assess suspected impacts and that no single constituent or parameter could be used alone to assess potential impacts.

7.4.2.4 Other Sources

In the EPA's *Retrospective Case Study in Northeastern Pennsylvania: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (U.S. EPA, 2014f), a pond was found to be impacted due to elevated chloride and TDS, along with strontium ratios (^{87}Sr/^{86}Sr) characteristic of Marcellus Shale produced water. Here, the suspected source of the impact was a well pad which had a hydrochloric acid spill, a possible produced water spill and been used for temporary storage of drill cuttings. The same mulidence fracturing impacts from constituents characteristic of produced water (TDS, chloride, sodium, barium, strontium and radium) found in three domestic wells located in an area with naturally occurring saline groundwater. Conversely, at a spring with organic chemical contamination but no associated chloride or TDS impacts, hydraulic fracturing activities were also ruled out.

An estimated 6,300 to 57,373 gal (24,000 to 217,280 L) of Marcellus Shale produced water was discharged through an open valve that drained a tank at XTO Energy Inc.'s Marquardt pad and flowed into a tributary of the Susquehanna River in November 2010 (U.S. EPA, 2016e; PA DEP, 2011c). Overland and subsurface flow of released fluids impacted surface water, a subsurface spring, and soil. Five hundred tons of contaminated soil were excavated, and an estimated 8,000 gal (30,000 L) of produced water was recovered (Science Applications International Corporation, 2010). Elevated levels of TDS, chloride, bromide, barium and strontium that indicated a release of produced water were present in the surface stream and a spring for roughly 65 days (U.S. EPA, 2016e). At that time the chloride concentration in the spring dropped below the state surface water standard of 250 mg/L. The impact extended a distance of approximately 1,400 ft (440 m) to the spring from the release point. Samples were taken in the tributary roughly 500 ft downstream from the spring, where chloride concentrations remained below the 250 mg/L standard throughout the sampling period, but were above the upstream concentrations (PA DEP, 2011c; Schmidley and Smith, 2011). Similarly, the total barium, total and dissolved iron, manganese and alkalinity concentrations remained below the Pennsylvania surface water quality standards at the downstream monitoring location throughout the monitoring period (Schmidley and Smith, 2011).

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[1] DIC is dissolved inorganic carbon.

[2] The full list was: Br vs. B, Cl vs. Mg, Cl vs. Br, Cl vs. HCO_3,Cl vs. Ca, Cl vs. K, Cl vs. Na, Cl vs. SO_4, Cl/Br, Cl/I, K/Rb, ^{87}Sr/^{86}Sr.

In Pennsylvania, discharges of brine were made into a storm drain that itself discharges to a tributary of the Mahoning River in Ohio. Analyses of the brine and drill cuttings that were discharged indicated the presence of contaminants, including benzene and toluene (U.S. Department of Justice, 2014). In California, an oil production company periodically discharged hydraulic fracturing wastewaters to an unlined sump for 12 days. It was concluded by the prosecution that the discharge posed a threat to groundwater quality (Bacher, 2013). These unauthorized discharges represent both documented and potential impacts on drinking water resources. However, data do not exist to evaluate whether such episodes are uncommon or whether they happen on a more frequent basis and remain largely undetected. Other cases of unpermitted discharges have been reported by various sources (Caniglia, 2014; Paterra, 2011).[1]

7.4.2.5 Data Compilation Studies

Three datasets were examined for produced water spill data. These included two published studies: a review of spills in Oklahoma that occurred prior to the onset of widespread high-volume hydraulic fracturing (Fisher and Sublette, 2005), and an EPA study of spills occurring between February 2006 and April 2012 on the well pads of hydraulically fractured wells (U.S. EPA, 2015m). The EPA spills study, *Review of state and industry spill data: characterization of hydraulic fracturing-related spills*, is described in Text Box 5-10. Because of data availability, EPA's study was dominated by data from Pennsylvania (21% of releases) and Colorado (48% of releases). Several difficulties are encountered in compiling and evaluating data on produced water spills and releases. Because states have differing minimum reporting levels, more spills are potentially reported in states with lower reporting limits.[2]

To include data from another state and to give results current to 2015, data from North Dakota were reviewed for this assessment.[3] Details on the procedures and results for non-produced water spills are given in Appendix Section E.5. The North Dakota Department of Health (NDDOH) collects data on environmental incidents and separately compiles oil field incidents; information is made available to the public at http://www.ndhealth.gov/EHS/Spills/. Of these incidents, most describe a release of oil, salt water, or other liquid. Of the remainder, a few describe releases of gas only.

For the period from November 2012 to November 2013, NDDOH reported 552 releases of produced water that were retained within the boundaries of the production or exploration facility and 104 that were not (North Dakota Department of Health, 2011). Thus, 16% of the releases were not contained within facility boundaries and had greater potential for impacting drinking water resources.

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[1] Section 8.4 discusses permitted discharges of wastewater.

[2] For example, two agencies in the state of California manage different databases that both store information on spills associated with oil and gas production (CCST, 2015a). CCST (2015a) reported that the databases contain inconsistencies as to the number of spills and the details regarding those spills (e.g., quantity, chemical composition of the wastewater) resulting in uncertainty on the impacts spills have on the environment.

[3] Wirfs-Brock (2015) presented an analysis of North Dakota spill data through 2013.

7.4.2.6 Frequency of Spills and Releases

The EPA analyzed these data and found that, in recent years (2010-2015), there were between five and seven produced water spills per hundred active production wells (Figure 7-7). Spills declined between 2014 and 2015 (from 846 to 609), although the number of production wells increased. A study of 17 states indicated that there was an overall reduction of 8% in spills from 2014 to 2015, and an increase of 9% in Texas (King and Soraghan, 2016). More details on the data analysis are given in Appendix Section E.5, which includes results on North Dakota oil and spills of other types, including hydraulic fracturing fluids (as noted in Chapter 5).

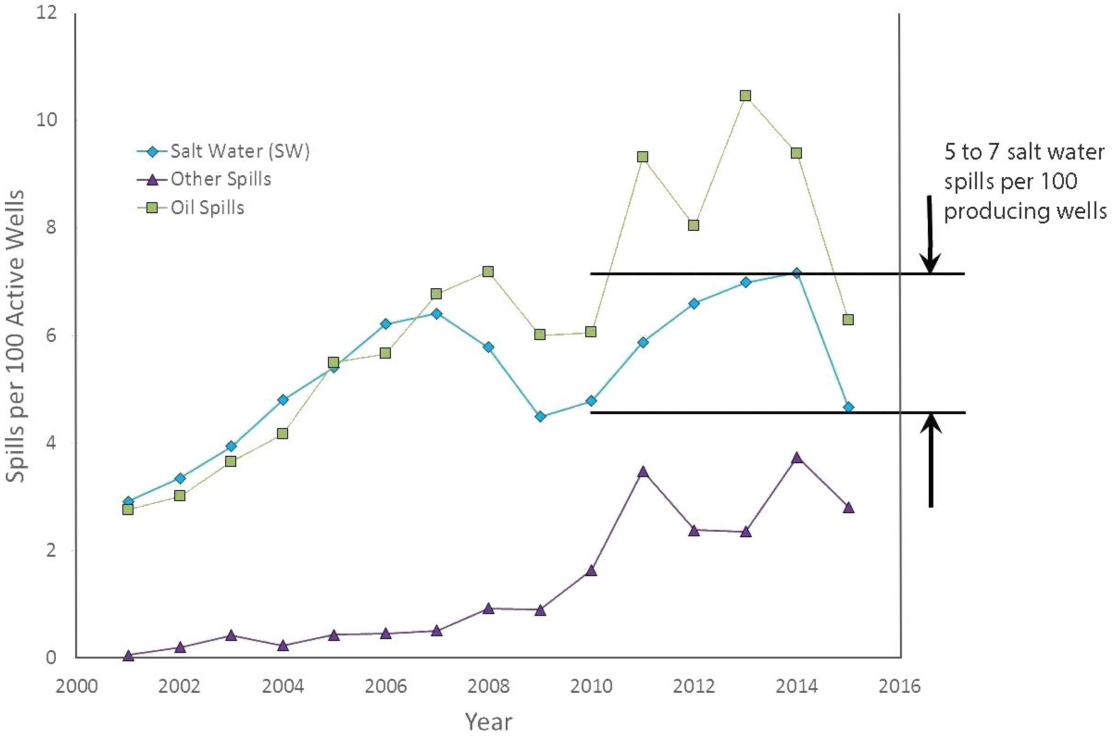

Figure 7-7. Produced water spill rates (spills per active wells) for North Dakota from 2001 to 2015 (Appendix Section E.5).

7.4.2.7 Produced Water Releases—Causes and Sources

The causes and sources identified for releases vary among the three datasets reviewed. North Dakota releases were dominated by leaks from various pieces of equipment, followed by “others,” and various overflows (Figure 7-8). While the release rate declined from 2014 to 2015, the causes remained ranked relatively in the same order; notably fewer releases were attributed to “other” and more to equipment failure in 2015. The EPA’s spills study found on- or near-well pad releases to be dominated by human error, unknown, and equipment failure (U.S. EPA, 2015m). The earlier

Oklahoma study was dominated by overflows, unpermitted discharges, and storms (Figure 7-9).[1] Storms can cause releases, as was noted after a major flood in northeastern Colorado that caused damage to produced water storage tanks releasing an estimated 43,000 gal (160,000 L) of produced water (COGCC, 2013).

The sources of releases are documented for the Oklahoma and EPA studies (Figure 7-10). The EPA cites storage, unknown, and hoses or lines as the major sources for its 225 well-pad releases. The earlier Oklahoma study cites unclassified, lines, and tanks as major sources of its 8,874 releases.

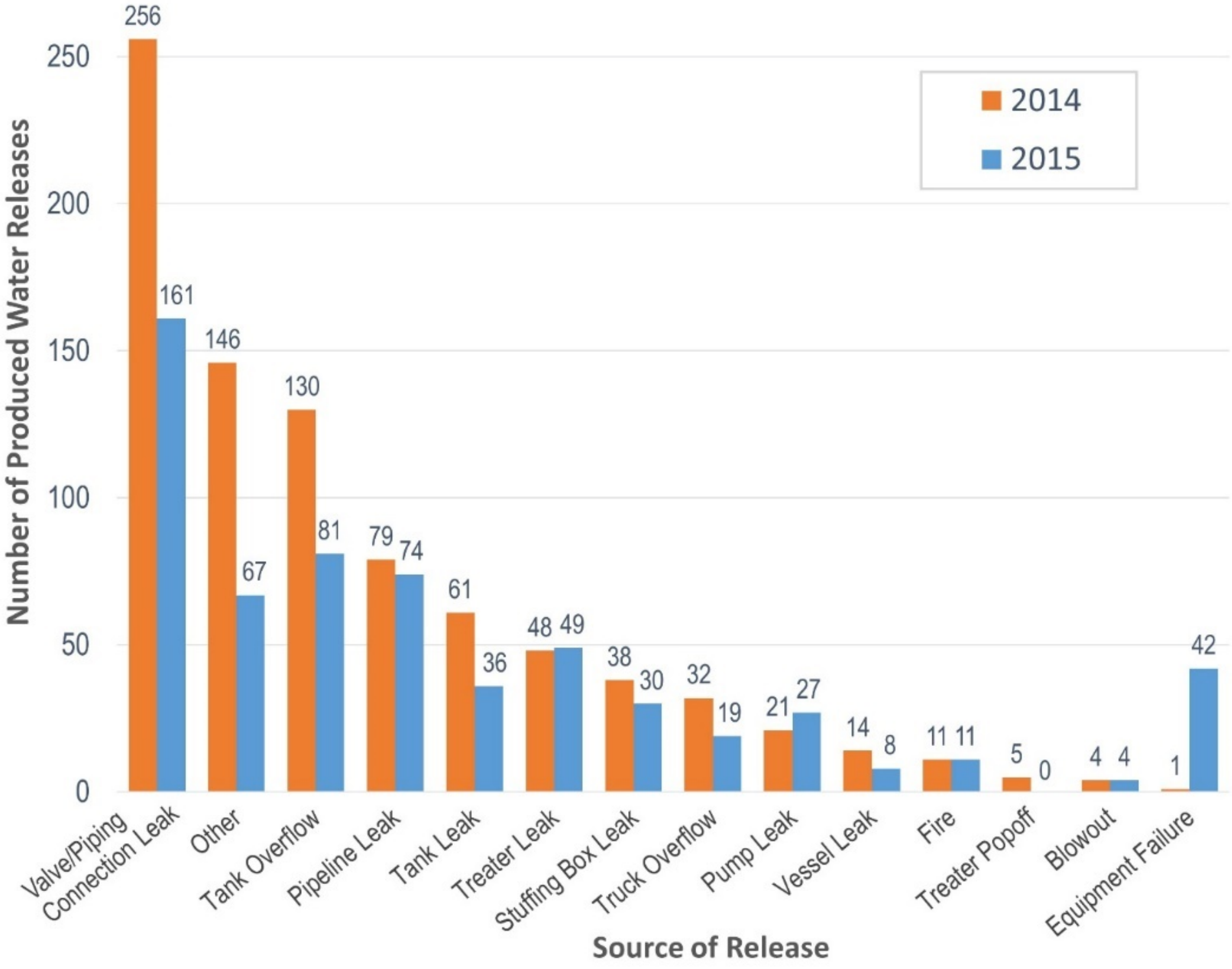

Figure 7-8. Number of produced water releases in North Dakota by cause for 2014 and 2015 (Appendix Section E.5).

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[1] Some of the causes in the three studies may be more similar than they appear, because the categorization used in the different studies overlap. For example, the EPA categorized overflows as “human error;” blowouts, vandalism and weather as “other;” and corrosion as “equipment failure,” while other studies listed these separately.

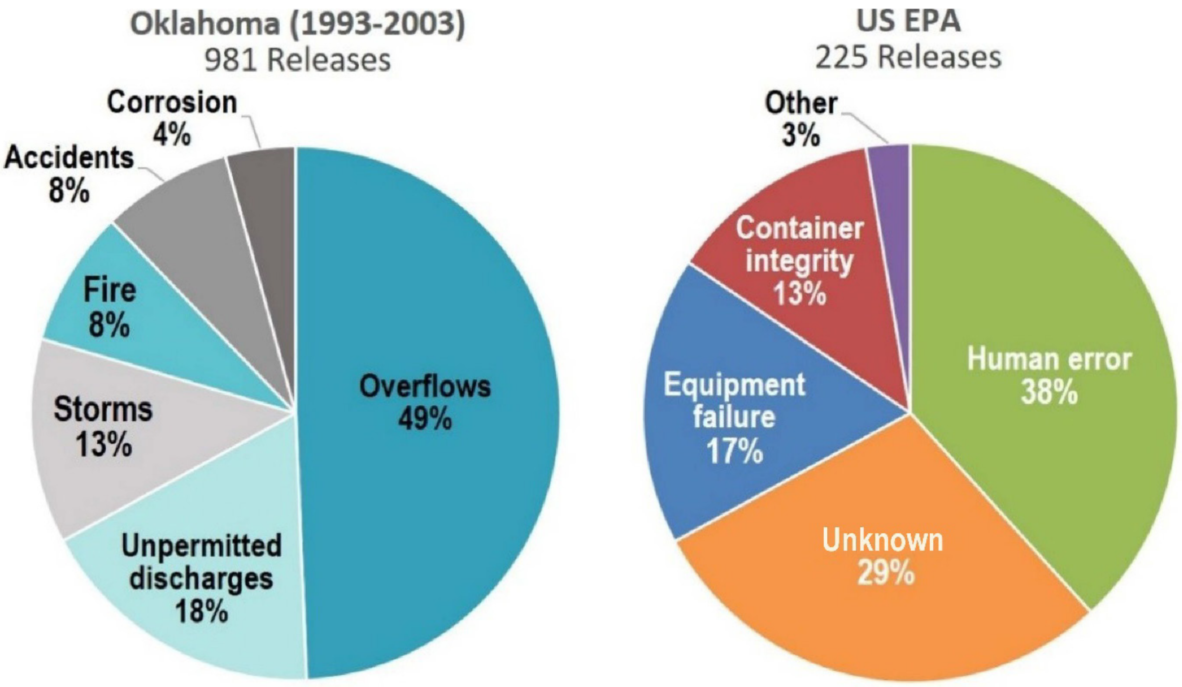

Figure 7-9. Distribution of spill causes in Oklahoma, pre-high volume hydraulic fracturing years of 1993-2003 (left) and in the EPA study of spills on production pads (right).
Data sources: left, Fisher and Sublette (2005); right, U.S. EPA (2015m).

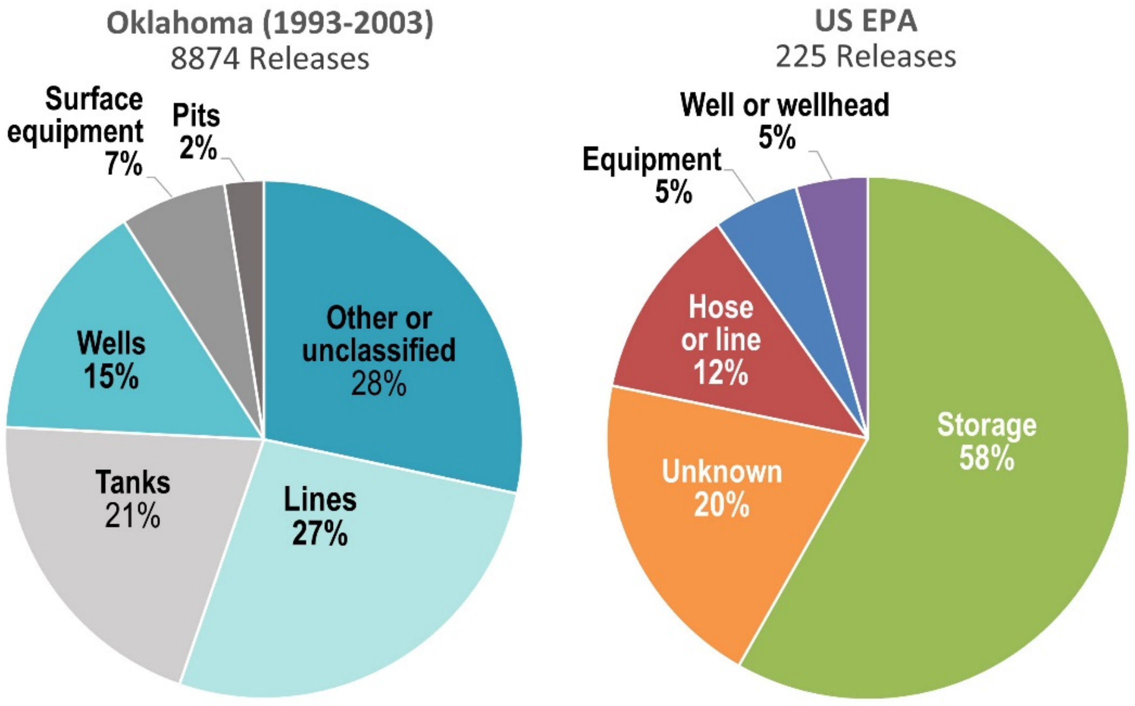

Figure 7-10. Distribution of spill sources in Oklahoma, pre-high volume hydraulic fracturing years of 1993-2003 (left) and in the EPA study of spills on production pads (right).
Data sources: left, Fisher and Sublette (2005); right, U.S. EPA (2015m).

7.4.2.8 The Volumes of Spilled Produced Water

The 2015 North Dakota spills were ranked from by the median volume, which is the level at which 50% of the spills are below this volume and 50% above (Figure 7-11).[1] Of the North Dakota spills in 2015, the highest median spill volume was caused by a blowout (2,400 gal, 91,000 L, left-most red box). The smallest median volume spill is approximately 10 times lower in volume (84 gal, 320 L). Spills larger than the median are of interest, because of their potential for impacting drinking water resources. The largest volume spill occurred from a pipeline break (2,900,000 gal, 11,000,000 L). The EPA spills study found the highest median volume spill was from equipment failure (1,700 gal, 6400 L), while the highest volume spill was due to container integrity (1,300,000 gal, 4,900,000 L) (Figure 7-12).

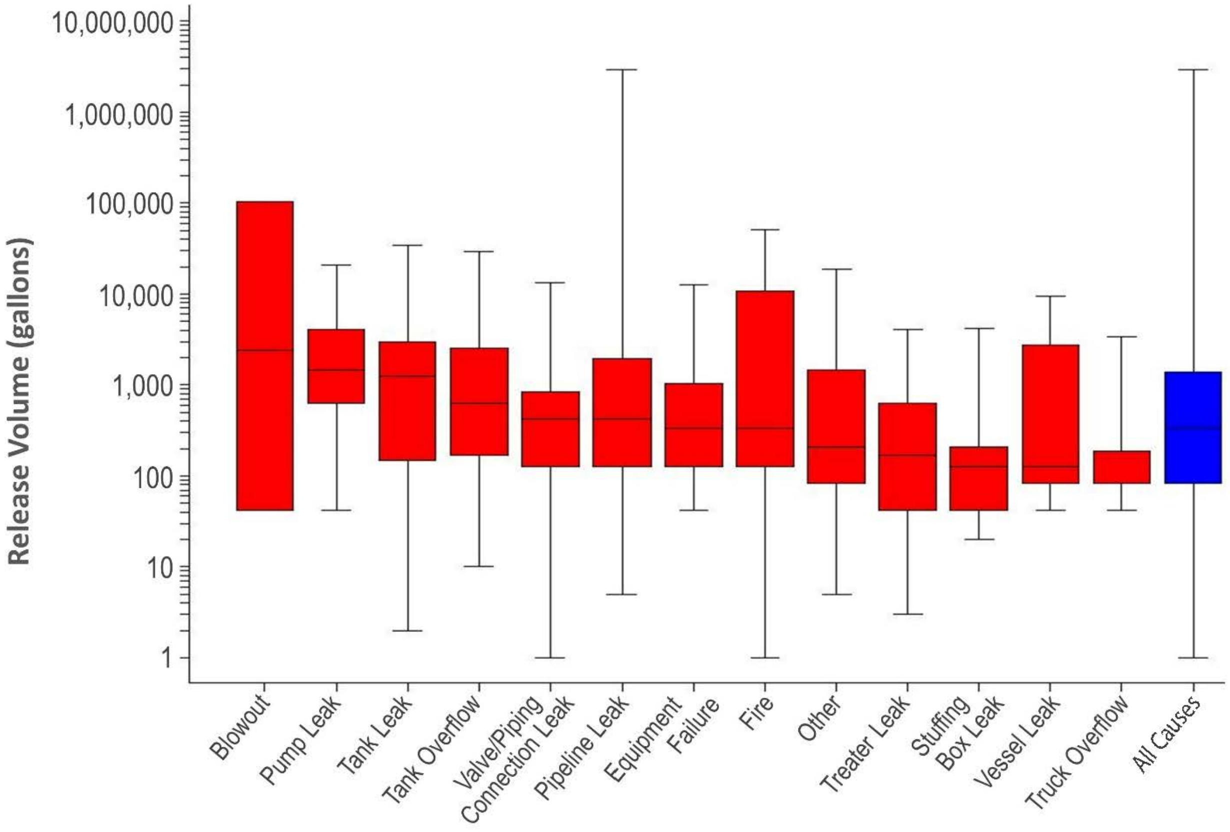

Figure 7-11. Volumes of 2015 North Dakota salt water releases by cause (leftmost 13 boxes in red), and all causes (last box in blue).

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[1] These figures are called "box" plots or "box and whisker" plots. The rectangle in the middle represents the range of data from the 25th to 75th percentile. The line across the box represents the 50th percentile, also known as the median. Fifty percent of the data are below the median. The lines extending above and below the boxes represent the range of data from minimum to maximum. These concepts are illustrated in Appendix Figure E-6.

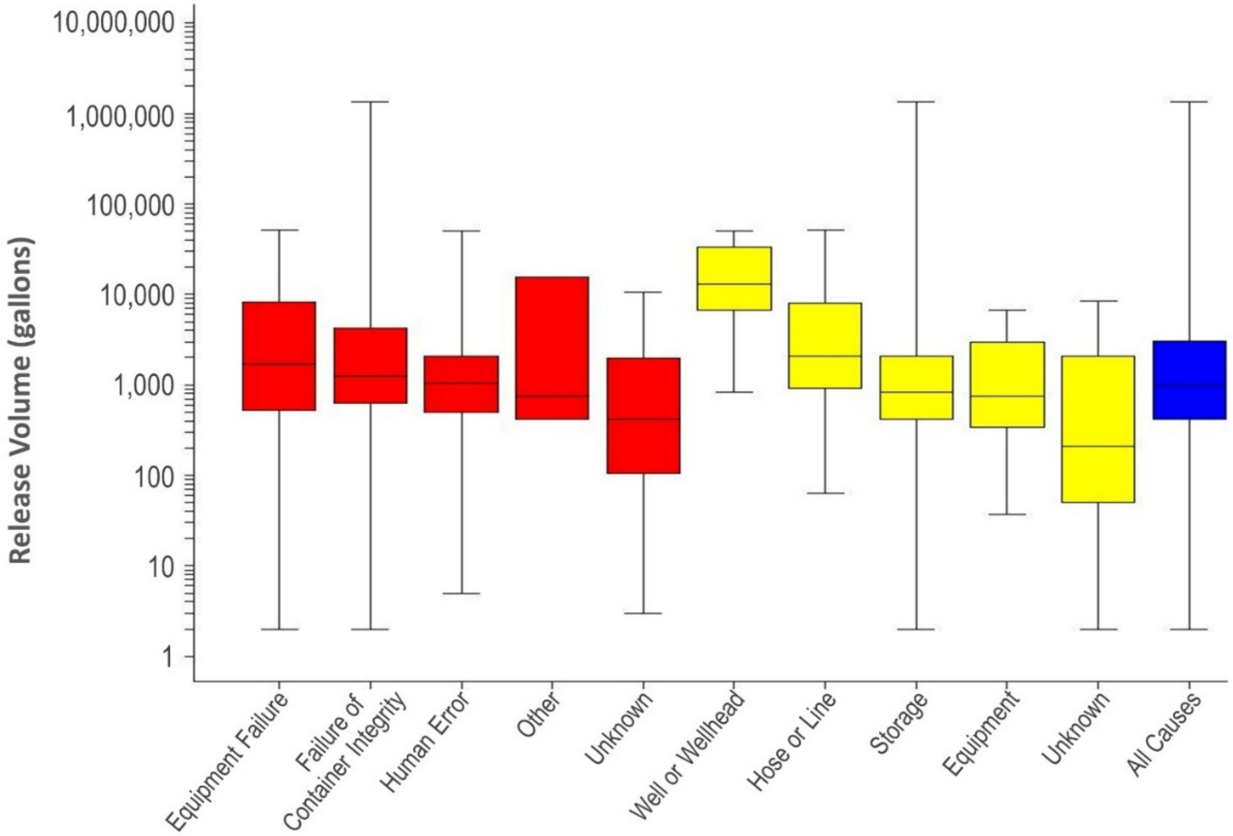

Figure 7-12. Volumes of produced water spills reported by the EPA for 2006 to 2012 by cause (the five left most boxes in red), source (the second five boxes in yellow), and all spills (blue). Calculated from Appendix B of U.S. EPA (2015m).

From the analyses, half of the spills are less than 1,000 gal (3,800 L) (EPA) and 340 gal (1,300 L) (North Dakota) (Figure 7-12, Figure 7-13, and medians in Table 7-7). The medians for the Oklahoma study were higher (overall 1,700 gal or 6,400 L; see Table 7-7 for yearly values) (Fisher and Sublette, 2005). These occurred in a different state and over an earlier time period, so a direct connection with the recent North Dakota and EPA results has not been made.

The skewed nature of the distributions are noted by the mean values being considerably higher than these medians (see Figure 7-13). In each case, this is caused by a small number of large spills. For 2015 in North Dakota, for example, there were 12 releases of 21,000 gal (79,000 L) or more; 5 of 42,000 gal (160,000 L) or more; and one of greater than 420,000 gal (1,600,000 L) (Appendix Table E-15). The largest spills from these data sets ranged from 1,000,000 gal (3,800,000 L) to 2,900,000 gal (11,000,000 L).

The EPA results give insight into recovery and reuse. Of the volume of spilled produced water, 16% was recovered for on-site use or disposal, 76% was reported as unrecovered, and the rest was unknown. The fewest spills occurred from wells and wellheads, but these spills had the greatest median volumes. Failure of container integrity was responsible for 74% of the volume spilled (U.S. EPA, 2015m).

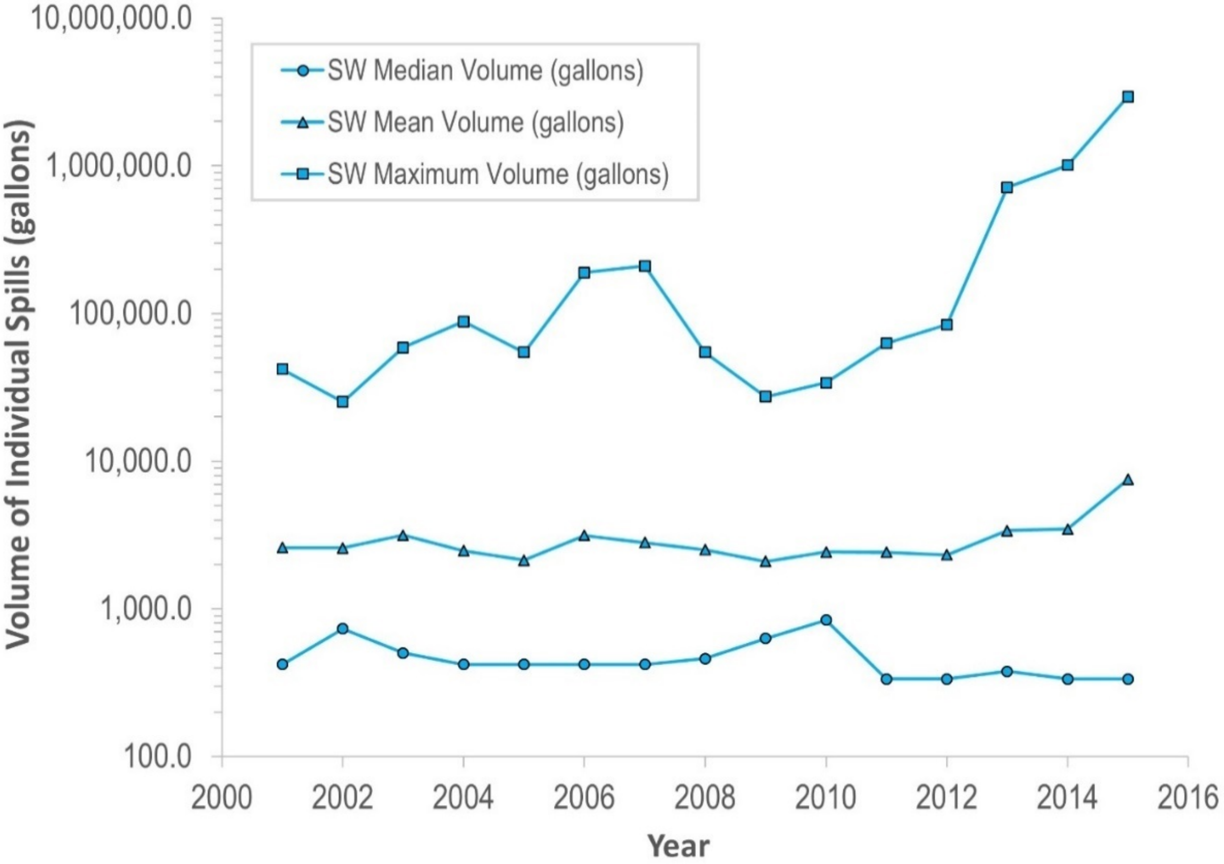

Figure 7-13. Median, mean, and maximum produced water spill volumes for North Dakota from 2001 to 2015.

Table 7-7. Summary of produced water release volumes.

Sources: U.S. EPA (2015m), Fisher and Sublette (2005), and Appendix Section E.5.

Study	Year(s)	Number		Minimum	25th percentile	Median	Mean	75th percentile	Maximum
		Total	Quantified	(gal)	(gal)	(gal)	(gal)	(gal)	(gal)
Oklahoma	1993-2002	7,916	2,365	0.0	630	1,700	7,000	4,200	3,400,000
	1993	373	161	0.4	420	1,500	3,900	4,200	46,000
	1994	844	333	0.4	420	1,600	5,400	4,200	84,000
	1995	913	333	0.0	420	1,500	3,700	4,200	63,000
	1996	880	333	4.2	630	2,100	6,500	4,200	420,000
	1997	806	270	0.4	630	1,900	6,000	4,200	120,000
	1998	825	236	2.1	798	4,900	2,100	4,200	105,000
	1999	886	218	10.5	840	2,100	6,600	4,200	120,000
	2000	853	155	4.2	840	2,100	5,600	5,040	210,000
	2001	826	144	21.0	840	2,100	31,000	6,510	3,400,000
	2002	710	182	0.8	630	1,700	5,500	3,276	130,000
U.S. EPA	2006-2012		225	2.1	420	1,008	10,920	2,982	1,344,000
North Dakota	2001		97	21.0	168	420	2,646	2,520	42,000
	2002		110	4.2	210	756	2,604	2,100	25,200
	2003		128	2.1	126	504	3,150	2,562	58,800
	2004		159	10.5	126	420	2,478	2,100	88,200
	2005		184	5.0	126	420	2,142	1,680	54,600
	2006		226	5.0	126	420	3,150	1,680	189,000
	2007		248	0.4	210	420	2,814	2,100	210,000

Study	Year(s)	Number		Minimum	25th percentile	Median	Mean	75th percentile	Maximum
		Total	Quantified	(gal)	(gal)	(gal)	(gal)	(gal)	(gal)
North Dakota, cont.	2008		248	8.4	84	504	2,520	2,058	54,600
	2009		208	2.1	126	630	2,100	2,100	27,300
	2010		255	0.1	126	840	2,478	2,310	34,020
	2011		381	2.1	126	336	2,436	1,680	58,800
	2012		543	7.1	84	336	2,310	1,260	84,000
	2013		700	2.1	126	378	3,402	1,428	714,000
	2014		846	0.8	84	336	3,528	1,470	1,008,000
	2015		609	0.8	84	336	7,560	1,386	2,940,000

7.4.2.9 Environmental Receptors and Transport

Data from the EPA (U.S. EPA, 2015m) were used to show that some spills were known to impact environmental receptors: soil (141 spills, 340,000 gal, or 1.3 million L); surface water (17 spills, 170,000 gal, or 640,000 L); surface water and soil (13 spills); and groundwater (1 spill, 130 gal, or 490 L).[1] Although 1 spill was identified as reaching groundwater, the possible groundwater impact of 107 of the spills was unknown.

In summary, 18 produced water spills reached surface water or groundwater, accounting for 8% of the 225 cases and accounting for approximately 170,000 gal (640,000 L) of produced water. Spills with known volumes that reached a surface water body ranged from less than 170 gal (640 L) to almost 74,000 gal (280,000 L), with median of 5,900 gal (22,000 L). In 30 cases, it is unknown whether a spill of produced water reached any environmental receptor.

An assessment conducted by the California Council on Science and Technology (CCST, 2015a) states that between January 2009 and December 2014, 575 produced water spills were reported to the California Office of Emergency Services of which nearly 18 percent impacted waterways (CCST, 2015a). These spills occurred in areas where production from both unconventional and conventional reservoirs occurs. Additional studies of spill impacts are presented in Appendix Section E.5.3.

Studies of Environmental Transport of Released Produced Water

The processes that affected the fate and transport of spilled produced water (Figure 7-14) are the same as those processes that impact the fate and transport of spilled chemicals (Section 5.8). Produced water spills differ from the chemical spills as they are always primarily spills of water containing multiple chemicals. Additionally, produced water of high salinity is denser than water and may alter transport and transformation properties of the chemicals and soils.[2] If a spill occurs prior to treatment in an oil and water separator, the produced water can be spilled along with oil. In the environment, oil is transported as a separate phase liquid as it is immiscible with water. The oil phase may become trapped (similarly to how oil is trapped in oil reservoirs) and serve as a slowly dissolving source of hydrocarbons to the environment.

For example, Whittemore (2007) described a site with relatively little infiltration due to moderate to low permeability of silty clay soil and low permeability of underlying shale units. Thus, most, but not all, of the historically surface-disposed produced water at the site flowed into surface drainages. Observed historic levels of chloride in receiving waters resulted from the relative balance of produced water releases and precipitation runoff, with higher concentrations corresponding to low stream flows. Persistent surface water chloride contamination was attributed to slow flushing and discharge of contaminated groundwater.

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[1] Quoted volumes.

[2] Appendix Section E.7 describes the estimation of chemical properties for organic chemical constituents of produced water for baseline conditions of low TDS. Elevated salinity, as is common for produced water, would alter these values.

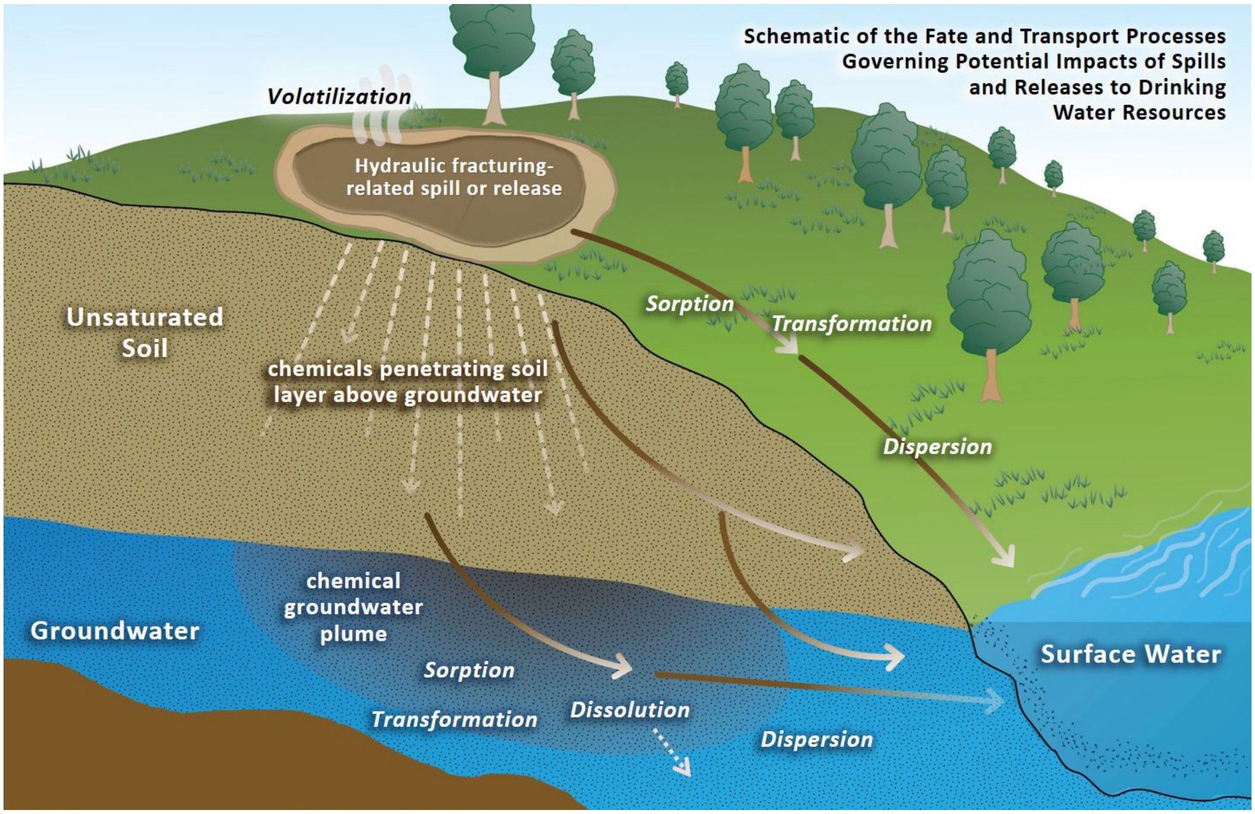

Figure 7-14. Schematic view of transport processes occurring during releases of produced water.

Because it is denser than freshwater, saline produced water can migrate downward through aquifers. Whittemore (2007) reported finding oilfield brine with a chloride concentration of 32,900 mg/L at the base of the High Plains aquifer. Where aquifers discharge to streams, saline stream water has been reported, although at reduced concentrations (Whittemore, 2007), likely due to diffusion within the aquifer and mixing with stream water. The stream flow rate, in part, determines mixing of substances in surface waters. High flows are related to lower chemical concentrations, and vice versa, as demonstrated for bromide in the Allegheny River (States et al., 2013).

7.5 Roadway Transport of Produced Water

Produced water is transported to treatment and disposal sites via pipeline, roadways, or railroad tankers. Accidents during transportation of hydraulic fracturing produced water are a possible mechanism leading to potential impacts to drinking water as truck-related releases have been reported. Nationwide data are not available, however, on the number of such accidents that result in impacts.

Crash rate estimates for Texas showed that commercial motor vehicle (CMV) crashes were correlated with oil and gas development activities over a recent period of increased oil and gas development (Quiroga and Tsapakis, 2015). As an example of the results, the number of new wells in the Permian Basin increased (by 61%) and so did rural CMV crashes (by 52%). For the Barnett Shale region, the number of new wells decreased (by 49%), and so did rural CMV crashes (by 34%). The correlations were strongest for the rural areas with oil and gas development (Permian and Eagle Ford).

Based on scenarios presented in Appendix Section E.8, the EPA estimated for this assessment the number of releases from truck crashes as having a chance of occurrence ranging between 1:110 and 1:13,000 over the lifetime of a producing well. The wide range of these estimates reflects both variable (distance and volume transported) and uncertain (crash rate) quantities. At 5,300 gal (20 m^3) per truckload, the volume from an individual spill would be low relative to the typical volume of water produced from a well. Several limitations are inherent in this analysis, including differing rural road and highway accident rates, differing transport distances, and differing amounts of produced water transported. Further, the estimates present an upper bound on impacts, because not all releases would reach or impact drinking water resources.

As for other types of impacts to drinking water resources, local effects can be significant despite the generally small numbers. For example, a brine-truck spill in Ohio resulted in concern for impacts to a drinking-water-source reservoir (Tucker, 2016).

7.6 Synthesis

Produced water is a by-product of oil and gas production and is that water that comes out of the well after hydraulic fracturing is completed and injection pressure is reduced. Produced water may contain hydraulic fracturing fluid, water from the surrounding formation, and naturally present hydrocarbons. Initially the chemistry of produced water reflects that of the hydraulic fracturing fluid. With time, the chemistry of the produced water becomes more similar to the water in the formation. Produced water is directly re-injected or stored at the surface for eventual reuse or disposal. Impacts to drinking water resources from produced water have been shown where spilled produced water entered surface water bodies or aquifers.

7.6.1 Summary of Findings

The volume and composition of produced water vary geographically, both within and among different production zones and with time and other site-specific factors. In most cases, there are high initial flow rates of produced water that last for a few weeks, followed by lower flow rates throughout the duration of gas production. The amount of fracturing fluid returned to the surface varies, and typically is less than 30%. In some formations (e.g., the Barnett Shale), the ultimate volume of produced water can exceed the volume of hydraulic fracturing fluid because of an inflow of water.

Knowledge of the composition of produced water comes from analysis of samples. Analysis of an individual sample is made much easier if the hydraulic fracturing and any equipment maintenance chemicals have been disclosed. Much of the chemical loading of produced water comes from naturally occurring material, both organic and inorganic, in the formation along with transformation products. As such, knowledge of produced water composition is uniquely dependent on sampling and analysis, which requires appropriate analytical methods. These are methods that can deal especially with high levels of TDS. Recently developed laboratory methods have greatly expanded the knowledge of organic chemicals in shale-gas and CBM produced waters, but these methods rely on advanced equipment and techniques. Routine methods of laboratory analysis do not detect many of the organic constituents of produced water.

The composition of produced water changes with time as the hydraulic fracturing fluid contacts the formation and mixes with the formation water. Typically it becomes more saline and more radioactive, if those constituents are present in the formation, while containing less DOC. The changing composition of produced water suggests that the potential concern for produced water spills also changes: initially the produced water may contain more hydraulic fracturing chemicals, later the concern may shift to the impact of high salinity water. Although varying within and between formations, shale and tight gas produced water typically contains high levels of TDS (salinity) and associated ionic constituents (bromide, calcium, chloride, iron, potassium, manganese, and sodium). Produced water can also contain toxic materials, including barium, cadmium, chromium, lead, mercury, nitrate, selenium, and BTEX. CBM produced water can have lower levels of salinity if its coal source was deposited under fresh water conditions, or if freshwater inflows to coal beds dilutes the formation water (Dahm et al., 2011). Many organic compounds have been identified in produced water. Most of these are naturally occurring constituents of petroleum. With the advent of advanced analytical techniques, more hydraulic fracturing fluid chemicals have been identified in produced water. These include some known tracer compounds, but others are known to exist whose identities have not yet been determined. Work has been done to identify environmentally benign tracers for assessing impacts, but these tracers have not been fully developed. Despite the presence in produced water of known hydraulic fracturing chemicals, the majority of organic and inorganic constituents of produced water come from the formation and cannot be minimized through actions of the operator. Throughout the formation-contact time, reactions occur between the constituents of the fracturing fluid and the formation.

Produced water spills have occurred across the country. From evaluation of data from across the United States and a focused study of North Dakota, the median produced water spill ranges from 336 to 1,000 gal (1,300 to 3,800 L). Although half of the spills are smaller than the median spill size, small numbers of much higher volume spills occur. In 2015, there were 12 spills in North Dakota greater than 21,000 gal (80,000 L), and one of 2,900,000 gal (11,000,000 L). From 2010 to 2015, there were approximately 5 to 7 produced water spills per hundred operating production wells. The major causes identified for these spills are container and equipment failures, human error, well communication, blowouts, pipeline leaks, and unpermitted discharges. Section 7.4.2 described impacts that were both of short and long term duration.

Highway transportation of produced water has resulted in crashes, but the impacts from these are unknown. Analysis of Texas crashes shows that as the oil and gas development activities increase, so do crashes, especially in rural areas. The EPA estimated the chance of a crash releasing produced water to range from 1:110 to 1:13,000.

7.6.2 Factors Affecting the Frequency or Severity of Impacts

The potential of spills of produced water to affect drinking water resources depends upon the release volume, duration, and composition, as well as watershed and water body characteristics. Larger spills of greater duration are more likely to reach a nearby drinking water resource than are smaller spills. Small releases, however, can impact resources where there are direct conduits from a source to receptor, such as fractures in rock. The composition of the spilled fluid also impacts the severity of a spill, as certain constituents are more likely to affect the quality of a drinking water resource.

Potential impacts to water resources from hydraulic fracturing related spills are expected to be affected by watershed and water body characteristics. For example, overland flow is affected by surface topography and surface cover. Infiltration of spilled produced water reduces the amount of water threatening surface water bodies. However, infiltration through soil can lead to groundwater impacts. Releases from pits can directly impact drinking water resources.

7.6.3 Uncertainties

The volume and some compositional aspects of produced water are known from published sources. The amount of hydraulic fracturing fluid returned to the surface is not well defined, because of the imprecise distinction between flowback and produced water. With regard to composition, TENORM and organics have the most limited data. Most of the available data on TENORM has come from the Marcellus Shale, where concentrations are typically high in comparison to the limited data available from other formations. Many organic constituents of produced water have been identified, and many of them are naturally occurring petroleum hydrocarbons. As methods improve and more data are collected, an increasing number of hydraulic fracturing fluid chemicals are being identified in produced water. Little is known concerning subsurface transformations and is reflected in only a few transformation products have been positively identified. Halogenation of organics has been noted, though.

Nationwide data on spills of produced water are limited in two primary ways: the completeness of reported data cannot be determined, and individual states' reporting requirements differ (U.S. EPA, 2015m). Therefore, the total number of spills occurring in the United States, their release volumes, and associated concentrations can only be estimated because of these underlying data limitations.

Spills vary in volume, duration, and composition, and most spill response focusses on immediate clean up, so several aspects of spills are not precisely characterized. The volume released is often a rough estimate, in part, because the spilled liquid spreads across the scene and is inherently difficult to measure. Simple measurements are often used to characterize the spill, rather than determining chemical concentrations (e.g., measuring electrical conductivity). As a consequence the suite of chemicals, and their concentrations, potentially impacting drinking water resources are usually unknown. Thus, the severity of impacts to drinking water resources is not usually well quantified.

Spills can originate from blowouts, well communication, aboveground or underground pipeline breaks, leaking pits, failed containers, human error (including unpermitted discharges, failure to detect spills, and failure to report spills) or unknown causes. The difference between these causes affects the location and size of the spill or release. For example, a container that fails may release a small amount of produced water, and be located on the well pad. A pipeline break may occur at a distance away from the well pad and release a larger amount of water from a bigger source (i.e., a pit). In addition, the factors governing transport of spilled fluid to a potential receptor vary by site: the presence and quality of secondary or emergency containment and spill response; the rate of overland flow and infiltration; the distance to a surface water body or drinking water well; and transport and fate processes. Impacts to drinking water resources from spills of produced water depend on environmental transport parameters, which can, in principle, be determined but are unlikely to be known or adequately specified in advance of a spill.

Because some constituents of produced water are constituents of natural waters (e.g., bromide in coastal surface waters) or can be released into the environment by other pollution events (e.g., benzene from gasoline releases, bromide from coal mine drainage), baseline sampling prior to impacts is one way to increase the certainty of an impact determination. Further sampling and investigation can be used to develop the linkage between a release and a documented drinking water impact. Appropriate sampling and analysis protocols, using quality assurance procedures, are essential for developing data that can withstand scrutiny. The EPA's northeastern Pennsylvania case study illustrates that the analytes that can be used to distinguish among types of water vary depending on the specifics of the situation. No single constituent or parameter could be used alone to assess impacts, and multiple lines of evidence were needed to assess the suspected impacts.

7.6.4 Conclusions

Produced water has the potential to affect the quality of drinking water resources if it enters into a surface water or groundwater body used as a drinking water resource. This can occur through spills at well pads or during transport of produced water. Specific impacts depend upon the spill itself, the environmental conditions surrounding the spill, water body and watershed characteristics, and the composition of the spilled fluid. The impacts from the majority of spills and releases is generally localized in extent as only the largest spills and releases impact large areas.

Chapter 8. Wastewater Disposal and Reuse

Abstract

This chapter addresses the practices and related impacts on drinking water resources that take place during the final stage of the hydraulic fracturing water cycle. This stage encompasses the management of wastewater, including disposal, reuse in hydraulic fracturing operations, or other uses. For this assessment, wastewater is defined as produced water from hydraulically fractured oil and gas wells that is managed by any of a number of strategies. The constituents of concern in hydraulic fracturing wastewaters that are most frequently noted include high total dissolved solids (TDS), chloride, bromide, and radionuclides (radium in particular). Other alkaline earth metals (e.g., barium), organics, and suspended solids, may be of concern as well.

Most hydraulic fracturing wastewater is managed by injection into Class II disposal wells. There are also “aboveground” management practices, which include reuse in subsequent hydraulic fracturing operations; treatment at a centralized waste treatment facility followed by reuse or discharge to surface water or a publicly owned treatment works; evaporation; irrigation; and direct discharge (under limited conditions). These practices can affect both surface water and groundwater.

Impacts on surface water arise from discharges of inadequately treated wastewater. In particular, bromide and iodide found in highly saline wastewaters can contribute to disinfection byproduct formation in downstream drinking water systems. If not removed during treatment, radium, metals, and organic compounds can also be discharged. Factors affecting the frequency and severity of impacts on surface waters include the wastewater’s composition, its volume, and the processes used to treat it (common wastewater treatment processes do not significantly reduce the high TDS content in hydraulic fracturing wastewaters). In addition, site-specific factors such as local hydrology, size of the receiving water body, and other activities taking place in a watershed can affect the severity of the impact.

Pits and impoundments used for storage or disposal can impact surface water or groundwater through spills, leaks, and infiltration through soils. The frequency and severity of such impacts depend on pit construction and maintenance as well as proximity to drinking water resources. Unlined pits or those with compromised liners can cause long-lasting impacts on groundwater. Depth to the water table, soil properties, and the contaminants in the wastewater also affect the likelihood of impacts.

Characterizing the impacts from wastewater management associated with hydraulic fracturing is challenging given gaps in the data. Specifically, there are limited data on the wastewater volumes managed, on the influent and effluent concentrations and volumes from facilities that treat wastewater from hydraulic fracturing operations, and on wastewater residual characteristics and management of those residuals. Further, there is inadequate monitoring of drinking water resources for specific contaminants associated with hydraulic fracturing wastewater. However, the data that are available have shown that management of hydraulic fracturing wastewater through aboveground practices has affected the quality of water resources.

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8. Wastewater Disposal and Reuse

8.1 Introduction

The final stage of the hydraulic fracturing water cycle encompasses disposal and reuse of hydraulic fracturing wastewater. For the purposes of this assessment, "hydraulic fracturing wastewater" is defined as produced water from hydraulically fractured oil and gas wells that is being managed using practices that include, but are not limited to, reuse in subsequent hydraulic fracturing operations, treatment and discharge, and injection into disposal wells.[1,2,3] Although the term "wastewater" is generally used in this chapter, when more specific information about a wastewater is known (e.g., a source indicates the wastewater is flowback), that information is also noted.

Wells producing from oil and gas reservoirs generate produced water during the course of their productive lifespan. This produced water includes the often large volumes of flowback generated immediately after fracturing in deep wells with long horizontal sections. Flowback estimates vary by formation and are noted in Section 7.2.1 to range from about 300,000 to 10 million gal (1.14 to 37.8 million L) per well (Mantell, 2013; U.S. GAO, 2012). This large volume of initial flowback necessitates having a wastewater management strategy in place before hydraulic fracturing is initiated. Also, the longer-term generation of produced water requires ongoing wastewater management.

The majority of wastewater generated from all oil and gas operations in the United States is managed via Class II injection wells (Veil, 2015). Injection may be for either disposal or enhanced recovery. As hydraulic fracturing activity expands or diminishes, choices regarding disposal practices can change in a given region due to factors such as the quality and volume of the fluids; regulations; available infrastructure; and the feasibility and cost of treatment, reuse, and disposal options.

Several articles have noted potential effects of hydraulic fracturing wastewater on water resources (Vengosh et al., 2014; Olmstead et al., 2013; Rahm et al., 2013; States et al., 2013; Vidic et al., 2013; Rozell and Reaven, 2012; Entrekin et al., 2011). One study used probability modeling that indicated water pollution risk associated with gas extraction in the Marcellus Shale is highest for the wastewater disposal aspects of the operation (Rozell and Reaven, 2012). These concerns arise from

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[1] The term "wastewater" is being used in this study as a general description of certain waters and is not intended to constitute a term of art for legal or regulatory purposes. This general description does not, and is not intended to, provide that the production, recovery, or recycling of oil, including the production, recovery, or recycling of flowback or produced water, constitutes "wastewater treatment" for the purposes of the Oil Pollution Prevention regulation (with the exception of dry gas operations), which includes the Spill Prevention, Control, and Countermeasure rule and the Facility Response Plan rule, 40 CFR 112 et seq.

[2] Disposal wells are Underground Injection Control (UIC) Class II wells, including those used for disposal (Class IID), enhanced oil recovery (Class IIR), and hydrocarbon storage (Class IIH).

[3] The term "reuse" is sometimes used to imply no treatment or basic treatment (e.g., media filtration) for the removal of constituents other than total dissolved solids (TDS), while "recycling" is sometimes used to convey more extensive treatment (e.g., reverse osmosis (RO)) to remove TDS (Slutz et al., 2012). In this document, the term "reuse" will be used to indicate use of wastewater for subsequent hydraulic fracturing, regardless of the level of treatment.

the elevated concentrations of chloride, bromide, radionuclides, and other constituents of concern found in many hydraulic fracturing wastewaters.

This chapter provides follow-on to Chapter 7, which discusses the per-well volumes of produced water (Section 7.2) and composition (Section 7.3), as well as the processes involved in its generation and impacts from a number of types of spills and releases. In this chapter, discussions are provided on management practices for hydraulic fracturing wastewater, available wastewater production information, and estimated aggregate volumes of wastewater generated for several states with active hydraulic fracturing (Section 8.2). As a complement to information on the composition of wastewaters in Chapter 7, Section 8.3 presents brief information on wastewater constituents and their relevance to wastewater management. Management methods used in recent years and their potential impacts on drinking water resources are described (Section 8.4). Based on background information provided in the earlier sections of the chapter, Section 8.5 discusses documented and potential impacts on drinking water resources from particular constituents, and a final synthesis discussion is provided (Section 8.6).[1]

8.2 Volumes of Hydraulic Fracturing Wastewater

This section provides a general overview of aggregate wastewater quantities generated in the course of hydraulic fracturing and subsequent oil and gas production, including estimates at regional and state levels. It also discusses methodologies used to produce these estimates and the associated challenges. (Chapter 7 provides a more in-depth discussion of the processes affecting produced water volumes and presents some typical per-well values and temporal patterns.) Wells also generate drilling fluid waste. Compared to produced water, however, drilling fluid wastewater can constitute a relatively small portion of the total wastewater produced (e.g., <10% in Pennsylvania during 2004-2013) (U.S. EPA, 2016d) and is not discussed further in this assessment.

Wastewater volume can be relevant to treatment costs, reuse options, and disposal capacities. IHS Global Insight suggests that as a general rule of thumb, the amount of flowback produced in the days or weeks after hydraulic fracturing is roughly comparable to the amount of produced water generated long-term over a span of years, which can vary considerably among wells (IHS, 2013). Thus, on a local level, operators can anticipate a relatively large volume of wastewater in the weeks following fracturing, with slower subsequent production of wastewater.

Wastewater volumes will most likely vary in the future as the amount and locations of hydraulic fracturing activities change and as existing wells age and move into the later phases of their production cycles. Substantial increases in wastewater production have occurred during times of increasing hydraulic fracturing activity. For instance, the average annual volume of wastewater

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[1] This chapter makes use of background information collected by the EPA's Office of Water (OW) as part of the development of its recent pretreatment standards for wastewater from unconventional oil and gas formations (U.S. EPA, 2016d). The pretreatment standards apply to wastewater from crude oil and natural gas produced by a well drilled into shale and tight formations. Coalbed methane is beyond the scope of those standards. In this chapter, we consider wastewater generated by the hydraulic fracturing of those unconventional oil and gas formations included in the background research done by OW. But we also consider wastewater generated by hydraulic fracturing in coalbed methane and conventional formations.

generated by all gas production (both shale gas and conventional) in Pennsylvania quadrupled from the 2001-2006 period to the 2008-2011 period (Wilson and Vanbriesen, 2012).

However, although the total volume of wastewater might be expected to generally increase and decrease as oil and gas drilling and production changes, it is not necessarily a direct correlation. Data from the Pennsylvania Department of Environmental Protection (PA DEP) (PA DEP, 2016b) show trends in volumes of wastewater compared to gas produced from wells in the Marcellus Shale in Pennsylvania (Figure 8-1). Although the data show some variation, they demonstrate a general positive correlation between the volume of wastewater and the amount of produced gas until early 2015. At that time, Baker Hughes weekly rig counts also began to drop, declining from 85 in early January 2014 to 24 in early June 2016 (Baker Hughes, 2016). This suggests that a decline in overall drilling activity (generally a measure of new wells) can be associated with a decline in wastewater production, although the exact timing depends on whether there is a time delay between drilling and completion of a well and the start of production from that well.

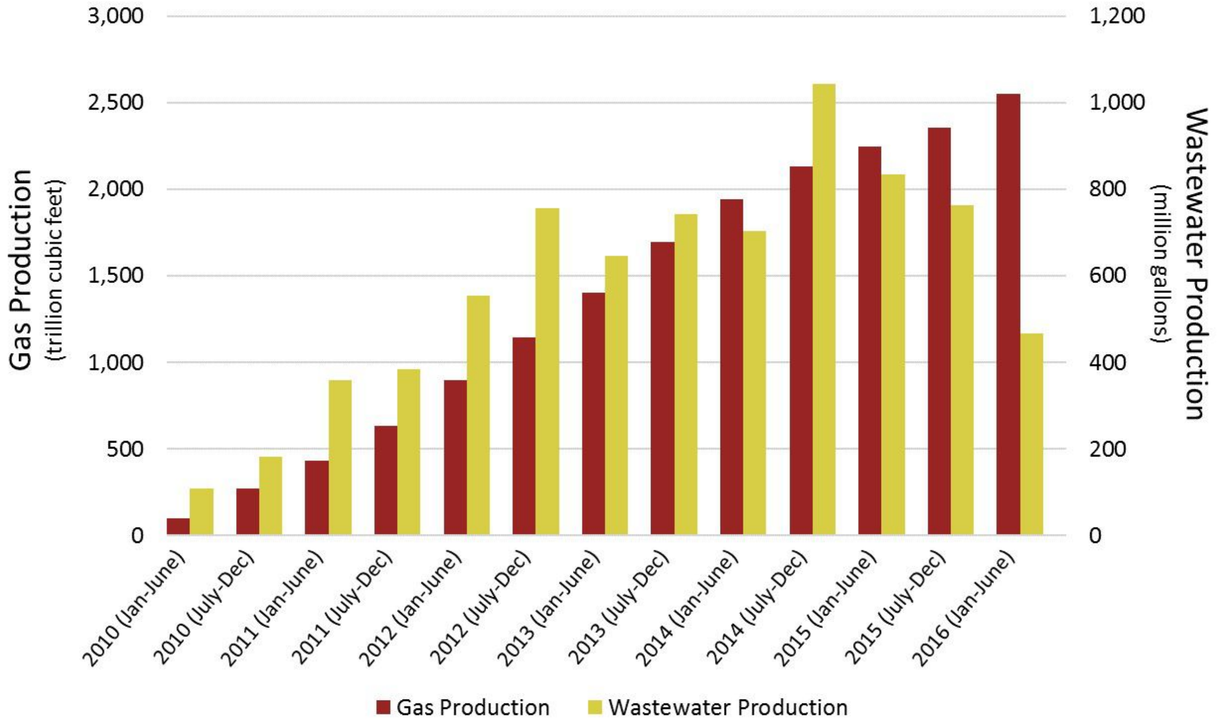

Figure 8-1. Wastewater (i.e., produced water and fracturing fluid waste) and produced gas volumes from unconventional (as defined by PA DEP) wells in Pennsylvania from January 2010 through June 2016.
Source: PA DEP (2016b).

Estimates of produced water compiled by Veil (2015) indicate that although oil and gas production in the United States increased by 29% and 22%, respectively, between 2007 and 2012, produced water volumes increased by less than 1%. There may be a number of factors contributing to this, including as noted by Veil (2015), a number of uncertainties associated with produced water estimates. First, wastewater generation varies from well to well, as do oil and gas production (see Chapter 7, Figure 7-1 for discussion of wastewater/produced water decline curves). The rates of decline in both wastewater volume and hydrocarbon production also vary among reservoirs. Additionally, some wells are drilled and completed but are not immediately put into production. Relationships between hydraulic fracturing activity, hydrocarbon production, and produced water volumes are likely reservoir- (and maybe production zone-) specific, and existing wells and production need to be considered to anticipate wastewater management needs.

8.2.1 National Level Estimate

Veil (2015) estimated that in 2012, U.S. onshore and offshore oil and gas production generated 889.59 billion gal (21.18 billion bbls) of produced water. This national-level estimate represents total oil and gas wastewater (from all oil and gas resources, and from wells hydraulically fractured and wells not hydraulically fractured). The estimate was compiled through a state-by-state analysis of survey data obtained from oil and gas agencies in the 31 states with active oil and gas production as well as the Department of Interior and U.S. EPA. However, Veil notes several issues with the data used for these estimates, including variability among states in data reporting, availability, and completeness. These issues may result in underestimation of the volumes of water produced (U.S. GAO, 2012). See Section **Error! Reference source not found.** for more discussion on methods of estimating wastewater volumes.

8.2.2 Regional/State Level Estimates

A limited number of studies have described the geographic variability in oil and gas wastewater volumes. Veil (2015) reported that the top ten states nationwide for wastewater production in 2012 included Texas (35% of total), California (15% of total), Oklahoma (11% of total), and Wyoming (11% of total). A study by the Bureau of Land Management (BLM) (Guerra et al., 2011) states that in 2008, more than 80% of all oil and gas wastewater was generated in the western United States, with Texas producing the highest volume and Wyoming the second highest. The BLM report notes substantial wastewater from CBM wells, in particular those in the Powder River Basin (Wyoming). Figure 8-2 summarizes the wastewater volumes for these western states, demonstrating the wide variability from state to state (likely reflecting differences in the number of oil and gas production wells/production activity and reservoir geology). Although the authors do not identify all wastewater contributions from production involving hydraulic fracturing, the regions with established oil and gas production are likely to have methods and infrastructure available for management of hydraulic fracturing wastewater.

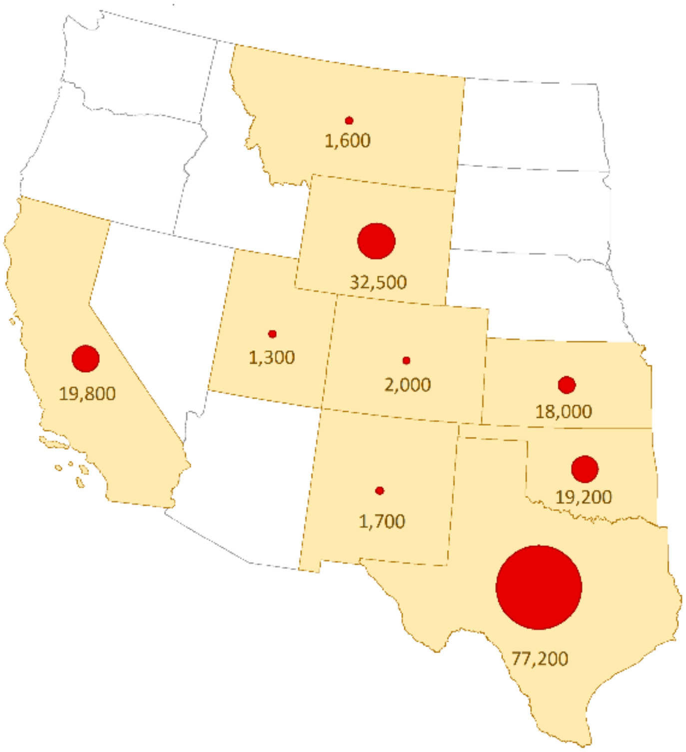

Figure 8-2. Wastewater quantities in the western United States (billions of gal per year).
Data from Guerra et al. (2011).

In the Marcellus region, waste data made public by the PA DEP have enabled analyses of wastewater volumes and trends since 2009. Estimates of produced water (including flowback or "fracing fluid waste" as well as "produced fluid") by Wunz (2015) and Shale Alliance for Energy Research Pennsylvania (SAFER PA, 2015) for 2014 are 1.73 and 1.64 billion gal (41.19 MMbl and 39.05 MMbl, respectively). The estimate compiled for this assessment is 0.65 billion gal (15.48 million bbls) for the first half of 2014 (Table 8-1). Variations among estimates reflect, among other factors, challenges in working with a dynamic database for which changes and corrections are ongoing.

Table 8-1 presents estimates of the volumes of hydraulic fracturing wastewater generated and the associated numbers of wells in North Dakota, Ohio, Pennsylvania, Texas (injected flowback only), and West Virginia. The data shown in this table were compiled for this assessment (except for West Virginia) and come primarily from records of produced water made publicly available on state websites.[1] These states are represented in Table 8-1 because the produced water volumes associated with hydraulic fracturing were readily identifiable. The data show that the increase in

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[1] Data used for Table 8-1 were downloaded from state agency websites and compiled as needed (in either Microsoft Excel or Microsoft Access) for each state except West Virginia. Once compiled, data were filtered if needed and summed to produce estimates of wastewater production by year and a count of the numbers of wells generating the wastewater. Data were downloaded up through 2014. (Note that 2014 data for Pennsylvania and Texas are for partial years.) Differences in the years presented for the states are due to differences in data availability from the state agency databases. For West Virginia, data are from a report by Hansen et al. (2013) that compiled available flowback data from West Virginia.

the number of wells producing wastewater and the volumes of wastewater produced are generally consistent with the timing of the expansion of high-volume hydraulic fracturing and track with the increase in horizontal wells seen in Figure 3-20.

Several states with mature oil and gas industries (California, Colorado, New Mexico, Utah, and Wyoming) make produced water volumes publicly available by well as part of their oil and gas production data, but they do not directly indicate which wells have been hydraulically fractured. Some states (Colorado, Utah, Wyoming, and New Mexico) specify the producing formation or the basin along with volumes of hydrocarbons and produced water. Determining volumes of hydraulic fracturing wastewater for these states is challenging because there is a possibility of either inadvertently including wastewater from wells not hydraulically fractured or of missing volumes that should be included. This may be a particular problem where state terminology regarding what constitutes an unconventional resource or hydraulically fractured well is ambiguous or possibly different from other states. Appendix Table F-1 provides estimates of wastewater volumes in California, Colorado, New Mexico, Utah, and Wyoming in regions where hydraulic fracturing activity is taking place, along with notes on data limitations. The data in Table 8-1 and Appendix Table F-1 illustrate the challenges in both compiling a national estimate of hydraulic fracturing wastewater and comparing wastewater production among states due to dissimilar data types, presentation, and availability.

8.2.3 Estimation Methodologies and Challenges

Compiling and comparing data on wastewater production at the wide array of oil and gas locations in the United States presents challenges associated with data reporting and availability. Different approaches have been used to estimate state-specific and national wastewater volumes. Data from state agency websites and databases can be a ready source of information, whether publicly available and downloadable or provided directly by agencies upon request.

Veil (2015) notes that the reported volumes of produced water (e.g., reported by well in state production data) can be inaccurate or imprecise because produced water is not monitored continuously. Therefore, reported volumes may be estimates. Other issues such as data transcription errors or extrapolation of data can also affect reported volumes (Veil, 2015).

Using produced water volumes from state records to estimate the volume of wastewater regionally or nationally presents additional challenges due to a lack of consistency in data collection, availability, usability, completeness, and accuracy (Malone et al., 2015; Veil, 2015; U.S. GAO, 2012). Due to what are sometimes significant differences in the types of data collected and the mechanisms, formats, and definitions used, data cannot always be directly compared from state to state. This makes it difficult to aggregate volume data, and estimates may be better and more useful at a local or state level. Larger-scale estimates across regions or between states should be interpreted carefully.

Table 8-1. Estimated volumes (millions of gal) of wastewater based on state data for selected years and numbers of wells producing fluid.

State	Basin	Principal lithologies	Data type	2000	2004	2008	2010	2011	2012	2013	2014	Comments
North Dakota	Williston	Shale	Produced water	2	3	130	790	1,900	4,500	8,500	9,700	From North Dakota Oil and Gas Commission website[a]. Data provided for six members of the Bakken Shale. Produced water includes flowback (reports are submitted within 30 days of well completion.)
			Wells	*161*	*152*	*844*	*2,083*	*3,303*	*5,036*	*6,913*	*8,039*	
Ohio	Appalachian	Shale	Primarily flowback	-	-	-	-	3	29	110	-	Data from Ohio DNR Division of Oil and Gas[b]. Utica data for 2011 and 2012. Utica and Marcellus data for 2013. Brine is noted by agency to be mostly flowback.
			Wells	-	-	-	-	*9*	*86*	*400*	-	
Pennsylvania	Appalachian	Shale	Flowback plus produced water (% flowback; % produced water)	-	-	-	180 (51%; 49%)	740 (46%; 54%)	1,100 (36%; 64%)	1,300 (27%; 73%)	650 (32%; 68%)	Waste data from PA DEP[c]. Second half of 2010 and first half of 2014. Data described as unconventional as defined by PADEP. Separate codes are provided by PA DEP for flowback and produced water.
			Wells	-	-	-	*1,232*	*2,434*	*4,039*	*5,015*	*5,150*	

State	Basin	Principal lithologies	Data type	2000	2004	2008	2010	2011	2012	2013	2014	Comments
Texas	Unspecified (entire state)	Shale, Sandstone	Flowback - injected volumes	-	-	-	-	490	2,200	3,100	2,000	Waste injection data from Texas Railroad Commission[d]. Monthly totals are provided for entire state. Oct - Dec for 2011, full years for 2012 and 2013, and Jan - Oct for 2014
West Virginia	Appalachian	Shale	Flowback - Estimated total disposed	-	-	-	120	110	59	-	-	Estimates from Hansen et al. (2013).[e]

[a] North Dakota Industrial Commission. Department of Mineral Resources. Bakken Horizontal Wells By Producing Zone: https://www.dmr.nd.gov/oilgas/bakkenwells.asp.

[b] Ohio Department of Natural Resources, Division of Oil and Gas Resources. Oil and Gas Well Production. http://oilandgas.ohiodnr.gov/production#ARCH1.

[c] PA DEP Oil and Gas Reporting website, https://www.paoilandgasreporting.state.pa.us/publicreports/Modules/Welcome/Agreement.aspx.

[d] Railroad Commission of Texas, Injection Volume Query, http://webapps.rrc.state.tx.us/H10/searchVolume.do;jsessionid=J3cgVHhK9nkwPrC7ZcWNMgyzF9LCYyR1NmvDy3F1QQ5wqXfcGNGN!1841197795?fromMain=yes&sessionId=143075601021612. Texas state data provide an aggregate total amount of flowback injected for the past few years. (Data on brine volumes injected do not differentiate hydraulically fractured wells and, therefore, well counts are not presented here.) These values are interpreted as estimates of generated flowback as based on reported quantities of “fracture water flow back” injected into Class IID wells.

[e] West Virginia flowback estimates from Hansen et al. (2013) are based on state data. Well counts that are explicitly associated with the flowback and total disposed volumes were not available.

To compile estimates of the production and management of hydraulic fracturing wastewater, there are additional challenges. Reporting of wastewater volumes may or may not include information that helps determine whether the producing well was hydraulically fractured (e.g., an indicator of resource type or formation). It also might not be clear whether volumes listed as 'produced water' include the flowback component. Some states (e.g., Colorado and Pennsylvania) include information on disposal and management methods along with production data, and others do not.

Given the limitations of comparing state databases, some studies have generated estimates of wastewater volume using water-to-gas and water-to-oil ratios along with the reports of hydrocarbon production (Murray, 2013). The reliability of any wastewater estimates made using this method would need to be evaluated in terms of the quality, timeframe, and spatial coverage of the available data, as well as the extent of the area to which the estimates will be applied. Water-to-hydrocarbon ratios are empirical estimates. Because these ratios show a wide variation among formations, reliable data are needed to formulate a ratio in a particular region.

Another approach to estimating wastewater volumes would entail multiplying per-well estimates of produced water production rates by the numbers of wells in a given area. Challenges associated with this approach include obtaining accurate estimates of the number of new and existing wells, along with accurate estimates of per-well water production both during the flowback period and during the production phase of the well's lifecycle. In particular, it can be challenging to correctly match per-well wastewater production estimates, which will vary by formation, with counts of wells, which may or may not be clearly associated with specific formations. Temporal variability in wastewater generation would also be difficult to capture and would add to uncertainty. Such an approach, however, may be attempted for order of magnitude estimates if the necessary data are available and reliable.

8.3 Wastewater Characteristics

Along with wastewater volumes, wastewater characteristics and the characteristics of residuals produced during treatment or storage are important for understanding the potential impacts of management and disposal of hydraulic fracturing wastewater on drinking water resources. This section provides brief highlights on several important constituents known to exist in hydraulic fracturing wastewaters and residuals. Chapter 7 provides more in-depth detail on the chemistry of produced water, and Chapter 9 discusses reference values and health effects associated with hydraulic fracturing wastewater constituents.

8.3.1 Wastewater

Wastewater composition is the result of naturally-occurring constituents originating in the formation solids and fluids as well as chemicals associated with the fracturing fluid. Discussion in this chapter focuses on constituents in hydraulic fracturing wastewater for which adequate information is available to assess documented and potential impacts on drinking water resources. There may also be unknown constituents in wastewaters for which analyses have not been performed. This is due, in part, to a lack of information on fracturing fluid ingredients identified as confidential business information (CBI). In addition, there are uncertainties about how fracturing fluid ingredients are degraded or removed in the subsurface. (See Chapter 5, Section 5.8 for a discussion of processes that can cause chemicals to degrade or transform in the subsurface.)

8.3.1.1 Total Dissolved Solids and Inorganics

Hydraulic fracturing wastewaters are generally high in total dissolved solids (TDS), especially those from shales and tight formations, with TDS values ranging from less than 1,000 mg/L to hundreds of thousands of mg/L (Section 7.3.4.4). The TDS in wastewaters from shale formations is typically dominated by sodium and chloride and may also include elevated concentrations of bromide, bicarbonate, sulfate, calcium, magnesium, barium, boron, strontium, radium, organics, and heavy metals (Chapman et al., 2012; Rowan et al., 2011; Blauch et al., 2009; Orem et al., 2007; Sirivedhin and Dallbauman, 2004).

Within each formation, the minimum and maximum values presented in Section 7.3.4.4 suggest spatial variation in TDS content that may need to be accommodated when considering management strategies such as reuse or treatment. In contrast to shales and sandstones, TDS values for wastewater from CBM formations are generally lower, with reported concentrations ranging from approximately 150 mg/L to 62,000 mg/L (DOE, 2014b; Dahm et al., 2011) (Appendix Table E-3). This results in fewer treatment challenges and a wider array of management options.

Constituents commonly found in TDS from hydraulic fracturing wastewaters may have potential health impacts or create treatment burdens on downstream drinking water systems if discharged at high concentrations to drinking water resources. Bromide, for example, can contribute to the increased formation of disinfection byproducts (DBPs) during drinking water treatment (Hammer and VanBriesen, 2012); see Section 8.5.1.

8.3.1.2 Organics

Less information is generally available about organic constituents in hydraulic fracturing wastewaters than about inorganic constituents, but there are now several studies reporting analyses of organic constituents (Chapter 7). The organic content in flowback waters can vary based on the chemical additives (e.g., biocides, antiscalants, gelling agents, breakers) used in hydraulic fracturing fluids and the chemistry of the formation, but the organics generally include polymers, oil and grease, volatile organic compounds (VOCs), and semi-volatile organic compounds (SVOCs) (Akob et al., 2016; Walsh, 2013; Hayes, 2009). Examples of other constituents detected include alcohols, naphthalene, acetone, and carbon disulfide, compounds that may be remnants of hydraulic fracturing fluid chemicals (Hayes and Severin, 2012b; Hayes, 2009) (Appendix E). Wastewater associated with CBM wells may have high concentrations of aromatic and halogenated organic contaminants potentially requiring treatment depending on how the wastewater will be managed (Pashin et al., 2014; Sirivedhin and Dallbauman, 2004). Concentrations of BTEX (benzene, toluene, ethylbenzene, and xylenes) in CBM produced waters are lower than in shale produced waters (Appendix Table E-9).

New research is focusing on transformation products generated in the subsurface; experimental work by Kahrilas et al. (2015) suggests that the biocide glutaraldehyde can be present in wastewaters along with its transformation products. Low molecular weight organic acids such as acetate, formate, and pyruvate have been detected in Marcellus wastewater, indicating microbial degradation of organic compounds in the fracturing fluid or formation (Akob et al., 2015).

8.3.1.3 Radionuclides

Radionuclides are constituents of concern in some hydraulic fracturing wastewaters, with most of the available data obtained for the Marcellus Shale in Pennsylvania (Appendix Table E-8). Results from a United States Geological Survey (USGS) report (Rowan et al., 2011) indicate that the predominant radionuclides in Marcellus Shale wastewater are radium-226 and radium-228. Radionuclides in produced fluids are considered 'technologically enhanced naturally-occurring radioactive material' (TENORM) because they have been exposed to the accessible environment.[1]

Although data regarding radionuclides in wastewater from formations other than the Marcellus Shale are limited, there is information on the naturally occurring radioactive material (NORM) in the formations themselves.[2] In particular uranium and thorium can be found in certain organic-rich black shales. High uranium content has been measured in the Marcellus, Barnett, Woodford, and other black shales (Swanson, 1955) (Section 7.3.4.6). Radium-226 and -228 are decay products of uranium and thorium and are soluble (Sturchio et al., 2001; Langmuir and Riese, 1985). Therefore wastewater from shales with high concentrations of uranium and thorium can contain radium, especially where TDS concentrations are also high (Rowan et al., 2011; Sturchio et al., 2001; Fisher, 1998). Section 7.3.3.2 provides further information on radionuclides in produced waters and in formations.

8.3.2 Constituents in Residuals

Depending on the wastewater and the treatment processes used, treatment residuals can consist of sludges, spent media (used filter materials), or brines. Residuals may require further treatment (e.g., dewatering sludges) prior to disposal (see Section 8.4.7 for further discussion on management of residuals). Residuals can contain constituents such as total suspended solids (TSS), TDS, metals, radionuclides, and organics. These constituents will be concentrated in the residuals, with the degree of concentration depending on the type of treatment employed. Processes such as electrodialysis and mechanical vapor recompression have been found to yield residuals with TDS concentrations in excess of 150,000 mg/L after treating waters with influent TDS concentrations of approximately 50,000 – 70,000 mg/L (Hayes et al., 2014; Peraki and Ghazanfari, 2014).

Also, TENORM in wastewaters can cause residual wastes to have gamma radiation emissions (Kappel et al., 2013). A laboratory study by Zhang et al. (2014b) estimated that the barium sulfate solids precipitated during treatment to remove barium and strontium from Marcellus Shale wastewater would also contain between 2,571 and 18,087 pCi/g of radium due to coprecipitation. Another similar study using mass balances calculated that sludge from a sulfate precipitation

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[1] Technologically Enhanced Naturally Occurring Radioactive Material (TENORM) is defined by the EPA as naturally occurring radioactive materials (NORM) that have been concentrated or exposed to the accessible environment as a result of human activities such as manufacturing, mineral extraction, or water processing.

[2] Naturally Occurring Radioactive Materials (NORM) are radioactive materials found in nature that have not been moved or concentrated by human activities.

process would have an average radium concentration of 213 pCi/g (Silva et al., 2012). In sludge from lime softening processes, Silva et al. (2012) estimated a radium-226 concentration of 58 pCi/g, a level that would necessitate disposal as a low-level radioactive waste.

8.4 Wastewater Management Practices and Their Potential Impacts on Drinking Water Resources

Operators have several strategies for management of hydraulic fracturing wastewaters (Figure 8-3), with the most common choice being disposal via Class IID wells (Veil, 2015; Clark et al., 2013; Hammer and VanBriesen, 2012). Other practices include reuse in subsequent hydraulic fracturing operations (with varying levels of treatment), treatment at a centralized waste treatment facility (CWT) (often followed by reuse), evaporation (in arid regions), irrigation (with no discharge to waters of the United States), and direct discharge for livestock or agricultural use (allowed west of the 98th meridian). Up until 2011, treatment of unconventional oil and gas wastewaters (as defined by PA DEP) at publicly owned treatment works (POTWs) was a common practice for wastewater management in the Marcellus region (Lutz et al., 2013); this is discussed further in Text Box 8-1.

The methods shown in Figure 8-3 represent wastewater management strategies, not all of which would be used at the same facility. Descriptions of incidents of unpermitted disposal and resulting legal actions have also been publicly reported (Chapter 7). However, such events are not generally described in the scientific literature, and the prevalence of this type of activity is unclear. Additional sources of information about potential impacts exist, but some records are sealed (e.g., litigation records) and are not publicly accessible.

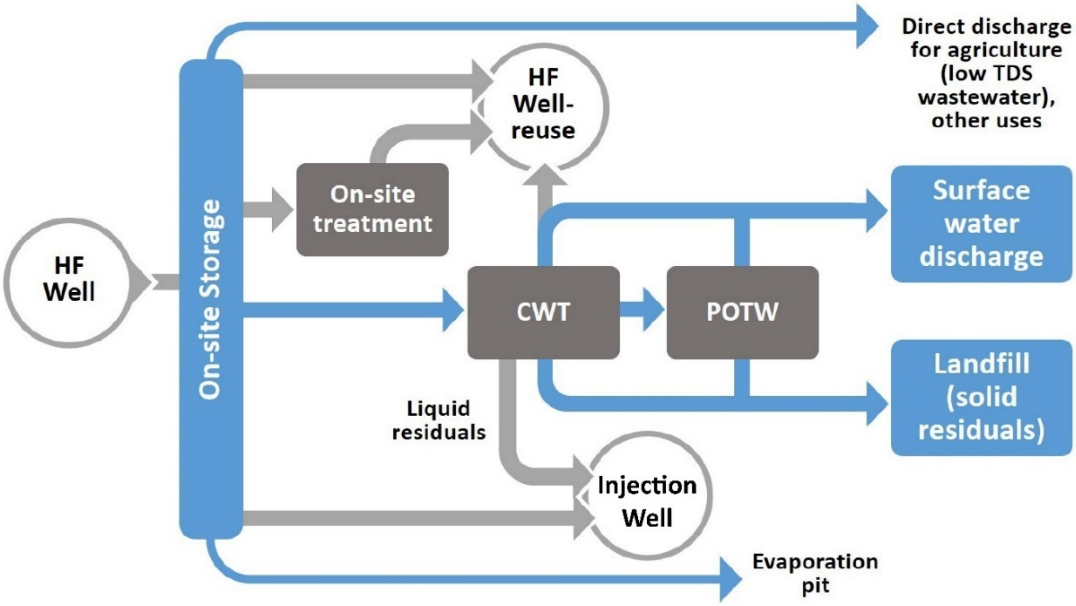

Figure 8-3. Schematic of wastewater management strategies.
Gray lines indicate management strategies that involve injection, either for reuse or disposal, and blue lines indicate management strategies that lead to other end points such as discharge, evaporation, landfills, or other uses.

Each of the wastewater management strategies can potentially lead to impacts on drinking water resources during some phase of their execution. Such impacts include, but are not limited to: accidental releases during transport (Chapter 7); discharges of treated wastewaters from CWTs or POTWs where treatment for certain constituents has been inadequate; migration of constituents to groundwater due to leakage from pits or land application of wastewaters; leakage from pits that reach surface waters (Chapter 7, Section 8.4.5); inappropriate management of liquid or solid residuals (e.g., leaching from landfills); or accumulation of constituents in sediments near outfalls of CWTs or POTWs that are treating or have treated hydraulic fracturing wastewater.[1]

A reliable census of oil and gas wastewater management practices nationwide is difficult to assemble due to a lack of consistent and comparable data among states. In addition, we do not know how often operators use more than one wastewater management strategy at a site (e.g., evaporation and injection), further complicating the tracking of wastewater management. As part of a data survey conducted by Veil (2015), some state agencies provided estimates of oil and gas wastewater volumes handled by several management practices (Table 8-2). These estimates illustrate how widespread injection for both enhanced recovery and for disposal is for managing oil and gas wastewater. The data also show regional differences in reuse and other practices. For hydraulic fracturing wastewaters, Table 8-3 illustrates nationwide variability in the primary wastewater management methods using qualitative and quantitative sources. Similar to Table 8-2, Table 8-3 shows disposal via underground injection predominates in most regions, and reuse is predominant in the Marcellus Region. (Table 8-3 does not include wastewater management in areas of CBM production.)

Management choices are affected by cost and a number of directly and indirectly related factors, including the chemical properties of the wastewater; the volume, duration, and flow rate of the wastewater generated; the feasibility of each option; the availability of necessary infrastructure; local, state, and federal regulations (Text Box 8-2); and operator discretion (U.S. GAO, 2012; NPC, 2011a). The economics (such as transport, storage, and disposal costs) and availability of treatment and disposal methods are of primary importance (U.S. GAO, 2012). For wastewater composition, there is limited information on the degradation or removal of fracturing fluid ingredients in the subsurface. Chemical disclosure requirements vary among states, and some fracturing fluid ingredients are claimed to be CBI. Therefore, the possible presence of unknown chemical constituents in wastewater contributes to uncertainty about the effectiveness and potential impacts of management strategies, particularly with regard to treatment efficacy.

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[1] The term surface water as used in this assessment refers to surface waters that meet the definition of waters of the United States under the CWA (House Bill No. 1950, 2011).

Table 8-2. Estimated percentages of wastewater managed by practice and by state.

Source: Veil (2015). Estimates do not identify interstate transport (e.g., wastewater transported from PA to OH or WV for injection into disposal wells). Thus, there may have been some double counting of volumes in both the generating and receiving states.

Management practice	**Percentage of produced water managed by practice and state (%)**											
	AR	**CA**	**CO**	**NM**	**ND**	**OH**	**OK**	**PA**	**TX**	**UT**	**WV**	**WY**
Injection for enhanced oil recovery	22	46	32	50 [d]	18	4.0	47	0	48	40	27	73
Injection for disposal	76	20	32	50 [d]	56	91	47	12	37	47	25	27
Surface discharge	0	2	10	no data	0	0	0	2.3	5.0 [f]	6	0	uncertain
Evaporation	0	21	9.0	no data	0	0		0	0	0	0	uncertain
Offsite commercial disposal	0.1 [a]	9	5.7 [c]	no data	26	Included in injection for disposal	6.0 [e]	0	10 [e]	7 [g]	28 [h]	uncertain
Beneficial reuse	1.1 [b]	no data	12 [b]	no data	0	5.0	0	85 (includes reuse for HF)	Est. 15-20 (flowback fluid)	0.5	uncertain	uncertain

[a] Land farm.

[b] Reuse for HF.

[c] Pits.

[d] Assumes even split with injection for enhanced oil recovery and injection for disposal.

[e] Injection.

[f] Fresh produced water.

[g] Evaporation ponds.

[h] Disposal wells.

Table 8-3. Management practices for wastewater from unconventional oil and gas resources.
Source: U.S. EPA (2016d).

Basin	Formation	Resource type	Reuse	Injection for disposal	CWT facilities	Notes	Available data[b]
Michigan	Antrim	Shale gas		XXX			Qualitative
Appalachian	Marcellus/Utica (PA)	Shale gas	XXX	XX	XX	Limited disposal wells in east	Quantitative
	Marcellus/Utica (WV)	Shale gas/oil	XXX	XX	X		Quantitative
	Marcellus/Utica (OH)	Shale gas/oil	XX	XXX	X		Mixed
Anadarko	Granite Wash	Tight gas	XX	XXX	X[a]		Mixed
	Mississippi Lime	Tight oil	X	XXX		Reuse/recycling limited but is being evaluated	Qualitative
	Woodford, Cana, Caney	Shale gas/oil	X	XXX	X[a]		Qualitative
Arkoma	Fayetteville	Shale gas	XX	XX	X[a]	Few existing disposal wells; new CWT facilities are under construction	Mixed
Fort Worth	Barnett	Shale gas	X	XXX	X[a]	Reuse/recycle not typically used due to high TDS early in flowback and abundance of disposal wells	Mixed
Permian	Avalon/Bone Springs, Wolfcamp, Spraberry	Shale/tight oil/gas	X	XXX	X[a]		Mixed
TX-LA-MS Salt	Haynesville	Tight gas	X	XXX		Reuse/recycle not typically used due to high TDS early in flowback and abundance of disposal wells	Mixed
West Gulf	Eagle Ford, Pearsall	Shale gas/oil	X	XXX	X		Mixed
Denver Julesburg	Niobrara	Shale gas/oil	X	XXX	X		Mixed
Piceance; Green River	Mesaverde/Lance	Tight gas	X	XX	X	Also managed through evaporation to atmosphere in ponds in this region	Qualitative

Basin	Formation	Resource type	Reuse	Injection for disposal	CWT facilities	Notes	Available data[b]
Williston	Bakken	Shale oil	X	XXX		Reuse/recycling limited but is being evaluated	Mixed

[a] CWT facilities identified in these formations are all operator-owned.

[b] This column indicates the type of data the EPA based the number of Xs on. In most cases, the EPA used a mixture of qualitative and quantitative data sources along with engineering judgment to determine the number of Xs.

XXX—The majority (≥50%) of wastewater is managed with this management practice; XX—A moderate portion (≥10% and <50%) of wastewater is managed with this management practice; X—This management practice has been documented in this location, but for a small (<10%) or unknown percent of wastewater. Blanks indicate the management practices have not been documented in the given location.

The availability and use of wastewater management strategies in a region can change over time as oil and gas production increases or decreases, regulations change, costs shift, and technologies evolve. Text Box 8-1 and Figure 8-4 illustrate shifting wastewater management practices in Pennsylvania as gas development in the Marcellus Shale increased and concerns over high-TDS discharges prompted a regulatory response. Reuse has increased substantially at well sites in Pennsylvania (labeled as "Reuse HF" in Figure 8-4) and wastewater management at CWTs has moved toward more facilities that provide wastewater for reuse and do not discharge (termed "zero-discharge facilities"). The estimated total reuse rate in Pennsylvania was 80% in 2012 and 90% in 2013 (PA DEP, 2015a). In contrast, wastewater disposal data in areas of Colorado where hydraulic fracturing takes place show a steady use of injection wells, an increase in surface water discharges, and a decrease in the use of on-site pits for evaporation since 2000 (Figure 8-5).

Another factor influencing reuse is the pace of hydraulic fracturing in the area. When hydraulic fracturing is active, demand for reuse is high. Some formations that are hydraulically fractured such as the Marcellus Shale and the Utica Shale are still in the early stages of development, with large potential resources not yet developed. For these plays, the need for wastewater treatment and/or reuse may remain high for decades to come, and the long-term wastewater management needs must be considered and addressed (SAFER PA, 2015).[1]

Researchers have developed optimization models to aid in the minimization of wastewater management costs as a part of comprehensive water management planning. For example, Yang et al. (2014) suggest an approach for reusing flowback in scheduled hydraulic fracturing events to minimize the operational costs of transportation, treatment, storage, and wastewater disposal. Another modeling study proposes an approach to minimize the total cost of water usage and wastewater treatment and disposal by optimizing capital costs (such as the costs of treatment units and storage pits) and operating costs for flowback management, treatment, storage, reuse, and wastewater disposal (Lira-Barragan et al., 2016).

Text Box 8-1. Temporal Trends in Wastewater Management – Experience of Pennsylvania.

Gross natural gas withdrawals from shale formations in the United States increased 518% between 2007 and 2012 (EIA, 2014b). This production increase has led to larger volumes of wastewater requiring appropriate management (Vidic et al., 2013; Gregory et al., 2011; Kargbo et al., 2010). The rapid increase in wastewater generated from hydraulically fractured oil and gas wells has led to many changes in wastewater disposal practices in the oil and gas industry. Changes have been most evident in Pennsylvania, which has experienced a more than 1,400% increase in natural gas production since 2000 (EIA, 2014b).

Lutz et al. (2013) estimated that total wastewater generation in the Marcellus region increased 570% between 2004 and 2013. The authors concluded that this increase has created stress on the existing wastewater disposal infrastructure. In 2010, concerns arose over elevated TDS in the Monongahela River

(*Text Box 8-1 is continued on the following page.*)

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[1] As noted in Chapter 3, oil and gas prices influence new drilling activity. However, the links between oil and gas prices and the generation of wastewater (as a byproduct of production) appear to be less direct.

Text Box 8-1 (continued). Temporal Trends in Wastewater Management – Experience of Pennsylvania

basin, and studies linked high TDS (and, in particular, high bromide levels) to elevated DBP levels in drinking water systems (PA DEP, 2011a). In response, PA DEP amended Chapter 95 Wastewater Treatment Requirements under the Clean Streams Law for new discharges of TDS in wastewaters. This regulation is also informally known as the 2010 TDS regulation. The regulation disallowed any new direct discharges to streams as well as direct disposal at POTWs of hydraulic fracturing wastewater and set limits on treated discharges from new CWTs of 500 mg/L TDS, 250 mg/L chloride, 10 mg/L barium, and 10 mg/L strontium. Existing discharges were exempt.

In April 2011, PA DEP announced a request that by May 19, 2011, gas drilling operators voluntarily stop transporting wastewater from shale gas extraction (i.e., unconventional resources as defined by PA DEP) to the eight CWTs and seven POTWs that were exempt from the 2010 TDS regulation.[1] Follow-up letters from PA DEP to the owners of the wells specified that the role of bromides from Marcellus Shale wastewaters in the formation of total trihalomethanes (TTHM) was of concern due to the their potential public health impacts (PA DEP, 2011a).

In response to the request, the oil and gas industry in Pennsylvania accelerated the switch of wastewater deliveries from POTWs to CWTs for better removal of metals and suspended solids (Schmidt, 2013). Effluent sampling at two POTWs that had accepted Marcellus Shale wastewater showed that concentrations of bromide, chloride, barium, strontium, and sulfate dropped after the April 2011 request (Ferrar et al., 2013); data based on two sampling events, one before and one after May 2011).

Between early and late 2011, although reported wastewater production more than doubled, Marcellus Shale drilling companies in Pennsylvania reduced their use of CWTs that were exempt from the 2010 TDS regulation by 98%, and direct disposal of Marcellus Shale wastewater at POTWs was "virtually eliminated" (Hammer and VanBriesen, 2012).

Along with the decreased discharges from POTWs, there has been increased reuse of wastewater in the Marcellus Shale region. From 2008-2011, reuse of Marcellus wastewater for hydraulic fracturing increased, POTW treatment volumes decreased, tracking of wastewater improved, and wastewater transportation distances decreased (Rahm et al., 2013). Maloney and Yoxtheimer (2012) analyzed data from 2011 and found that reuse of flowback increased to 90% by volume. Eight percent of flowback was sent to CWTs. Brine water, which was defined as formation water, was reused (58%), disposed via injection well (27%), or sent to CWTs (14%). Of all the fluid wastes in the analysis, brine water was most likely to be transported to other states (28%). Maloney and Yoxtheimer (2012) also concluded that wastewater disposal to municipal sewage treatment plants declined nearly 100% from 47,221 bbls in the first half of 2011 to 408 bbls in the second half.

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[1] An unconventional formation was defined in 2011 by the state of Pennsylvania as "A geological shale formation existing below the base of the Elk Sandstone or its geologic equivalent stratigraphic interval where natural gas generally cannot be produced at economic flow rates or in economic volumes except by vertical or horizontal wellbores stimulated by hydraulic fracture treatments or by using multilateral wellbores or other techniques to expose more of the formation to the wellbore." The EPA defines unconventional oil and gas as crude oil and natural gas produced by a well drilled into a shale and/or tight formation (including, but not limited to, shale gas, shale oil, tight gas, and tight oil). For the purpose of the rule, the definition of UOG does not include CBM (U.S. EPA, 2016d).

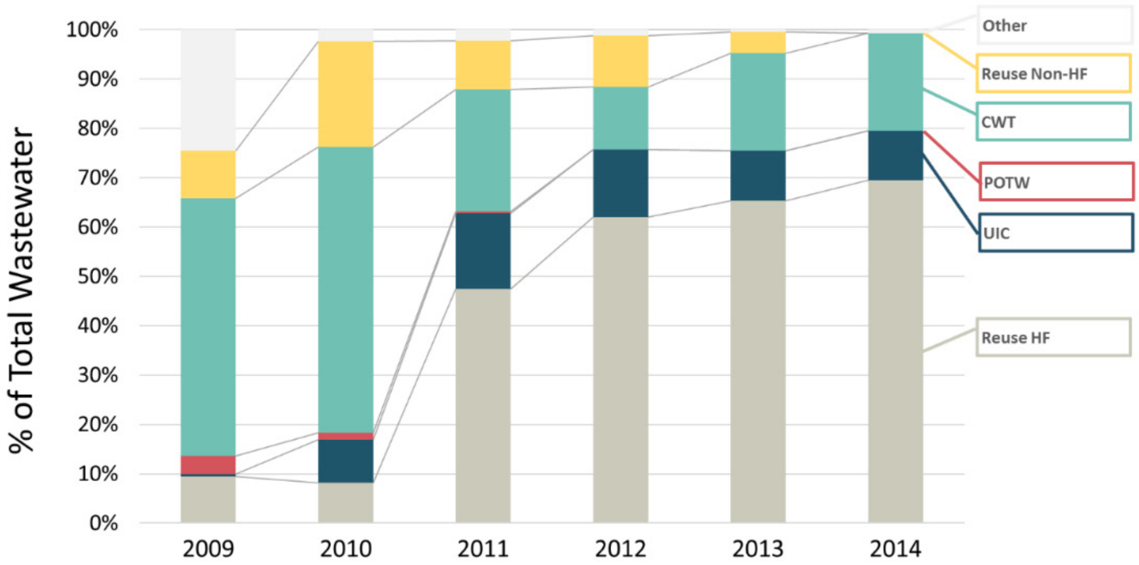

Figure 8-4. Percentages of total unconventional wastewater (as defined by PA DEP) managed via various practices for the second half of 2009 through the first half of 2014.

The volume sent to POTWs in 2013 was 0%. Note also that a majority of wastewater sent to CWTs is subsequently reused, so that when combined with "Reuse HF," the total reuse rate was approximately 90% in 2013. "Reuse HF" indicates on-site reuse. Source: Waste data from PA DEP (2015a).

Text Box 8-2. Regulations Affecting Wastewater Management.

Regulations affect wastewater management options and vary geographically as well as over time. At the Federal level, the EPA has promulgated national technology-based regulations, known as effluent limitations guidelines and standards (ELGs), for the oil and gas extraction industry, which can be found in 40 U.S. Code of Federal Regulations (CFR) Part 435. These ELGs do not apply to CBM discharges which are subject to technology based limits developed by permit writers on a case-by-case "best professional judgment" basis. The Onshore subcategory of the oil and gas, ELGs 40 CFR 125.3, Subpart C, prohibits the discharge of wastewater pollutants to waters of the United States from onshore oil and gas extraction facilities, with one exception in the arid west as discussed below. This "zero-discharge standard" means that, unless the exception applies, oil and gas wastewater pollutants cannot be discharged directly to waters of the United States. Operators have met this requirement through underground injection, reuse, or transfer of wastewater to POTWs and/or CWTs. The EPA finalized a rule in June 2016 that would prohibit operators from sending wastewater from unconventional oil and gas extraction to POTWs. Operators can continue to send wastewater to CWTs, which are subject to regulation under a separate set of ELGs in 40 CFR Part 437.

In addition, Subpart E of the oil and gas ELGs establishes an exception to the zero discharge standard west of the 98th meridian (the arid western portion of the continental United States), allowing discharges of produced water from onshore oil and gas extraction facilities to waters of the United States if the produced water has a use in agriculture or wildlife propagation when discharged into navigable waters. The term "use in agricultural or wildlife propagation" means that: (1) the produced water is of good enough quality to be used for wildlife or livestock watering or other agricultural uses; and (2) the produced water is actually put to

(*Text Box 8-2 is continued on the following page.)*

Text Box 8-2 (continued). Regulations Affecting Wastewater Management.

such use during periods of discharge (40 CFR 135.51(c)). Produced water discharged under this exception must not exceed an oil and grease concentration of 35 milligrams per liter (mg/L). Subpart E does not allow for discharge from sources other than produced water (i.e., drilling muds, drill cuttings, produced sands) to waters of the United States.

In addition to the technology-based limitations discussed above, the Clean Water Act (CWA) and the EPA's implementing regulations also require that permits include more stringent limits as necessary to meet applicable water quality standards. CWA Section 301(b)(1)(C); 40 CFR 122.44(d)(1).

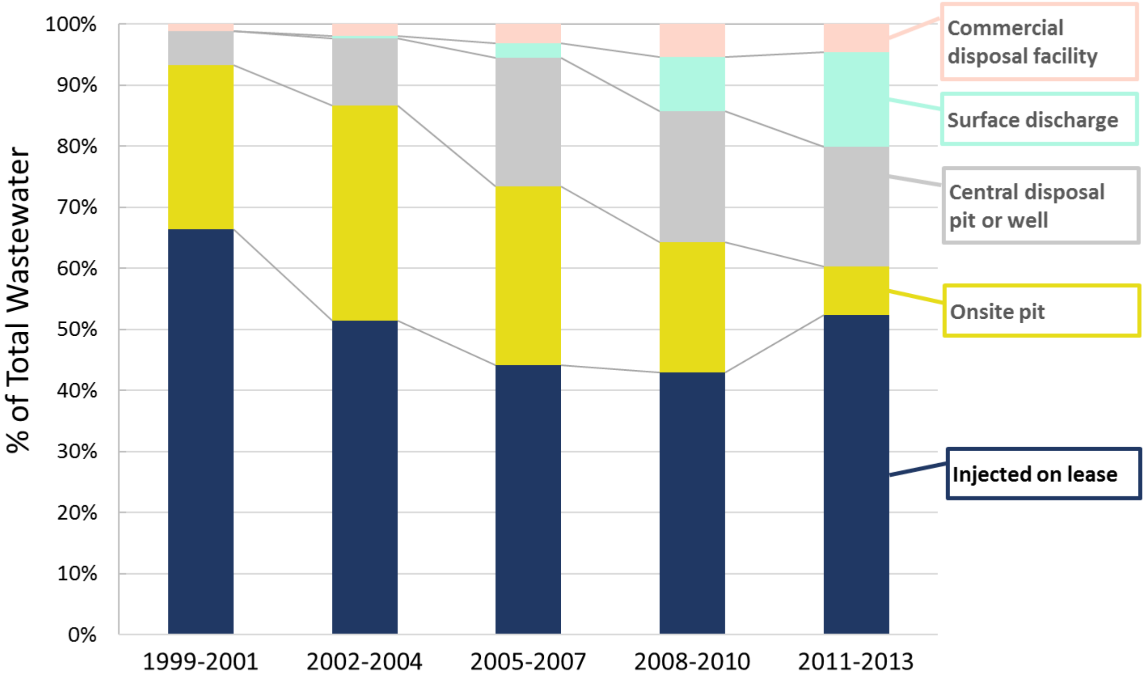

Figure 8-5. Management of wastewater in Colorado in regions where hydraulic fracturing is being performed.

See footnote for details on disposal codes.[1] Production data from Colorado Oil and Gas Conservation Commission (COGCC, 2015).

The following sections provide an overview of hydraulic fracturing wastewater management methods, with some discussion of the geographic and temporal variations in practices and their impacts on drinking water resources. In addition to currently used treatment and disposal methods, this section also briefly describes past treatment of hydraulic fracturing wastewater at

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[1] Codes for wastewater disposal from COGCC are described by Veil (2015) as follows:

- Commercial disposal facility: water sent to commercial pits.
- On-site pit: most water evaporates, or excess water is hauled to disposal wells.
- Central disposal pit: Central facilities owned by a single producer to handle water from multiple wells (some recycled, much is injected).
- Injected on lease: Injected into wells, roughly half for enhanced recovery.
- Surface discharge: water is either fresh or treated to acceptable standards and discharged to surface water.

POTWs. More in-depth descriptions of treatment technologies applicable to hydraulic fracturing wastewater are available in Appendix F.

8.4.1 Underground Injection

Oil- and gas-related wastewater may be disposed of via Class II injection wells (disposal wells are referred to as Class IID whereas enhanced recovery wells are referred to as Class IIR) regulated by the UIC Program under the SDWA.[1] Nationwide, injection wells receive a large percentage of wastewater from the oil and gas industry, including wastewater associated with hydraulic fracturing. Veil (2015) estimates that in 2012, U.S. oil and gas production from onshore wells generated over 863 billion gal (20.56 billion bbls or 3.27 trillion L) of produced water, and of that volume, information on management was available for 97%. The study estimated that about 93% was injected into Class II wells, with about 47% injected into Class IID wells and 46% injected into Class IIR wells.[2]

The above national estimates are for the oil and gas industry as a whole. A good national estimate of the amount of hydraulic fracturing wastewater injected into Class II wells is difficult to develop due to lack of available information and data on injection of hydraulic fracturing wastewater. Management of hydraulic fracturing wastewater is not well tracked or made publicly available in many states (Pennsylvania being a notable exception). The local availability of Class IID wells along with generally low reuse rates, however, are consistent with Class IID wells being a primary means of wastewater management in many areas with hydraulic fracturing activity.

According to recently released data from 2012 and 2013, there are about 26,400 active Class IID wells in the United States, with more than 65% of these located in Texas, Oklahoma, and Kansas (Table 8-4). In Pennsylvania, on the other hand, there are currently nine operating disposal wells, and only three of these are commercially operated wells (at one facility) (SAFER PA, 2015). The location and number of Class IID wells is in part determined by geology (including depth and permeability of geologic formations appropriate for injection), permitting, and historical demand for disposal of oil and gas wastewater. The large Class IID well capacity in Texas, for example, is consistent with the availability of formations with suitable geology and the demand for wastewater disposal associated with a mature and active oil and gas industry. In contrast, injection plays a relatively small role in Marcellus Shale wastewater management in Pennsylvania—about 10% in 2013 and the first half of 2014 (PA DEP, 2015a).

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[1] States may be given federal approval to run a UIC program under SDWA. UIC Class II wells include those used for disposal (Class IID), enhanced oil recovery (Class IIR), and hydrocarbon storage (Class IIH).

[2] Because some states surveyed by Veil (2015) do not distinguish between volumes injected for disposal versus enhanced recovery, assumptions and analyses were used in the study to estimate the two types of injection in some states.

Table 8-4. Distribution of active Class IID wells across the United States.
Data are primarily from 2012 and 2013. Source: U.S. EPA (2016d).

Geographic region (from the EIA)	State	Number of active disposal wells[a]	Average disposal rate per well (gpd/well)[b]	State disposal rate (MGD)
Alaska	Alaska	45	182,000	8.2
East	Illinois	1,054	—[c]	—[c]
	Michigan	772	16,200	13
	Florida	14	246,000	3.4
	Indiana	208	7,950	1.7
	Ohio	190	8,570	1.6
	West Virginia	64	6,970	0.45
	Kentucky	58	4,650	0.27
	Virginia	12	17,500	0.21
	Pennsylvania	9	6,380	0.057
	New York	10[d]	33.7	0.00034
Gulf Coast/Southwest	Texas	7,876	52,100	410
	Louisiana	2,448	40,300	99
	New Mexico	736	48,600	36
	Mississippi	499	24,200	12
	Alabama	85	53,300	4.5
Mid-Continent	Kansas	5,516	25,600	140
	Oklahoma	3,837	35,900	140
	Arkansas	640[e]	25,400	16
	Nebraska	113	19,100	2.2
	Missouri	11	2,270	0.025
	Iowa	3	—[c]	—[c]
Northern Great Plains	North Dakota	395	53,300	21
	Montana	199	32,700	6.5
	South Dakota	15	17,400	0.26

Geographic region (from the EIA)	State	Number of active disposal wells[a]	Average disposal rate per well (gpd/well)[b]	State disposal rate (MGD)
Rocky Mountains	Wyoming	335	107,000	36
	Colorado	292	48,800	14
	Utah	118	83,400	9.8
West Coast	California	826	86,800	72
	Nevada	10	54,600	0.55
	Oregon	9	—[c]	—[c]
	Washington	1	—[c]	—[c]
Total		**26,400**	**41,300**	**1,050**

Abbreviations: gpd—gal per day; MGD—million gal per day.

[a] Number of active disposal wells is based primarily on data from 2012 to 2013.

[b] Typical injection volumes per well are based on historical annual volumes for injection for disposal divided by the number of active disposal wells during the same year (primarily 2012 to 2013 data).

[c] Disposal rates and volumes are unknown.

[d] These wells are not currently permitted to accept extraction wastewater from production in unconventional reservoirs.

[e] Only 24 of the 640 active disposal wells in Arkansas are in the northern half of the state, close to the Fayetteville Shale.

The decision to inject hydraulic fracturing wastewater into Class IID wells depends in part on cost, including transportation costs. Therefore, the distance between the production well and a disposal well is an important consideration. For oil and gas producers, underground injection is a low cost management strategy unless significant trucking is needed to transport the wastewater to a disposal well (U.S. GAO, 2012).

Evaluation of documented or potential impacts on drinking water resources associated with disposal at Class IID injection wells is outside of the scope of this assessment. However, disposal wells play a significant role in the overall management of hydraulic fracturing water nationwide, and their availability and capacity are integral factors in determining which wastewater management strategies are used by operators in a given region. Should the feasibility of managing wastewater via underground injection become limited or less economically advantageous, operators will need to adjust their wastewater management programs. They may evaluate and implement other local practices such as sending wastewater to a CWT for treatment and discharge or reuse.

Recent events and studies, for example, have documented a link between wastewater injection and seismic activity in some locations in several states, including Oklahoma, Colorado, New Mexico, Arkansas, and Ohio (Weingarten et al., 2015; Wong et al., 2015). The Oklahoma Geological Survey (Andrews and Holland, 2015) “considers it very likely that the majority of recent earthquakes, particularly those in central and north-central Oklahoma, are triggered by the injection of produced water in disposal wells.” Walsh and Zoback (2015) correlated wastewater injection from production wells (including hydraulically fractured wells) into Oklahoma's Arbuckle formation to the steep increase in seismic events observed in that state. Farther west, in the Raton Basin of southern Colorado and northern New Mexico, Rubinstein et al. (2014) presented several lines of evidence linking injection well disposal of CBM produced water to seismic events. Horton (2012) attributed a swarm of earthquakes in Northern Arkansas to hydraulic fracturing wastewater injection, and in a study evaluating multiple states in the mid-continent region, Weingarten et al. (2015) demonstrated a relationship between Class II wells (including both Class IID and Class IIR wells) and seismicity.

The local availability of Class IID wells and the capacity to accept large volumes of wastewater could be affected by these recent findings concerning seismic activity associated with injection (U.S. EPA, 2014c). Between 2011 and 2016, some state UIC programs modified their Class II wastewater injection regulations and permitting requirements. At least eight states (Arkansas, Colorado, Illinois, Kansas, Ohio, Oklahoma, Texas, and West Virginia) consider an assessment of seismicity in their Class II programs and have regulatory provisions for banning or shutting injection wells and/or modifying injection volumes and pressures if evidence indicates that a well is near a fault and/or is contributing to seismic activity.

As an example, Oklahoma has recently taken steps to reduce the risk of induced seismicity by implementing a regional strategy intended to reduce wastewater injection in certain regions (OCC OGCD, 2016). These actions affect over 10,000 square miles and 600 wastewater injection wells in western and central Oklahoma. The measures are intended to reduce wastewater injection in the area by 40% below 2014 totals, which will affect wastewater management and disposal practices across this large area.[1]

In terms of potential impacts on drinking water resources, Class IID facilities are subject to the same general considerations regarding wastewater storage and handling as other wastewater management sites and facilities (e.g., CWTs). Changes in surface water or groundwater quality due to general wastewater handling at these facilities may be another factor affecting wastewater management practices in some locations or regions. For example, Kell (2011) identified eight groundwater contamination incidents in Texas between 1993 and 2008 due to water releases from storage facilities associated with Class II well sites. A recent study by the United States Geological Survey documented impacts on surface water from hydraulic fracturing wastewater at a Class II disposal well site in central West Virginia (Akob et al., 2016). Water samples collected downstream from the facility were indicative of wastewater from hydraulic fracturing operations handled at the site. The authors documented elevated specific conductance and elevated TDS, sodium, chloride, barium, bromide, strontium, and lithium concentrations, and different strontium isotope ratios compared to those found in upstream, background waters. The study concluded that activities at the wastewater facility have affected water quality in a nearby stream. The pathways for the movement of wastewater into the local stream include several possibilities (e.g., leaks from storage ponds and tanks, transportation activities, previous site history).

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[1] For additional information on strategies and initiatives regarding wastewater injection and inducted seismicity, see the following: KDHE (2014), States First Initiative (2014), and U.S. EPA (2014c).

8.4.2 Publicly Owned Treatment Works

POTWs are designed to treat local municipal wastewater and indirect discharges from industrial users. POTWs are also used to treat wastewater and other wastes from oil and gas operations in some eastern states. Although this is not a common method of treatment for oil and gas wastewaters in the United States, the scarcity of injection wells for waste disposal in Pennsylvania drove the need for disposal alternatives (Wilson and Vanbriesen, 2012). When development of the Marcellus Shale began, POTWs were used to treat wastewater originating from these oil and gas wells (Kappel et al., 2013; Soeder and Kappel, 2009). However, elevated concentrations of constituents in wastewater from the Marcellus region (halides, heavy metals, organic compounds, radionuclides, and salts) can pass through the treatment processes commonly used in POTWs and be discharged to receiving waters (Cusick, 2013; Kappel, 2013; Lutz et al., 2013; Schmidt, 2013). In addition, sudden, extreme salt fluctuations can disturb POTW biological treatment processes (Linarić et al., 2013; Lefebvre and Moletta, 2006).

The annual reported volume of oil and gas wastewater treated at POTWs in the Marcellus Shale region peaked in 2008 and has since declined significantly (Figure 8-6). As discussed in Text Box 8-1, this was in response to an April 2011 request from PA DEP asking operators to cease sending Marcellus Shale wastewater to 15 POTWs and CWTs that were exempt from the 2010 TDS regulation (Rahm et al., 2013). Although operators complied with the request in May 2011, non-Marcellus oil and gas produced water continued to be processed at these facilities (Ferrar et al., 2013; Lutz et al., 2013; Wilson and Vanbriesen, 2012).[1] In August 2016, the EPA finalized pretreatment standards prohibiting discharges of unconventional wastewater pollutants to POTWs (U.S. EPA, 2016d).

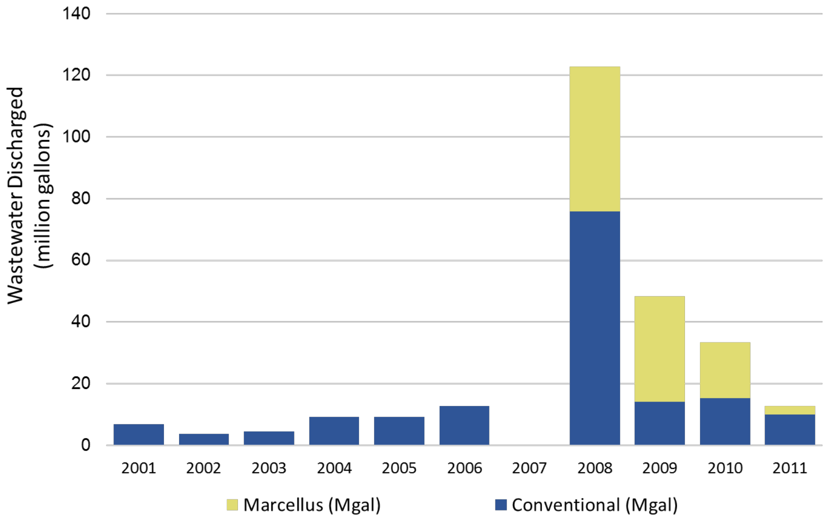

Figure 8-6. Oil and gas wastewater volumes discharged to POTWs from 2001-2011 in the Marcellus Shale. ("Conventional" is indicated by the authors as non-Marcellus wells and described as vertically drilled to shallower depths in more porous formations.)
Due to an unrecoverable data loss at the PA DEP, records for 2007 were not available. Source: Lutz et al. (2013).

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[1] POTWs in Pennsylvania have likely been accepting waste considered conventional by Pennsylvania but unconventional by others based on the EPA's broader definition (Text Box 8-1).

8.4.3 Centralized Waste Treatment Facilities

A CWT facility is generally defined as one that accepts industrial materials (hazardous or non-hazardous, solid, or liquid) generated at another facility (off-site) for treatment or recovery (EPA, 2000). (Wastewater may also be treated at on-site mobile or semi-mobile facilities; see Appendix F for additional information.) The decision to treat hydraulic fracturing wastewater at a CWT and the level of treatment used depends upon several factors, such as a lack of proximity to Class II disposal wells; whether the wastewater might be reused for additional hydraulic fracturing jobs; the water quality needed if it will be reused; whether the treated wastewater can be discharged under the Subpart E agricultural and wildlife use exception in the arid west; and the water quality needed if it will be discharged to the waters of the United States. As a group, CWTs that accept oil and gas wastewater offer a wide variety of treatment capabilities and configurations (Text Box 8-3 and Appendix F).

Text Box 8-3. Wastewater Treatment Processes.

The constituents prevalent in hydraulic fracturing wastewater include TDS, TSS, radionuclides, organic compounds, and metals (Section 8.3 and Chapter 7). If the ultimate disposal or use of the wastewater necessitates treatment, a variety of technologies can be employed to remove or reduce these constituent concentrations.

The most basic treatment needed for oil and gas wastewaters, including those from hydraulic fracturing operations, is separation to remove TSS and oil and grease. This is accomplished through separation technologies including settling, skimming, hydrocyclones, dissolved air or induced gas flotation, media filtration, or biological aerated filters (Igunnu and Chen, 2014; Duraisamy et al., 2013; Barrett, 2010; Shammas, 2010).

Other treatment processes that may be used include media filtration after chemical precipitation for hardness and metals (Boschee, 2014); adsorption technologies for organics, heavy metals, and some anions (Igunnu and Chen, 2014); a variety of membrane processes (microfiltration, ultrafiltration, nanofiltration, reverse osmosis (RO)); and distillation technologies for metals and organics (Drewes et al., 2009).

Advanced processes, such as RO, or distillation methods, such as mechanical vapor recompression (MVR), are needed if the system requires significant reduction in TDS (Drewes et al., 2009; LEau LLC, 2008; Hamieh and Beckman, 2006). However, RO is typically only capable of treating TDS concentrations less than 35,000 mg/L (Shaffer et al., 2013), whereas distillation can effectively treat higher TDS waters (Hayes et al., 2014; Drewes et al., 2009). Extremely high TDS waters may require a series of advanced treatment processes, which can be very costly.

An emerging technology in hydraulic fracturing wastewater treatment is electrocoagulation, which has been used in mobile treatment systems to remove organics, TSS, and metals (Halliburton, 2014; Igunnu and Chen, 2014).

Appendix F provides more in-depth descriptions of technologies used to treat for hydraulic fracturing wastewaters and the constituents they remove. Also, Appendix Table F-4 provides an overview of influent and effluent results and removal percentages for constituents of concern at oil and gas treatment facilities reported in the literature (both conventional and unconventional) and the specific technology(ies) used to remove them. Section 8.4.7 discusses solid and liquid residuals, including treatment-related wastes.

The treated effluent from a CWT can be reused in hydraulic fracturing operations (also called zero-discharge), discharged directly to a receiving water under a National Pollutant Discharge Elimination System (NPDES) permit, discharged indirectly to a POTW, or a combination of these. Some CWTs may be configured so that they can either (1) partially treat the waste stream to suit the needs of operators who reuse it or (2) use more advanced treatment (i.e., TDS removal) if the treated wastewater will be discharged. Generally, the former option is less costly for the CWT, and some facilities that have permits to discharge do not do so continuously, opting to direct as much of the wastewater as possible for reuse. There are also CWTs permitted to discharge that do not have TDS removal capabilities. However, these facilities must still meet TDS discharge limits specified by their state. Appendix F contains additional information on treatment configurations, including examples of processes at several facilities treating oil and gas wastewater.

Facilities discharging treated wastewater to waters of the United States or POTWs are regulated under the Clean Water Act (CWA). For zero-discharge facilities, some states, including Pennsylvania and Texas, have adopted regulations to control permitting of these facilities or to encourage treatment and reuse. The PA DEP issues permits that allow zero-discharge CWTs to treat and release water back to oil and gas industries for reuse (see the Eureka Resources Facility in Williamsport, PA listed in Appendix Table F-6 as an example of a zero-discharge facility).[1]

In developing this assessment, we looked at NPDES permit information for several CWTs in the eastern United States treating wastewater from the Marcellus region and one near the Fayetteville Shale in Arkansas. The facilities include those with and without TDS removal capabilities, and some are undergoing upgrades to implement TDS removal. Some of the permits reviewed for this assessment are current, and others are expired and may be in the process of renewal. The permits require monitoring (with or without limits) for a range of constituents that may include chloride, TDS, TSS, total strontium, total barium, oil and grease, heavy metals, 5-day biological oxygen demand (BOD5), and a range of organic compounds (e.g., phenol, cresol, BTEX, phthalates), with the specific constituents varying by permit. Sample types for the facilities are generally 24-hour composites. The newer permits set limits for several important constituents such as chloride, TDS, TSS, total barium, total strontium, oil and grease, and a number of heavy metals. Bromide is generally either not included or is required to be reported but with no limit specified. However, limits on TDS will reduce bromide concentrations. Some permits require monitoring for total radium, uranium, and gross alpha, but no limits are specified. Note that these facilities do not necessarily discharge consistently because treated wastewater can be sent for reuse.

Although there are CWTs serving hydraulic fracturing operations throughout the country, the majority serve Marcellus Shale operations in Pennsylvania (Boschee, 2014). Of the 74 CWT facilities identified by the EPA (U.S. EPA, 2016d) as having accepted or having the ability to accept hydraulic fracturing wastewater (not counting facilities treating CBM wastewater), 40 are located in Pennsylvania (Table 8-5). Most are zero-discharge facilities, and many do not have treatment processes for TDS removal. Although several Pennsylvania facilities are permitted to discharge, Wunz (2015) found few that currently discharge (two CWTs in Pennsylvania, one in West Virginia,

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[1] The facility is also permitted for indirect discharge to the Williamsport Sewer Authority.

Table 8-5. Number, by state, of CWT facilities that have accepted or plan to accept wastewater from unconventional oil and gas activities.

Source: U.S. EPA (2016d).

State	Unconventional formation(s) served	Zero discharge CWT facilities[a]		CWT facilities that discharge to a surface water or POTW[a]		CWT facilities with multiple discharge options[a]		Total known facilities
		Non-TDS removal	TDS removal	Non-TDS removal	TDS removal	Non-TDS removal	TDS removal	
AR	Fayetteville	2	0	0	0	0	1	**3**
CO	Niobrara, Piceance Basin	3 (1)	0	0	0	0	0	**3**
ND	Bakken	0	1 (1)	0	0	0	0	**1**
OH	Utica, Marcellus	10 (7)	0	1	0	0	0	**11**
OK	Woodford	2	0	0	0	0	0	**2**
PA	Utica, Marcellus	22	7(3)	8	0	0	3 (1)	**40**
TX	Eagle Ford, Barnett, Granite Wash	1	3	0	0	0	0	**4**
WV	Marcellus, Utica	4 (2)	0	0	0	1	1	**6**
WY	Mesaverde and Lance	0	2	0	0	0	2	**4**
Total		**44**	**13**	**9**	**0**	**1**	**7**	**74**

[a] Information is current as of 2014; it is possible that since 2014, some listed CWT facilities have closed and/or new CWT facilities not listed have begun operation. The number of facilities includes those that have not yet opened but are under construction, pending permit approval, or are in the planning stages. Facilities that are not accepting hydraulic fracturing wastewater but plan to accept it in the future are noted parenthetically and not included in the sum of total known facilities. Facilities handling CBM wastewater are not represented here.

and one in Ohio). According to EPA research (U.S. EPA, 2016d), the number of CWT facilities serving operators in the Marcellus and Utica Shales has increased since the mid-2000s, growing from roughly five in 2004 to over 40 in 2013. A similar trend has been noted for the Fayetteville Shale region in Arkansas, where there are fewer Class IID injection wells compared to the rest of the state (U.S. EPA, 2016d).

In other regions, a small number of newer facilities have emerged in the last several years, most often with TDS removal capabilities. In Texas, for example, two zero-discharge facilities with TDS removal capabilities are available to treat wastewater from the Eagle Ford Shale (beginning in 2011 and 2013), and one zero-discharge facility with TDS removal is located in the Barnett Shale region (operational since 2008). In Wyoming, there are four facilities in the region of the Mesaverde/Lance formations that started operating between 2006 and 2012. Two are zero-discharge facilities, and two have multiple discharge options; all are capable of TDS removal (U.S. EPA, 2016d).

Few states maintain a comprehensive list of CWT facilities, and the count provided by the EPA (U.S. EPA, 2016d) includes facilities that do not currently but plan to accept wastewater from unconventional formations. Therefore, the data in Table 8-5 do not precisely reflect the number of facilities currently handling hydraulic fracturing wastewaters. Other sources indicate either use of, or interest in, development of treatment facilities in other regions such as the Barnett Shale region (Hayes and Severin, 2012b), the Fayetteville (Veil, 2011), and other areas in Texas and Wyoming (Boschee, 2014, 2012). In addition, news releases and company announcements indicate that other wastewater treatment facilities are being planned (Greenhunter, 2014; Geiver, 2013; Purestream, 2013; Alanco, 2012; Sionix, 2011).

Use of specific types of CWTs has and will continue to shift due to drivers such as availability and cost of other disposal options (e.g., disposal wells), operator demand for reuse and the associated quality needed, developments in treatment, treatment costs, and regulatory changes. Practices in Pennsylvania over the last several years provide such an example. Between 2010 and 2013, the percentage of Marcellus wastewater treated at CWTs dropped from 52% to 20% (Figure 8-4), and the percentage of wastewater reused on-site rose to 65%, reflecting a shift in practice among operators. Among the percentage of the wastewater sent to CWTs, the portion sent to zero-discharge facilities for subsequent reuse rose from 10% to 65%. This is consistent with an increased emphasis on reuse in Pennsylvania. (See Section 8.4.4 for a discussion on reuse as a waste management practice.)

8.4.3.1 Relationship to Potable Surface Waters

Figure 8-7 shows the relationship between Pennsylvania potable water supplies and the CWTs that lie in their upstream watersheds. These surface waters, including streams, rivers, and waterbodies (e.g., lakes and reservoirs) have been evaluated by the PA DEP for attainment of a designated use of potable water supply as per the CWA Section 305(b) reporting and Section 303(d) listing. Ninety-four percent of the waterbodies and 98% of the streams and rivers were attaining their designated use in 2016. These stream segments may or may not currently have intakes for drinking water treatment plants. The map also shows the locations and types of CWTs that either currently accept unconventional oil and gas wastewater (as defined by PA DEP) or have accepted such wastewater

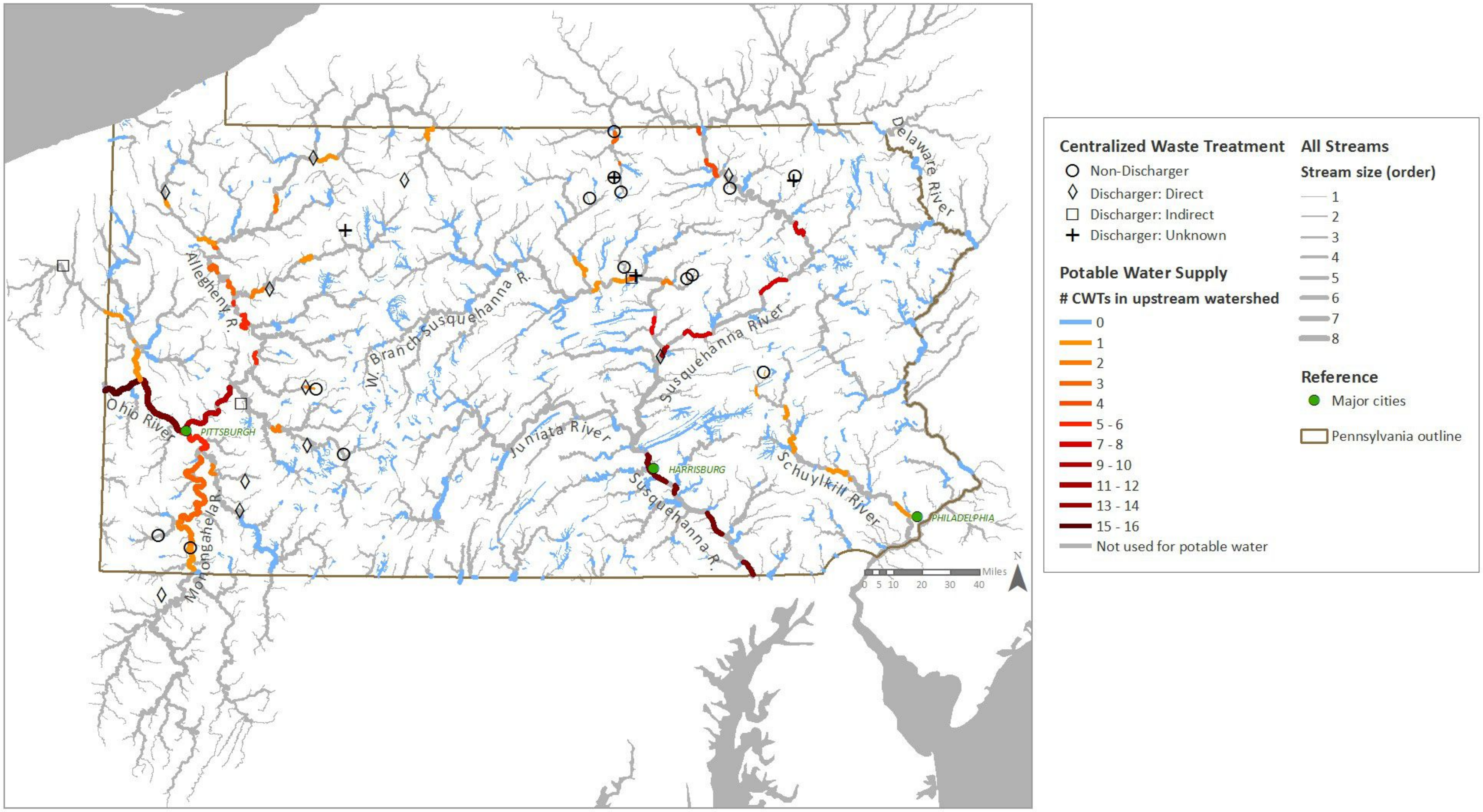

Figure 8-7. Map showing Pennsylvania surface water designated as potable water supplies and upstream CWTs.

Surface waters are colored orange to red to indicate the number of CWTs located in the upstream watershed. Blue surface waters have no upstream CWTs, and light gray lines show those not designated as potable water supplies. Symbols show the locations of CWTs that currently accept or have accepted unconventional oil and gas wastewater. Data sources: U.S. EPA (2016d), U.S. EPA (2016f), and PA DEP (2016b).

within approximately the last five years.[1] CWTs represented include both dischargers (direct and indirect) as well as zero-discharge facilities. For some facilities, we were not able to determine if the facility was zero-discharge or if it has a NPDES permit. The surface waters have been color-coded to indicate the number of CWTs that are located upstream. Darker red indicates more CWTs located in the upstream watershed, while blue indicates no upstream CWTs. Softer grey lines show portions of the stream network not designated for potable water supply. The thickness of the line indicates the size of the stream or river, categorized by the "stream order" designation.

The map provides a general illustration of how CWTs are situated within catchments in Pennsylvania, showing their spatial and general hydrologic relationships to streams that can serve as potable water supplies. The map shows that a given stream or waterbody may have a number of CWTs upstream, potentially contributing to combined impacts on surface water if there are spills or inadequately treated discharges. Note that the upstream catchment areas are large for the major rivers. Therefore, some rivers, such as the Ohio or Susquehanna, have as many as 15 or 16 upstream CWTs, although most are located far away. The map does not represent the effects of dilution on either discharges or spills; such an evaluation would necessitate currently unavailable data required to do a complete analysis of water quality. Note that many of the CWTs are zero-discharge facilities, and those that are permitted to discharge may do so intermittently. However, the storage and handling of wastewater at CWTs could impact nearby surface water through leaks and spills.

To more completely place these facilities in a watershed context, other types of discharges that could be occurring upstream should be taken into consideration. Impacts from hydraulic fracturing wastewater may be more problematic if there are additional pollutant sources within the watershed, increasing the cumulative effects of discharges and spills. For example, an EPA source apportionment study (U.S. EPA, 2015o) evaluated the relative contributions of bromide, chloride, nitrate, and sulfate from CWTs primarily treating hydraulic fracturing wastewater to the Allegheny River Basin and to two downstream public water system intakes. The study considered that the Allegheny River and its tributaries also receive runoff and discharges from an array of sources that include acid mine drainage and mining operations, coal-fired electric power stations, industrial wastewater treatment plants, and POTWs. It was concluded that CWTs treating oil and gas wastewater and coal-fired power plants with flue gas desulfurization were the primary contributors of bromide and chloride at the intakes (see Section 8.5.1 for further discussion), while nitrate and sulfate contributions were from POTWs and Acid Mine Drainage (U.S. EPA, 2015o).

8.4.3.2 Potential Impacts from CWTs

The potential impacts of managing hydraulic fracturing wastewater at CWTs depend on whether the CWT adequately treats for constituents of concern prior to discharge to surface water or a POTW, and whether treatment residuals are managed appropriately. Historically, CWTs have not

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[1] The list of CWTs used to develop this map is based on best available data, including information in the technical development document supporting the new EPA unconventional oil and gas effluent limitation guidelines (U.S. EPA, 2016d) as well as data from PA DEP waste records. This information was supplemented with other publicly available descriptions of the facilities. The information may, however, not be complete, and the symbols may not definitively reflect the discharge status of a facility.

included processes to treat for constituents that are difficult to remove, such as the high concentrations of TDS found in wastewater from unconventional reservoirs. As a result, impacts on drinking water resources have included increased suspended solids and chloride concentrations downstream of discharging facilities that were accepting hydraulic fracturing wastewater (Olmstead et al., 2013) and elevated bromide concentrations and radium concentrations in CWT effluent (Warner et al., 2013a); see Sections 8.5.1 and 8.5.2. In addition, spills and leaks can occur in pits or impoundments associated with the storage of treated wastewater at CWTs (impacts related to spills and leaks from pits and impoundments are discussed in Section 8.4.5). Wastewater being transported by truck or pipeline to and from a CWT can also present a vulnerability for spills or leaks (Easton, 2014) (Chapter 7).

While selection of appropriate treatment processes is critical for CWTs that discharge to surface waters, there are also two important issues related to completeness of treatment that can have an impact. First, there may be unknown constituents in the wastewater. The effectiveness of treatment cannot be evaluated for constituents for which the wastewater has not been tested. This makes it challenging to know the degree to which effluent from a CWT is protective of public health. Second, even an efficient treatment process may not be able to reduce the concentrations of some constituents to levels that allow for discharge to a drinking water resource if influent concentrations are so high that they exceed the capabilities of the treatment technology(ies) to meet those discharge limits. For example, a facility described by Kennedy/Jenks Consultants (2002) removed a high percentage of boron (88%), but the effluent concentration of 1.9 mg/L (average influent concentration of 16.5 mg/L) was not low enough to meet California's action level of 1 mg/L. Thus, the influent concentration must be considered together with removal efficiency to determine whether the effluent quality will meet the requirements dictated by end use or by regulations.

Relatively few studies describe the ability of individual treatment processes to remove constituents from hydraulic fracturing wastewater. For this assessment, simple estimated effluent concentrations were calculated for several combinations of unit treatment processes, wastewater constituents, and influent concentrations (details are given in Appendix Table F-3). The purpose of the analysis was to illustrate the relative capabilities of a number of treatment processes and not to represent a complete treatment system. As an example, the estimates suggest that if wastewater contains radium with a concentration in the thousands of pCi/L, a 95% removal rate with chemical precipitation may result in an effluent that exceeds 100 pCi/L. Treatment of the same wastewater via distillation or reverse osmosis could result in effluent concentrations in the tens of pCi/L. This analysis suggests that attention should be paid to the capabilities of a planned treatment system for the full range of anticipated wastewater compositions.

To gain a better understanding of impacts, the USGS has conducted sampling for a wide array of water quality parameters in surface water and groundwater in the Monongahela River Basin in West Virginia to establish baseline water-quality conditions (Chambers et al., 2014). Future water quality sampling can be compared to this baseline to assess impacts from hydraulic fracturing activities. To address past impacts, Pennsylvania, having experienced water quality impacts on receiving streams due to discharges of high-TDS effluent modified their regulations to address these issues by setting water quality standards for CWT dischargers (Mauter and Palmer, 2014; Shaffer et al., 2013). (See Text Box 8-1.)

8.4.4 Wastewater Reuse for Hydraulic Fracturing

The reuse of hydraulic fracturing wastewater for subsequent hydraulic fracturing operations has increased in some regions of the country in recent years (Boschee, 2014, 2012; Gregory et al., 2011; Rassenfoss, 2011).[1] This practice is driven by factors that include cost (including treatment costs), the lack of availability of other management options (e.g., Class II disposal wells), and changes to state regulations (Boschee, 2014; Shaffer et al., 2013). Wastewater quality is a consideration; some constituents pose challenges for reuse and may necessitate treatment. For example, high concentrations of barium and sulfate can lead to scaling, and the presence of some constituents in wastewater can hinder crosslinking (Akob et al., 2016; Boschee, 2014). Hydraulic fracturing fluid formulations that can use high TDS waters (e.g., as high as 150,000 mg/L to over 300,000 mg/L) facilitate reuse with minimal treatment (Boschee, 2014; Mauter and Palmer, 2014). See Chapter 5 for more information regarding the chemical composition of hydraulic fracturing fluids and Appendix F for more discussion of considerations for reuse.

Reuse can be accomplished by blending either untreated or minimally treated hydraulic fracturing wastewater with fresh water to lower the TDS content (Boschee, 2014). Wastewater may be reused at a site with multiple wells, eliminating the need for transport to a CWT (Lester et al., 2015; Easton, 2014). Alternatively, wastewater can be treated at a CWT and then taken by operators for mixing with other water sources for reuse (Easton, 2014). Flowback may be preferable to later-stage produced water for reuse because of its lower TDS concentration. Also, it is typically generated in larger quantities from a single location as opposed to water produced later on, which is generated in smaller volumes over time from many different locations (Barbot et al., 2013; Maloney and Yoxtheimer, 2012). Reuse can reduce the costs associated with water acquisition and produced water management. Such economic and logistical benefits can be expected to inform ongoing wastewater management decisions.

Costs can be the most significant driver for reuse. For example, the costs of transporting wastewater from the generating well to the treatment facility and then to the new well can be weighed against the costs for transport to alternative locations (e.g., a disposal well). Trucking large quantities of water can be relatively expensive—from \$0.01 to \$0.19 per gallon (\$0.50 to \$8.00 per bbl)—rendering on-site treatment technologies and reuse economically competitive in some settings (Dahm and Chapman, 2014; Guerra et al., 2011). Reuse rates may also be driven by wastewater production rates compared to the demand for reuse, with both production and demand increasing in a region if more wells go into production or decreasing as plays mature (Lutz et al., 2013; Hayes and Severin, 2012b; Slutz et al., 2012). Other logistics to consider include proximity of the water sources for aggregation and sequencing of completion schedules (Mauter and Palmer,

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[1] Reused hydraulic fracturing wastewater is discussed in Chapter 4 of this report (Water Acquisition) as well as in this chapter, though in a different context. The wastewater reuse rate described in this chapter is the amount or percentage of generated hydraulic fracturing wastewater that is managed through use in subsequent hydraulic fracturing operations. In contrast, Chapter 4 discusses reused wastewater as a source water and as one part of the base fluid for new fracturing fluid.

2014). A small survey by Mauter and Palmer (2014) indicates that the scheduling of well completions is complex, requiring optimization of labor, contractual issues, equipment usage, and water storage capacity among other factors. Boschee (2014) notes that in the Permian Basin, older conventional wells are linked by pipelines to a central disposal facility, facilitating movement of treated water to areas where it is needed for reuse. Companies drilling fewer wells or located in more remote areas may find reuse difficult because of challenges in consolidating wastewater from their wells or accessing wastewater from centralized facilities.

Regulations may also encourage reuse. For example, in 2013, the Texas Railroad Commission adopted rules eliminating the need for a permit when operators reuse on their own lease or transfer the fluids to another operator for reuse (Rushton and Castaneda, 2014). Any information on wastewater management practices in Texas that becomes available for the years after 2013 will allow evaluation of whether reuse has in fact increased.

A summary of reuse practices throughout the United States is hampered by the limited amount of data available for many regions of the country. However, current data indicate that extensive reuse takes place in the Marcellus region. Several studies using data from PA DEP data show that total reuse rates of oil and gas wastewater in Pennsylvania have risen over the last several years to between 85 and 90% (Table 8-6). This includes wastewater sent to CWTs to treat for reuse as well as reuse at the well sites without transfer to a CWT (labeled as "Reuse HF" in Figure 8-4). In particular, reuse of Marcellus wastewater at well sites in Pennsylvania has risen from about 8% in the second half of 2010 to nearly 70% in the first half of 2014 (PA DEP, 2015a). Schmid and Yoxtheimer (2015) report more recent data stating that in 2014, approximately 85% of Marcellus hydraulic fracturing wastewater was reused. Of that amount, 78% occurred on-site, and 22% was via CWTs.

Table 8-6. Estimated percentages of reuse of hydraulic fracturing wastewater.

Play or basin	Source and year	2008	2009	2010	2011	2012	2013	2014
East Coast[a]								
Marcellus, PA	Rahm et al. (2013)	9	8	25 – 48	67 – 80			
Marcellus, PA	Ma et al. (2014)		15 - 20				90	
Marcellus, PA	Shaffer et al. (2013)					90		
Marcellus, PA	Schmid and Yoxtheimer (2015)							85
Marcellus, PA	Hansen et al. (2013)	9	6	20	56			
Marcellus, PA	Maloney and Yoxtheimer (2012)				71.6			
Marcellus, PA	Tiemann et al. (2014)				72	87		

Play or basin	**Source and year**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Marcellus, PA	Rassenfoss (2011)			~67 (general estimate) 96 (one company)				
Marcellus, PA	Wendel (2011)			75-85	90			
Marcellus, PA	Lutz et al. (2013)	13 (prior to 2011)			56			
Marcellus, PA (SW region)	Rahm et al. (2013)	~10	~15	~25-45	~70-80			
Marcellus, PA (NE region)	Rahm et al. (2013)	0	0	~55-70	~90-100			
Marcellus, WV	Hansen et al. (2013)			88	73	65 (partial year)		
Gulf Coast and Midcontinent								
Fayetteville	Veil (2011)			20 (single company target)				
Barnett	Rahm and Riha (2014), Nicot et al. (2012)				5 (general estimate – appears to cover recent years)			
Eagle Ford	Nicot and Scanlon (2012)				0	20 (estimate based on interviews)		
East Texas	Nicot and Scanlon (2012)				5			
Haynesville	Horner et al. (2014)						0	
Haynesville	Rahm and Riha (2014)				5 (general estimate – appears to cover recent years)			

Play or basin	Source and year	2008	2009	2010	2011	2012	2013	2014
West Coast and Upper Plains								
Denver-Julesburg (Weld County), CO	Sumi (2015)					54 (flow-back only)		
Bakken	Horner et al. (2014)						0	

[a] Studies focusing on the Marcellus Shale use waste data reports from PA DEP.

Reuse in the Marcellus region is higher in the northeastern part of Pennsylvania than in the southwestern portion where easier access to Class IID wells in Ohio makes disposal by injection more feasible (Rahm et al., 2013). Outside of the Marcellus region, reuse rates are lower. Ma et al. (2014) note that only a small amount of reuse is occurring in the Barnett Shale. Reuse has not yet been pursued aggressively in New Mexico or in the Bakken (North Dakota) (Horner et al., 2014; LeBas et al., 2013). Other sources, however, indicate growing interest in reuse, as evidenced in specialized conferences (e.g., "Produced Water Reuse Initiative 2014" on produced water reuse in Rocky Mountain oil and shale gas plays), and available state-developed information on reuse (e.g., fact sheet by the Colorado Oil and Gas Conservation Commission) (Colorado Division of Water Resources et al., 2014).

If hydraulic fracturing activity slows in an area that is currently reusing wastewater, demand for the wastewater may decrease and wastewater management practices may shift. Analysis by Wunz (2015) and data in Figure 8-1 suggest a decline in wastewater production in Pennsylvania. Wunz (2015) also notes that in the future, there could be a trend of more wastewater coming from late-stage produced water and less from flowback as more wells are in the production phase and fewer wells are being fractured. If the demand drops relative to production due to fewer wells being drilled and fractured, then the "excess" produced water will need to be managed by other means. Alternatives to reuse may include increased transport to disposal wells (e.g., those in Ohio), development of more disposal wells in Pennsylvania, or advanced treatment and discharge to surface water via CWTs that have TDS removal capabilities (SAFER PA, 2015; Wunz, 2015; Silva et al., 2014a).

8.4.4.1 Potential Impacts from Reuse

For companies employing reuse as a wastewater management strategy, surface spills and leaks can occur during wastewater transport to and from a treatment facility or from storage tanks/pits located at the treatment facility or at the well site. Releases may be due to failed infrastructure such as tank or pipe ruptures, from natural disasters such as floods or earthquakes, or incidents such as overfills, improper operations, or vandalism (CCST, 2015a; NYSDEC, 2011). If the spill or leak is not contained or otherwise mitigated, these releases could reach groundwater or surface water (CCST, 2015a; NYSDEC, 2011). See Chapter 7 for more discussion on types of spills associated with hydraulic fracturing activities, including storage and transport. See Section 8.4.5 for discussion of storage pits and associated impacts on drinking water resources.

With reuse there is the potential for accumulation of dissolved solids such as salts and TENORM in the wastewater over successive reuse cycles (see Section 7.3.4.6 and Section 8.5.2 for more information about TENORM). Because wastewater is often reused with minimal treatment, constituents resulting from time spent in the subsurface remain in the wastewater and can increase during additional hydraulic fracturing. This potentially concentrated wastewater can pose a bigger issue if a breach occurs in an on-site pit or tank storing this wastewater while awaiting reuse (Section 8.4.5; Chapter 7).

The issue of concentrating contaminants during reuse has not yet been quantitatively evaluated in the literature. Also, it is not known how much this problem would be mitigated due to the dilution of wastewater when reused as new fracturing fluid. Estimates of the percentages of reused wastewater in new fracturing fluids in Pennsylvania range from about 2% in 2009 to as much as 22% in 2013 (SRBC, 2016; Schmid and Yoxtheimer, 2015) (Chapter 4). However, data from Pennsylvania's TENORM study (PA DEP, 2015b) showed radium in some hydraulic fracturing fluids, presumably from a reused wastewater component. As reused wastewater continues to accumulate contaminants, the water will eventually need to be managed, either through treatment or injection.

8.4.5 Storage and Disposal Pits and Impoundments

The use of pits and impoundments as part of a wastewater management strategy is a historic as well as current practice in the oil and gas industry. These structures are either used for temporary storage (on-site at oil and gas production wells or off-site at CWTs or disposal wells) or they are intended for permanent disposal (evaporation or percolation). There are a variety of terms to describe these structures depending upon their use (Richardson et al., 2013); "pits," "impoundments," and "reserve pits" are some of the more common terms associated with wastewater management. The terms "impoundment" or "pond" are often used to refer to large area holding structures and are also used by some states for specific applications such as holding "freshwater" for fracturing fluid formulation (Quaranta et al., 2012). Definitions and terminology are not standardized and vary from state to state (Richardson et al., 2013). For the purposes of this section, the nomenclature will defer to the term used by the original author/regulating authority.

States govern the use and permitting of pits under their jurisdiction. Regulations vary from state to state regarding the circumstances in which pits can be used (e.g., chemical composition of the fluid), how they should be constructed, and whether they must be lined (e.g., proximity to drinking water resources and/or chemical composition of the fluid) (Richardson et al., 2013). Most states restrict the use of wastewater pits in environmentally sensitive areas. To avoid contamination events, some states are moving toward requiring closed loop systems (i.e., tanks) or injection wells rather than using pits for hydraulic fracturing wastewater storage. For example, Pennsylvania has modified their regulations (published October 8, 2016) to ban the use of pits for temporary storage of unconventional (as defined by PA DEP) wastewaters; many operators have already moved to closed-loop systems (PA DEP, 2016a). This development is particularly notable because of

Pennsylvania's heavy reliance on reuse for wastewater management, necessitating both on-site and off-site storage.

8.4.5.1 Locations and Numbers of Pits

The locations and number of existing pits (both for storage and for disposal) are not well documented in all states, and in the data found, pits associated with hydraulic fracturing operations were not specifically identified. With respect to larger pits for storage or disposal of wastewater, some states (e.g., Utah and Oklahoma) provide locational data on their websites. In 2016, the state of California began posting the number of active and inactive oil field produced water "ponds" (defined as unlined surface impoundments), both permitted and unpermitted, on their website. The July 2016 posting showed that 64% (682) of the 1,065 unlined ponds identified in the Central Valley and Central Coast of California were active. Of the active ponds, 21% (144) were not permitted (CA Water Board, 2016). Active ponds are primarily found in the southern San Joaquin Valley (CCST, 2015a). The EPA Region 8 conducted a survey of pits associated with oil and gas operations in Colorado, Montana, North Dakota, South Dakota, Utah, and Wyoming from 1996 through 2002. Results indicated there were approximately 28,000 pits at that time (U.S. EPA, 2003b).

In the absence of an inventory of pits in Pennsylvania, the organization SkyTruth led an effort using volunteers to produce a map of pits believed to be associated with drilling and hydraulic fracturing the Marcellus Shale (Manthos, 2014). The identification of pits was based on USDA aerial imagery taken in 2005, 2008, 2010, and 2013. SkyTruth acknowledges the uncertainties associated with identifying pits based on aerial images and volunteer labor. They have described their methodology as including multiple reviewers and QA/QC procedures. The study cannot differentiate ponds for drilling fluids and fracturing fluids from those for wastewater. Their preliminary findings indicate that the estimated number of ponds rose from 11 in 2005 to 529 in 2013, with the structures themselves increasing in size from a median size of 3,713 ft^2 (345 m^2) in 2005 to 66,844 ft^2 (6,210 m^2 in 2013. SkyTruth also notes that impoundments are not permanent and that of 581 ponds delineated in 2010, only 116 of them were found in the images from 2013.

Evaporation ponds, referred to as Commercial Oil Field Waste Disposal Facilities (COWDFs), are a waste management strategy most commonly used in the western states such as Utah, Wyoming, and Colorado (USFWS, 2014). According to a 2016 list of approved COWDFs posted by the Utah Division of Oil, Gas, and Mining (Utah Division of Oil, 2016), 20 facilities in Utah are approved to accept produced water. All are in the eastern part of the state where the Uinta and Paradox basins are found (unconventional shale formations). The Wyoming Department of Environmental Quality website, accessed in 2016, lists 35 active COWDFs (WDEQ, 2016b). The increase in hydraulic fracturing activity in Wyoming has resulted in significant increase in wastewater disposed of in COWDFs (USFWS, 2014). Data from the Colorado Oil & Gas Conservation Commission includes eight active evaporation pits, five of which are unlined (COGCC, 2016). Ninety-five other active pits are listed in Colorado, with descriptors such as "production," "multi-well pit," "skim," or "produced water." Seventy-one of these are unlined, and 22 have synthetic liners. Eleven pits are located in

Garfield County, where there is hydraulic fracturing activity. The Colorado data do not distinguish pits at centralized commercial facilities from on-site pits.

8.4.5.2 Unlined Storage Pits and Percolation Pits

Whether an unlined pit is designed and intended to percolate wastewater into the ground for disposal or if it is built for storage, it provides a pathway for wastewater to infiltrate into the subsurface and potentially reach groundwater. Such pits have been used historically for conventional oil and gas wastewater. More recently, they have received wastewater in areas where hydraulic fracturing takes place. States such as Montana and Wyoming allow unlined pits to be used for storage if the quality of the waste fluid meets specified limits and the pit is not in close proximity to environmentally sensitive areas such as drinking water resources, wetlands, and floodplains (Kuwayama et al., 2015b; Richardson et al., 2013).

In the past, several states have allowed unlined pits designed to dispose of wastewater via percolation into the subsurface. For example, until July 2015, percolation pits were permitted for wastewaters from hydraulically fractured wells in the Central Valley Region in California (Grinberg, 2016). The California Department of Conservation's Division of Oil, Gas, and Geothermal Resources (DOGGR) listed "evaporation-percolation" as the management method for almost 60% (190 million gal) of the wastewater generated via well stimulation in Kern County between 2011 and 2014 (CCST, 2015a). However, according to DOGGR's 2015 report addressing well stimulation activities in Kern County from January 1, 2014 through September 30, 2015, evaporation/percolation was not employed as a disposal option during that period (98% of the produced water was disposed of via operator-owned Class II injection wells, 1.75% was disposed of via commercial Class II injection wells, and 0.16% was reused).

While the practice of disposal via percolation pits has been discontinued in most states, as of July 2016, Wyoming's regulations still allow the use of percolation for disposing produced water specific to CBM operations in the Powder River Basin. To be permitted, the operator must demonstrate that the disposed fluid will comply with water quality standards of the Department of Environmental Quality (WYOGCC, 2015).

8.4.5.3 Evaporation Ponds

Evaporation is a simple water management strategy involving transporting wastewater to a pond or pit with a large surface area and allowing passive evaporation of the water from the surface (NETL, 2014; Clark and Veil, 2009). As discussed above, this disposal option, often referred to as a COWDF, is practical for drier climates of the western United States. Evaporation ponds have been used for oil and gas wastewater disposal in Montana, Colorado, Utah, New Mexico, and Wyoming (Veil et al, 2004). However, New Mexico no longer allows the use of pits for disposal (NM EMNRD OCD, 2013), and in Montana, evaporation ponds are no longer allowed because they do not put extracted water to a beneficial use (NRC, 2010). Figure 8-8 shows an example of a lined evaporation pit in Montana (DOE, 2006).

Figure 8-8. Lined evaporation pit in the Battle Creek Field (Montana).
Source: DOE (2006). Reproduced with permission from ALL Consulting.

As the water component of the wastewater is subject to evaporation, the fluid remaining in the pond becomes concentrated, and a sludge layer is formed. Remaining residual brines in the pond can be collected and disposed of via an underground injection well, and the solids can be taken to a landfill (see Section 8.4.7 for more details). In cold, dry climates, a freeze-thaw evaporation method has also been used to purify water from oil and gas wastewater (Boysen et al., 1999).

Nowak and Bradish (2010) describe the design, construction, and operation of two large commercial evaporation facilities in Southern Cross, Wyoming and Danish Flats, Utah. Each facility includes 14,000 gal (53,000 L) three-stage concrete receiving tanks, a sludge pond, and a series of five-acre (20,234 m^2) evaporation ponds connected by gravity or force-main underground piping. The Wyoming facility, which opened in 2008, consists of two ponds with a total capacity of approximately 84 million gal (2 million bbls or 318 million L). The Utah facility, open since 2009, consists of 13 ponds with a total capacity of approximately 218.4 million gal (5.2 million bbls or 826.6 million L). Each facility receives 0.42 to 1.47 million gal (10,000 to 35,000 bbls; 1.59 million to 5.56 million L) of wastewater per day from oil and gas production companies in the area.

Evaporation ponds or pits are subject to state regulatory agency approval and must meet state standards for water quality and quantity (Boysen et al., 2002).

8.4.5.4 Impacts and Potential Impacts from Pits and Impoundments

Pits containing hydraulic fracturing wastewater have the potential to impact drinking water resources if spills and overflows cause runoff to surface water or if wastewater percolates through the soil and reaches groundwater. In addition to contaminants in the wastewater itself, wastewater that reaches groundwater may mobilize constituents in pit bottoms or soils, and it may also reach hydrologically connected surface water. These impacts are amplified with increasing pit/impoundment size (Quaranta et al., 2012). Percolation may be accidental (through tears or improper installation of liner) or by design in unlined pits (Sumi, 2004).

Compromised pit liners can result in leaks, and extreme weather events, such as floods, can cause pits to overflow. An analysis of three state databases (New Mexico, Oklahoma, and Colorado) where pits and tanks have been used for storage of hydraulic fracturing wastewater found that for pits, the most common causes of spills were from overflows and liner malfunctions (Kuwayama et al., 2015b). For instance, of the 106 pit-related spills reported in New Mexico between 2000 and 2014, 33% were due to overflows and 26% were caused by liner malfunctions. Of the 62 tank spills reported, 44% were due to leaks, and 27% were related to overfilling (Kuwayama et al., 2015b). The types of constituents in pits that may be of concern from such events include VOCs, metals, TDS, oil, and TENORM (Kuwayama et al., 2015b).

Operational factors also influence potential impacts from pits and impoundments. These can include water level management (influent, seepage, spillage), the length of time water is stored in the pit/impoundment, the composition of the water, the local climate (rainfall and/or evaporation), and the transmission method (piped or delivered in an open channel) (NRC, 2010).

Construction and Capacity Issues

Construction requirements typically include specifications for features that can reduce the potential for impacts on groundwater or surface water. These can include liner specifications, depth to groundwater, secondary containment, setback requirements, freeboard, leak detection, and water quality monitoring (Kuwayama et al., 2015b).[1,2] For example, in a 2012 review of 19 states with shale gas development or potential for shale gas development, many states had setback requirements for pits in sensitive areas including surface water, wetlands, and floodplains. As of December 2015, however, 12 of the 19 states surveyed did not include setback requirements in their regulations. Many states did address the vertical separation of pits from the water table (e.g., 20 in (0.5 m) to seasonal high water table in PA; 10 ft (3 m) in WY; 50 ft (15 m) in NM) (Kuwayama et al., 2015b).

Despite construction standards, impacts on groundwater or surface water due to overflows, liner breaches, and other construction issues have been documented. In 2007 in Knox County, Kentucky, retention pits holding hydraulic fracturing flowback fluids overflowed into Acorn Fork Creek during the development of four natural gas wells (CCST, 2015a; Papoulias and Velasco, 2013). The incident caused the pH of the creek to drop from 7.5 to 5.6 and the conductivity to increase from 200 to 35,000 µS/cm. In addition, organics and metals including iron and aluminum formed precipitates in the stream. Fish and aquatic invertebrates were killed or distressed in the area of the stream affected by the release (Papoulias and Velasco, 2013).

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[1] Setback is the distance between the pit and a stream, lake, building, or other feature or structure that needs protection.

[2] Freeboard is the vertical distance between the level of the water in an impoundment and the overflow elevation (an outfall or the lowest part of the berm).

Similarly, in 2009, Marcellus wastewater stored in an impoundment from a hydraulic fracturing operation in Washington County, Pennsylvania overflowed the bank of the impoundment and reached surface water (a tributary of Dunkle Run) (CCST, 2015a). NRC (2010) reported continuous overfilling of an impoundment in the Powder River Basin (Wyoming) with CBM produced water, resulting in significant erosion of a seasonal water channel. The CBM operator was required through litigation to manage flows to the impoundment to prevent overflows. The literature did not report specific impacts on groundwater or surface water from the Pennsylvania or Wyoming incidents.

In Pennsylvania in 2010, pit liner failure was reported to have impacted groundwater through leakage of Marcellus wastewater from six impoundments (Colaneri, 2014). Ziemkiewicz et al. (2014) note that a study of 15 pits and impoundments in West Virginia found that slope stability and liner deficiencies were common problems. Construction quality control and quality assurance were often inadequate; the authors found a lack of field compaction testing, use of improper soil types, excessive slope lengths, buried debris, and insufficient erosion control, although no breaches were reported. A statistical analysis of oil and gas violations in Pennsylvania found that structurally unsound impoundments or inadequate freeboard were the second most frequent type of violation, with 439 instances in the period from 2008 to 2010 (Olawoyin et al., 2013).

Unlined Pits

Impacts on groundwater from historic and current uses of unlined pits in the oil and gas industry have been documented. In a review of records spanning 25 years (1983 – 2007), 63 incidents of private water supply contamination from the infiltration of saline fluids from unlined or inadequately constructed reserve pits were identified in Ohio (Kell, 2011). The same study (Kell, 2011) identified 57 legacy (pre-1984) incidents in Texas involving groundwater contamination from unlined produced water disposal pits. Such pits were phased out in Texas by 1984, prompting a move towards disposal of oil and gas wastewater in disposal wells.

Kern County, California has experienced impacts on groundwater associated with unlined percolation pits. A 2014 study notes that there are hundreds of pits across Kern County and elsewhere in the state, stretching state resources for regulatory oversight (Grinberg, 2014). Past sampling of water in percolation pits has shown exceedances of California's Tulare Lake Basin Plan (Basin Plan), which specifies maximum levels permitted for discharges of oil field well wastewater to unlined ponds overlying groundwater (Grinberg, 2014).[1] For example, the McKittrick 1 and 1-3 pits are large percolation pits in Kern County near oil fields where most of the hydraulic fracturing in California takes place (Grinberg, 2014). The pits are situated close to a number of important resources. They are located within a few miles of the Kern River Flood Channel, the California State Water Project, farmland, and are in an area of high quality groundwater (Grinberg, 2014). Sampling of fluids in the pits dating back to 1997 showed consistent exceedances of Tulare Basin Plan standards for TDS, chlorides, and boron. Sampling also revealed the presence of BTEX, gasoline range organics (GRO), and diesel range organics (DRO) (MTA, 2014). Sampling of three monitoring

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[1] The Basin Plan sets limits for salinity (1,000 μmhos/cm measured as electrical conductivity), chloride (175 mg/L), and boron (1 mg/L) (California Regional Water Quality Control Board Central Valley Region, 2015).

wells indicated that in 2004, a plume had migrated at least 4,000 ft (1,000 m) from the pits and was still detected in test wells in 2013. As of July 1, 2015, California's Code of Regulations includes a provision that no longer allows the use of pits, including percolation pits, for fluids produced from stimulated wells (Grinberg, 2016).

Unlined pits that were used from the 1960s until the mid-1990s for disposal of drilling muds and flowback and produced waters associated with hydraulic fracturing operations have been linked to groundwater contamination in Pavillion, Wyoming (Digiulio and Jackson, 2016; AME, 2015). A report by the Wyoming Oil and Gas Conservation Commission (WYOGCC) (WYOGCC, 2014a) summarizes site investigations and reclamation activities conducted by WOGCC, the Wyoming Department of Environmental Quality (WDEQ), and Encana Oil and Gas for pits in the Pavillion Well Field. The report includes information on samples collected between 2006 and 2013 from shallow groundwater in the vicinity of the pits. Some sites had detections for one or more of the following contaminants: GRO, DRO, BTEX, and/or naphthalene. Of the shallow groundwater sites with detections, some were associated with pits located within one-quarter mile of a domestic well. One of these sites exceeded clean-up levels established by the WDEQ Voluntary Remediation Program for DRO (13,000 µg/L) and benzene (110 µg/L).[1] The report noted that there was insufficient evidence to determine whether or not drinking water supply wells in the vicinity of the pits were contaminated by disposal of hydraulic fracturing wastewater in those pits (WYOGCC, 2014a).

Other examples in the literature include the detection of VOCs in groundwater downgradient of an unlined pit containing oil and gas wastewater near the Duncan Oil Field in New Mexico (Sumi, 2004) (Section 8.5). Groundwater impacts downgradient of an unlined pit in Oklahoma included high salinity (3500-25,600 mg/L) and the presence of VOCs (Kharaka et al., 2002). Neither New Mexico nor Oklahoma currently allows unlined pits for disposal or storage (OCC OGCD, 2015; NM EMNRD OCD, 2013).

Mobilization and Transport of Constituents

Groundwater impacts may result not just from constituents in the wastewater but also from mobilization of existing constituents in the soil or sediment. A CBM produced water impoundment in the Powder River Basin of Wyoming was studied for its impact on groundwater (Healy et al., 2011; Healy et al., 2008). Infiltration of water from the impoundment was found to create a perched water mound in the unsaturated zone above bedrock in a location with historically little recharge. Elevated concentrations of TDS, chloride, nitrate, and selenium were found at the site, with one lysimeter sample exceeding 100,000 mg/L of TDS (Healy et al., 2008). Most of the solutes found in the groundwater mound did not originate with the CBM produced water, but rather were the consequence of dissolution of previously existing salts and minerals (Healy et al., 2011).

Generally, the deeper that wastewater can move into an aquifer, as impacted by the volume and timing of the release, the longer the duration of contamination (Whittemore, 2007). Kharaka et al. (2007) reported on studies at a site in Oklahoma with one abandoned and two active unlined pits.

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[1] WDEQ cleanup levels are derived from a combination of promulgated levels (MCL, state-assigned water quality standards) and risk-based cleanup level concentrations (WDEQ, 2016a).

Produced water from these pits penetrated 10 to 23 ft (3 to 7 m) thick shale and siltstone units, creating three plumes of high-salinity water (5,000 to 30,000 mg/L TDS). The impact of these plumes on the receiving water body (Skiatook Lake) was judged to be minimal, although the estimate was based on a number of notably uncertain transport quantities (Otton et al., 2007).

Vadose (unsaturated) zone transport was illustrated at a site in Oklahoma where two abandoned pits were major sources for releases of produced water and oil. Saline water from the pits flowed through thin soils and readily percolated into underlying permeable bedrock. Deeper, less-permeable bedrock was contaminated by salt water later in the history of the site, presumably due to fractures. The mechanisms proposed were vertical movement through permeable sand bodies, lateral movement along shale fractures, and possibly increased clay permeability due to the presence of highly saline water (Otton et al., 2007).

Summary

Collectively, the above examples show that regardless of the purpose of pits (storage or disposal), they present a potential pathway for wastewater constituents to impact groundwater or surface water. Good construction standards and practices, including liners, adequate freeboard, and setbacks, are important for minimizing potential impacts on both surface water and groundwater. Proper monitoring and maintenance (e.g., avoiding overfilling, maintaining the integrity of liners and berms) are also important for protecting surface water and groundwater. Unlined pits, in particular, can lead to groundwater contamination. This can be long-lasting, as evidenced by legacy impacts from older pits. Most states have phased out unlined disposal pits and unlined storage pits, but if such pits are still in use, they can provide ongoing potential sources of groundwater contamination (CCST, 2015a; Grinberg, 2014).

8.4.6 Other Management Practices and Issues

Additional strategies for wastewater management in some states include directly discharging to surface waters and land application. In particular, wastewater from CBM fracturing and production generally has lower TDS concentrations than wastewater from other types of unconventional formations and more readily lends itself to other uses.

8.4.6.1 Land Application and Road Spreading

Road spreading has been used as a disposal option for high-TDS wastewaters (brines) from conventional oil and gas production. Road spreading can be done for dust control and de-icing. Although recent data are not available, an American Petroleum Institute (API) survey estimated that approximately 75.6 million gal (1.8 million bbls or 286.2 million L) of wastewater was used for road spreading in 1995 (API, 2000). The API estimate does not specifically identify hydraulic fracturing wastewater. There is no current nationwide estimate of the extent of road spreading using hydraulic fracturing wastewater.

Road spreading with hydraulic fracturing wastewater is regulated primarily at the state level (Hammer and VanBriesen, 2012) and is prohibited in some states. For example, with annual approval of a plan to minimize the potential for pollution, PA DEP allows spreading of brines from conventional (as defined by PA DEP) wells for dust control and road stabilization. Hydraulic fracturing flowback, however, cannot be used for dust control and road stabilization (PA DEP, 2011b). In West Virginia, use of gas well brines for roadway de-icing is allowed per a 2011 memorandum of agreement between the West Virginia Division of Highways and the West Virginia Department of Environmental Protection, but the use of "hydraulic fracturing return fluids" is not permitted (Tiemann et al., 2014; West Virginia DEP, 2011).

Concerns about road application center on contaminants such as barium, strontium, and radium. A report from PA DEP analyzed several commercial rock salt samples and compared results with contaminants found in Marcellus Shale flowback samples. The results noted elevated barium, strontium, and radionuclide levels in Marcellus Shale brines compared with commercial rock salt (Titler and Curry, 2011). Another study found increases in metals (radium, strontium, calcium, and sodium) in soils ranging from 1.2 to 6.2 times the original concentrations (for radium and sodium, respectively), attributed to road spreading of wastewater from conventional oil and gas wells for de-icing (Skalak et al., 2014).

Potential impacts on drinking water resources from road spreading have been noted by Tiemann et al. (2014) and Hammer and VanBriesen (2012). These include potential effects of runoff on surface water and migration of brines to groundwater. Snowmelt can carry salts and other chemicals from the application site, and transport can increase if application rates are high or rain occurs soon after application (Hammer and VanBriesen, 2012). Research on the impacts of conventional road salt application has documented long-term salinization of both surface water and groundwater in the northern United States (Kelly, 2008; Kaushal et al., 2005). When conventional oil field brine was used in a controlled road spreading experiment, elevated chloride concentrations were detected in shallow groundwater (Bair and Digel, 1990). The amount of salt attributable to road application of hydraulic fracturing wastewaters has not been quantified.

To evaluate land application of solid wastes from oil and gas production, a laboratory study mimicking land spreading of conventional oilfield scales and sludges indicated that 20% of the radium in barite sulfate scales was released by microbial processes during incubation with soil (Matthews et al., 2006; Swann et al., 2004). Although the radium was then complexed with the soil, it would be more mobile and more bioavailable than when it was associated with the barite. Overall, potential effects on drinking water resources from land spreading are not well understood, including the amounts of hydraulic fracturing wastes that are managed by land spreading.

8.4.6.2 Management of Coalbed Methane Wastewater

Many, but not all, CBM wells are hydraulically fractured to enhance recovery, using fluids that range from water alone to more complex gel formulations with proppant (e.g., Engle et al., 2011; McCartney, 2011; NRC, 2010; Halliburton, 2008; U.S. EPA, 2004a). The literature indicates that hydraulic fracturing of CBM formations is being conducted in the San Juan, Raton, Piceance, and Uinta Basins, among others. Literature such as NRC (2010) notes that hydraulic fracturing may not be common in the Powder River Basin. Additionally, when CBM well stimulation does take place, it can be accomplished using very simple hydraulic fracturing fluid formulations (Chapter 3).

Wastewater from CBM wells can be managed like other hydraulic fracturing wastewater discussed above. However, the wastewater from CBM wells can also be of higher average quality (typically lower TDS content) than wastewater from other hydraulically fractured wells. The lower TDS content makes it more suitable for certain management practices and uses. A number of management strategies have been proposed or implemented, with varying degrees of treatment required depending on the quality of the wastewater and the intended use (Hulme, 2005; DOE, 2003, 2002). Although specific volumes managed through the practices discussed below are not well documented, qualitative information and considerations for feasibility are available and presented. The discussion below covers both dilute and higher-TDS wastewater from CBM formations.

The quality of CBM wastewater plays a large role in how the wastewater is managed. The TDS content can range from an average of nearly 1,000 mg/L in the Powder River Basin to an average of about 14,000 mg/L (and as high as approximately 62,000 mg/L) in the Black Warrior Basin (Appendix Table E-3). Data sources from about 2002 through 2008 indicate that operators in some basins such as the San Juan, Uinta, and Piceance, and Raton (in New Mexico), where TDS is typically higher compared to other basins (e.g., Powder River), manage most wastewater by injection into disposal wells (NRC, 2010; U.S. EPA, 2010a).

Discharge to rivers and streams, a management option governed by the CWA, may be permitted in cases where wastewater is of high quality.[1] To be discharged, the wastewater must meet technology-based effluent limitations established by the permitting authority on a case-by-case "best professional judgment" basis as well as any more stringent limitations necessary to meet applicable water quality standards. For example, as a means of protecting high-quality waters of the state, the Montana Supreme Court ruled in 2010 that treatment is required for all CBM produced water prior to discharge to surface water (NRC, 2010).

A 2008 EPA survey of CBM operators found that of the projects represented in the results, direct discharge to surface water was by far most prevalent in the Powder River Basin but was also reported as a management practice in the Green River, Raton, Black Warrior, Cahaba, Illinois, and Appalachian basins (U.S. EPA, 2013e, 2010a).[2] Discharges to surface water can provide habitat maintenance, restoration of wildlife-waterfowl fishery habitat, and flow augmentation to benefit downstream water users. However, hydrologic changes from such discharges could also have unanticipated effects on ecosystems previously adapted to intermittent streamflow.

Some CBM wastewater can be put to agricultural use, including livestock and wildlife watering, and crop irrigation. Livestock watering with CBM wastewater can be done using on-channel or off-channel impoundments, and irrigation is an area of active research (e.g., Engle et al., 2011; NRC, 2010). However, wastewater from some higher-salinity CBM basins (e.g., San Juan, Uinta, and Piceance) would need blending or treatment before such uses. Irrigation with treated CBM

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[1] Although discharge to rivers and streams is generally prohibited under the EPA's oil and gas ELGs, the ELGs do not apply to CBM.

[2] These reports did not describe certain non-discharging wastewaters management strategies in basins with few operators in order to preserve CBI. The reports also do not provide information on hydraulic fracturing activities in the basins. Not also that results are presented by numbers of projects, which may vary in the number of wells they contain.

wastewater would be most suitable on coarse-textured soils for cultivation of salt-tolerant crops (DOE, 2003). NRC (2010) remarks that "use of CBM produced water for irrigation appears practical and sustainable," provided that appropriate measures are taken such as selective application, dilution or blending, appropriate timing, and rehabilitation of soils.

Although CBM wastewater is generally lower in TDS than wastewater associated with shale gas development, it can still have higher TDS concentrations than stream water. This poses concerns regarding the sodium adsorption ratio (SAR) for agricultural soils. A USGS study performed trend analysis of water quality at sampling sites in the Tongue and Powder River watersheds (Powder River Basin) (Sando et al., 2014). One of the study objectives was to determine possible effects of CBM produced water particularly in areas where the water was discharged to impoundments or upper reaches of in-stream channels for infiltration. Trend analysis showed potential effects of CBM production on downstream water quality (increases in sodium, alkalinity, and SAR) in the main-stem Powder River but found mixed results at the Tongue River sites (some appeared to be impacted by CBM activities while others did not) (Sando et al., 2014).

Sando et al. (2014) found that CBM pumping rates (i.e., discharge of produced water) were high relative to streamflow in the Powder River Basin. For the three main-stem Powder River sites, the CBM pumping rates were 26-34% of the 2001-2010 median streamflows. For one site in the Little Powder River watershed, the CBM pumping rate was 360% of 2001-2010 median streamflow. This underscores that in arid climates in the western United States, permitted discharges from CBM activities (whether hydraulically fractured or not) at a particular site may be large relative to the size of the receiving water and may sometimes dominate flows.

As noted above, a degree of treatment is needed (or required) for some uses. Plumlee et al. (2014) examined the feasibility, treatment requirements, and potential costs of several hypothetical uses for CBM wastewater. In several cases, costs for these uses were projected to be comparable to or less than estimated disposal costs. In one case study, use of CBM wastewater for streamflow augmentation or crop irrigation could potentially cost between \$0.26 and \$0.27 per bbl. For comparison, reported disposal costs in 2000-2001 ranged from \$0.01 per bbl for a pipeline collection system with impoundment to \$2.00 per bbl for hauling to disposal or treatment. The 2010 NRC report (NRC, 2010) noted that 15 to 18% of CBM produced water in the Powder River Basin was being treated to reduce SAR in order to satisfy NPDES permits for discharge.[1] If wastewater is treated to address SAR, reported costs are approximately \$0.12 to \$0.60/bbl (NRC, 2010).

The applicability of particular uses may be limited by ecological and regulatory considerations as well as the irregular nature of CBM wastewater production (voluminous at first, and then declining and halting after a period of years). Legal issues, including overlapping jurisdictions at the state level and senior water rights claims in over-appropriated basins (in western states) can also determine the use of CBM wastewater (Wolfe and Graham, 2002).

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[1] SAR is the relative proportion of sodium to other cations in water. It is also an indication of risk to soil from alkalinity. The higher the SAR, the less suitable the water is for irrigation, and long-term use can damage soil structure.

8.4.6.3 Other Documented Uses of Hydraulic Fracturing Wastewater

Uses of wastewater from shales or other hydraulically fractured formations face many of the same possibilities and limitations as those associated with wastewater from CBM operations. The biggest difference is in the quality of the water. Wastewaters vary widely in water quality, with TDS values from shale and tight sand formations ranging from less than 1,000 mg/L TDS to hundreds of thousands of mg/L TDS (DOE, 2006) (Chapter 7). Wastewaters on the lower end of the TDS spectrum could be reused in many of the same ways as CBM wastewater, depending on the concentrations of potentially harmful constituents and applicable federal, state, and local regulations. High TDS wastewaters have more limited uses, and pre-treatment may be necessary (Shaffer et al., 2013; Guerra et al., 2011; DOE, 2006). Agricultural and wildlife uses are subject to the produced water daily effluent discharge limit of 35 mg/l for oil and grease.[1]

Potential uses for wastewater in the western United States include livestock watering, irrigation, streamflow supplementation, fire protection, road spreading, and industrial uses, with each having their own water quality requirements and applicability (Guerra et al., 2011). Guerra et al. (2011) summarized the least conservative TDS standards for five possible uses in the western United States that include 500 mg/L for drinking water (the drinking water secondary maximum contaminant level (SMCL)), 625 mg/L for groundwater recharge, 1,000 mg/L for surface water discharge, 1,920 mg/L for irrigation, and 10,000 mg/L for livestock watering. The authors estimated that wastewater from 88% of unconventional wells in the western United States could be used for livestock watering without TDS removal based on a maximum TDS concentration of 10,000 mg/L. However, wastewater from only 10% of unconventional wells could be used for surface discharge without treatment for TDS based on the least conservative standard among the western states of 1,000 mg/L TDS (Guerra et al., 2011). Guerra et al. (2011) indicate that in several basins in the western United States (e.g., Wind River, Green River, and Powder River), wastewater from 50% or more of oil and gas wells is suitable for agricultural use. In other basins (e.g., San Juan, Piceance, and Permian) over 50% of oil and gas wastewater is unsuitable for use without treatment. A 2006 Department of Energy (DOE) study pointed out that the quality necessary for use in agriculture depends on the plant or animal species involved and that in the Bighorn Basin in Wyoming, low-salinity wastewater is used for agriculture and livestock watering after minimal treatment to remove oil and grease (DOE, 2006).

Although TDS is a common criterion for water quality, there are also recommended limits or considerations for some metals, alkalinity, and nitrate in water for use in livestock watering, and for metals, SAR, electrical conductivity (ECw), and pH for water for irrigation (Guerra et al., 2011). Also, using TDS/salinity as the primary criterion may not be appropriate if wells contributing to the produced water have undergone hydraulic fracturing or if maintenance chemicals are being used on the well.

The water quality standards and monitoring requirements for direct discharge for use in irrigation or livestock watering include few specifications. In California, the California Council on Science and Technology (CCST, 2015a) notes that the testing and treatment required by the regional water

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[1] 40 CFR 435.52(b).

quality control boards prior to use of produced water for irrigation do not include assessment for chemicals associated with hydraulic fracturing and that there are no policies prohibiting the use of hydraulic fracturing wastewaters for irrigation.

In the Wind River Basin in Wyoming, three NPDES permits were appealed by environmental groups due to concerns that the permits failed to address maintenance and hydraulic fracturing chemicals (Natural Resources Defense Council, 2015; PEER, 2015). The environmental groups argued that the EPA's regulations do not allow for the discharge of produced water containing chemicals from well treatment, and that, moreover, the EPA lacked sufficient information regarding the well treatment chemicals to determine whether the discharge would be "good enough quality" for wildlife and agricultural use, as required under the ELG regulations. As an example, the environmental groups pointed to MSDS information provided upon request for six maintenance products, which included toxic chemicals such as ethylene glycol, benzyl chloride, isopropanol, naphthalene, benzene, and xylene, among others. This raised concerns that produced water permitted for direct discharge may contain toxic chemicals or their degradation products. Ultimately, pursuant to a settlement agreement with the environmental groups and permittees, the EPA issued modified permits that included additional conditions for handling of and reporting about well stimulation and well maintenance chemicals.

8.4.7 Management of Solid and Liquid Residuals

Solid and liquid residuals associated with hydraulic fracturing wastewater are formed from treatment processes at CWTs, buildup of sludges in tanks and pits, and scale formation on pipes and equipment. These residuals must be managed and disposed of properly to avoid impacts on ground and surface water resources. (Note that drill cuttings and drilling muds are outside the scope of this chapter.)

8.4.7.1 Solid Residuals

The solid residuals produced at a CWT depend on the constituents in the untreated water and the treatment processes used and are likely to contain TSS, TDS, metals, radionuclides, and organics. Solid residuals can consist of sludges (from precipitation, filtration, settling units, and biological processes), spent media (filter media, adsorption media, or ion exchange media), and other material such as spent filter socks used to remove gross particulates. In addition, solids that accumulate in storage tanks and pits and scale that deposits on equipment are part of the residual load from a site. These residuals can constitute a considerable fraction of solid waste in an oil or gas production area.

Handling and disposal of residual sludges from treatment processes can present some of the biggest challenges associated with these technologies (Igunnu and Chen, 2014). Additional treatment may be applied to solid residuals including thickening, stabilization (e.g., anaerobic digestion), and dewatering processes prior to disposal. The solid residuals are then typically sent to a landfill, land spread on-site, or incinerated (Morillon et al., 2002). Land spreading is a waste management method in which wastes are spread over the soil surface and tilled into the soil to allow the hydrocarbons in the wastes to biodegrade (Smith et al., 1998); note that inorganic constituents (e.g., salts, metals, metalloids, and radionuclides) will not degrade. In addition, pits or impoundments that have reached the end of their useful life have accumulated residuals. Practices used to decommission these pits include draining and leveling the pit in place or land farming the residual materials into the ground (Rich and Crosby, 2013), although more information is needed on the potential for these practices to affect water resources.

A particular concern for the management of residual wastes is TENORM that originates from the geologic formation and was present in the produced water (SAFER PA, 2015). Studies have found TENORM in solid residuals at oil and gas operations including the filter cake (PA DEP, 2015b), filter socks (Harto et al., 2014), and pit sludges (Rich and Crosby, 2013). Researchers have assessed Marcellus produced water samples, finding that many with low barium and high radium-226 levels would generate sludges that exceed the maximum acceptable radium-226 activity for nonhazardous landfill disposal in Pennsylvania (Silva et al., 2014b; Silva et al., 2014a). In scales that build up on hydraulic fracturing and treatment equipment and sludges that accumulate in tanks and pits, radium can coprecipitate with barium, strontium, or calcium sulfates (Smith et al., 1999). (See Section 8.5.2 for additional discussion of TENORM associated with residuals.)

The accumulation of TENORM in the solids generated can limit or preclude landfills as a disposal option. Walter et al. (2012) point out that wastes containing TENORM can be problematic due to the possibility of radon emissions from the landfill. Regulatory limits on permissible radionuclide levels accepted at non-hazardous landfills vary by state (Silva et al., 2014a).[1] Some states have volumetric limitations on TENORM in their landfill permits (e.g., Colorado). Also, some states write criteria, such as gamma exposure rates (radiation) and radioactivity concentration limits, into permits for many landfills that are permitted to accept TENORM. Silva et al. (2014a) note that there are 50 nonhazardous (RCRA-D) disposal facilities in Pennsylvania, but no TENORM disposal facilities. Texas and other states have disposal facilities for TENORM.

8.4.7.2 Liquid Residuals

Liquid residuals include concentrated brines (from membrane or evaporation processes) and regeneration or cleaning chemicals (from ion exchange, adsorption, and membrane processes) (Fakhru'l-Razi et al., 2009). Practices for managing liquid residual streams from treatment processes are generally the same as for untreated hydraulic fracturing wastewaters, although the treated volumes are smaller, resulting in lower costs (Hammer and VanBriesen, 2012). Concentrations of contaminants in liquid residuals, however, will be higher. The most common disposal method is injection into disposal wells.

If the liquid is not injected into a disposal well, treatment to remove salts would be required for surface water discharge to meet NPDES permit requirements and protect the water quality for downstream users such as drinking water utilities (Section 8.5). Because some constituents of concentrated liquid residual waste streams can pass through or impact municipal wastewater treatment processes (Linarić et al., 2013; Hammer and VanBriesen, 2012), these residuals would

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[1] Examples of permissible radionuclide levels at non-hazardous landfills: Pennsylvania requires alarms to be set at all municipal landfills, with a trigger set at 10 μR/hr above background radiation. Texas sets a radioactivity limit, requiring that any waste disposed by burial contains less than 30 pCi/g radium or 150 pCi/g of other radionuclides.

not be appropriate for discharge to a POTW. Elevated salt concentrations, in particular, can have detrimental effects on microbiological treatment at municipal wastewater systems, such as activated sludge treatment (Linarić et al., 2013).

Liquid residuals can also be mixed with a solidifying agent such as Portland cement and then disposed of in landfills, or they can undergo advanced treatment processes to generate products such as road salt or industrial chemicals (SAFER PA, 2015).

8.4.7.3 Potential Impacts from Solid and Liquid Residuals

Residual wastes have the potential to impact the quality of drinking water resources if contaminants leach to groundwater or reach surface water. In a recent study by PA DEP, radium was detected in leachate from 34 of 51 landfills that accept waste from the oil and gas industry (Marcellus in particular). Radium-226 concentrations ranged from 54 to 416 pCi/L, and radium-228 ranged from 2.5 to 1,100 pCi/L (PA DEP, 2015b). (See also Section 8.5.2 and see Chapter 9 for health effects associated with radium). Countess et al. (2014) studied the potential for a wide array of elements to leach from sludges generated at a CWT handling hydraulic fracturing wastewater in Pennsylvania. Tests used strong acid solutions (to simulate the worst case scenario) and weak acid digestions (to simulate environmental conditions). The data illustrate the possibility of leaching of these constituents from landfills. The extent of leaching varied by constituent and by fluid type, but the authors concluded that boron, bromide, calcium, magnesium, manganese, silicon, sodium, and strontium had high potential to migrate from the residual solids, with bromide and sodium having the highest leaching potential (Countess et al., 2014). (See also Section 5.8 in Chapter 5 for discussion of the processes governing the movement of constituents in the subsurface.)

In another study assessing the leaching behavior of residuals from hydraulic fracturing operations, Sharma et al. (2015) found that alkali metals, alkaline earth metals, and bromide had the highest leaching potential of the constituents tested. The authors also found that disposing of hydraulic fracturing residuals along with other solids (e.g., at a municipal landfill) produces a greater leaching potential than if the residuals are disposed of by burying or land disposal designed for solely the hydraulic fracturing residuals. This is due to the more acidic leachate formed at the co-disposal locations (Sharma et al., 2015).

Sang et al. (2014) studied the potential for hydraulic fracturing fluid to mobilize colloidal particles in the soil. The study used microspheres and sand particles as surrogates for contaminant particles. The authors note that the chemistry of hydraulic fracturing fluid favors transport of colloids and mineral particles through rock cracks, and they found that infiltration of flowback fluid can transport existing pollutants such as heavy metals, radionuclides, and pathogens, in unsaturated soils (Sang et al., 2014). Heavy metals can also move through soil. Although not specific to hydraulic fracturing wastes, Camobreco et al. (1996) report high levels of heavy metal transport in soil columns, with 12% recovery for lead, 15% for copper, 23% for zinc, and 30% for cadmium (Camobreco et al., 1996).

Residuals, whether liquid or solid, are the most concentrated wastes and waste streams associated with hydraulic fracturing operations. Contaminants in the produced water will accumulate in the sludges in storage tanks/pits, in scale on the equipment, and in treatment facilities. Proper management and disposal of these highly concentrated wastes is critical to minimize the potential for impacts on water resources.

8.5 Potential Impacts of Hydraulic Fracturing Wastewater Constituents on Drinking Water Resources

The previous section discussed the potential impacts of specific wastewater management strategies on drinking water resources. The severity of impacts, however, depends largely on the constituents in the wastewater, the concentrations of those constituents, and their health and ecological effects. This section will discuss the potential impacts of several specific types of hydraulic fracturing wastewater constituents on drinking water resources.

The impacts or potential impacts discussed in the literature are heavily focused on discharges from CWTs, including treated wastewater that is discharged indirectly through POTWs. Available evidence suggests that the effects of hydraulic fracturing on surface water quality are related to discharges of partially treated wastewater (Kuwayama et al., 2015a). Other avenues of contamination for both surface water and groundwater include leaks from pits and impoundments, landfill leachate, and leaching from contaminated sediments and other improperly managed solid wastes.

As noted, an important consideration regarding the potential impacts of hydraulic fracturing wastewater on receiving water is whether there are constituents of concern known to have health effects or that can give rise to compounds with health effects. See Chapter 9 for discussion of the health effects of wastewater constituents. For some classes of constituents, such as DBP precursors, considerable research exists regarding concentrations in the waste stream and impacts on downstream drinking water treatment plants or the finished drinking water after treatment. For other constituents, information is limited, especially within the context of hydraulic fracturing activities. There may also be unknown constituents because some ingredients in the original hydraulic fracturing fluids are claimed to be CBI. The following subsections identify several classes of constituents known to occur in hydraulic fracturing wastewater, discuss whether potential impacts are likely, and detail information gaps.

8.5.1 Bromide, Iodide, and Chloride

Halides, including bromide, chloride, and iodide, are commonly found in high-TDS hydraulic fracturing wastewater. As noted in Section 8.3.1.1, chloride is a regulated contaminant with a secondary MCL of 250 mg/L. Bromide and iodide are not regulated, but are of concern due to their role in the formation of DBPs (Parker et al., 2014; Krasner, 2009). (See Appendix F for information on DBP formation.) High-TDS wastewaters from the Marcellus Shale have been the focus of concern due to the state's history of treating these wastewaters at POTWs (without pretreatment) and at CWTs without TDS removal capabilities (Text Box 8-1). Discontinuing the practice of sending shale gas wastewater to POTWs without pretreatment (States et al., 2013), and compliance with the new EPA pretreatment standards for discharges of unconventional oil and gas wastewaters helps mitigate this problem. This section describes the role of some constituents in high-TDS fluids in the formation of DBPs and provides more details on the effects on surface waters as observed in Pennsylvania. The lessons learned and steps taken in the Marcellus region can provide valuable knowledge for operators and state agencies in other parts of the country that treat and discharge high-bromide and high-iodide wastewaters.

8.5.1.1 Influence of Bromide and Iodide on Formation of Disinfection Byproducts

Disinfection byproducts (DBPs) are formed when organic material comes in contact with disinfectants (e.g., chlorine, chloramine, chlorine dioxide, or ozone). Of particular concern are DBPs formed in the presence of halides (e.g., bromide or iodide). The type of DBP formed depends on the organic precursors in the source water and the disinfectant used. Regulated DBPs include total trihalomethanes (TTHM), five haloacetic acids (HAA5), bromate, and chlorite. There are, however, many additional DBPs that are not regulated and may in fact be of greater concern than the regulated species. Brominated forms of DBPs, for example, are considered to be more toxic and carcinogenic than chlorinated species (McGuire et al., 2014; Parker et al., 2014; States et al., 2013; Krasner, 2009; Richardson et al., 2007). Another halide, iodide is also found in some hydraulic fracturing wastewater (Chapter 7), and although its effects have not been as well documented as those associated with bromide, iodide raises some of the same concerns regarding formation of toxic DBPs as bromide (Xu et al., 2008).

Studies have found that elevated bromide levels in water correlate with increased DBP formation in the drinking water that is delivered to customers (also called “finished drinking water”) (Obolensky and Singer, 2008; Matamoros et al., 2007; Hua et al., 2006; Yang and Shang, 2004). Harkness et al. (2015) studied the chemical composition of flowback, produced waters, treated wastewaters, instream flows downstream from discharges, and accidental spill sites. The study found high concentrations of bromide and iodide in the flowback and produced waters, concluding that the elevated levels of these constituents could promote the formation of toxic brominated and iodinated DBPs in downstream drinking water systems (Harkness et al., 2015).

In terms of the resulting DBP formation, laboratory experiments using hydraulic fracturing wastewater from the Marcellus and Fayetteville shales and river water from the Allegheny and Ohio rivers suggest that a relatively small portion of hydraulic fracturing wastewater can notably affect DBP formation (Parker et al., 2014). In particular, trihalomethanes (THM; a category of DBPs) were shown to shift towards greater brominated and iodinated species with a little as 0.01% hydraulic fracturing wastewater in disinfected samples. Modeling work by Landis et al. (2016) evaluated the impact of CWT discharges on DBP formation at a drinking water system and suggested that although only a 3% increase in overall TTHM formation was predicted, the model predicted a decrease in chlorinated THM and a substantial shift toward a higher percentage of the more-toxic brominated THMs (Landis et al., 2016).

States et al. (2013) found a strong correlation between bromide concentrations in source water from the Allegheny River in Pennsylvania and the percentage of brominated THMs in finished water at a drinking water facility using Allegheny source water. Bromide concentrations in the river water measured during the study ranged from less than 25 μg/L to 299 μg/L. The authors noted that source water containing 50 μg/L of bromide resulted in treated drinking water with approximately

62% of total THMs consisting of brominated species. When the source water contained 150 μg/L bromide, the brominated THM percentage was 83% (States et al., 2013).

Pope et al. (2007) reported that increased bromide levels are the second best indicator of DBP formation, with pH being the first. Furthermore, bromine (which may be formed from bromide in the water during disinfection) reacts as much as ten times faster and more efficiently with DBP precursors than chlorine (Westerhoff et al., 2004). These studies show that increased bromide concentration in a drinking water resource shifts the DBP formation towards more-toxic brominated forms.

If disinfection is accomplished using ozonation instead of or in addition to chloramination or chlorination, bromide and iodide in the source water can form two additional constituents: bromate and iodate. Iodate, although formed during disinfection by ozonation, is not considered a DBP and is non-toxic (Allard et al., 2013). Bromate, however, is a DBP of concern and has an MCL of 0.010 mg/L (U.S. EPA, 1998).

Another category of DBP that is not regulated is the nitrogenous DBPs, including nitrosamines. Data are lacking on the formation of nitrogenous DBPs specifically linked to hydraulic fracturing wastewater, but their formation is possible. During chloramination, bromide can enhance the formation of the nitrosamine N-nitrosodimethylamine (NDMA) in waters containing the precursor dimethylamine (DMA) (Le Roux et al., 2012; Luh and Mariñas, 2012). As with some other non-regulated DBPs, nitrogenous DBPs may be more toxic than the regulated ones (Harkness et al., 2015; McGuire et al., 2014; Parker et al., 2014).

As discussed in Section 8.4 and Text Box 8-3, removal of dissolved solids, including chloride and bromide, requires advanced treatment processes such as reverse osmosis (RO), distillation, evaporation, or crystallization. Unless the treatment plant receiving the high-TDS wastewater employs processes specifically designed to remove these constituents, effluent discharge may contain high levels of bromide and chloride. Drinking water systems with intakes downstream of these discharges may receive water with correspondingly higher levels of bromide and chloride and may have difficulty complying with SDWA regulations related to DBPs.

8.5.1.2 Effects on Receiving Waters

Studies show that discharges from oil and gas wastewater treatment facilities can elevate TDS, bromide, and chloride levels in receiving waters, and potential impacts may be detectable far downstream (> 1km) of an outfall (States et al., 2013; Warner et al., 2013a; Wilson and Van Briesen, 2013). The work by Landis et al. (2016) in the Allegheny River mentioned above is consistent with these findings. The authors studied the impacts of a CWT accepting oil and gas wastewater on water quality at a downstream drinking water intake. They found that compared to data from upstream (background) locations, bromide concentrations at the intake were increased by 53% at low streamflow and 22% during high streamflow.[1]

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[1] Background samples are those taken from locations upstream of, and therefore unaffected by, permitted facilities.

Elevated TDS, chloride, and bromide can serve as indicators of potential influence from hydraulic fracturing wastewater in surface water and can also raise concerns about DBP formation in downstream drinking water systems. Elevation of bromide has been shown to place a burden on downstream drinking water systems. The Pittsburgh Water and Sewer authority (PWSA) drinking water system concluded that elevated bromide in their source water led to elevated TTHMs in their finished drinking water, with a substantial increase in the percentage of brominated TTHMs (States et al., 2013). The utility modified their treatment process and proposed improvements to their storage facilities to address the elevated TTHM levels in the distribution system (Chester Engineers, 2012).

Conversely, changes in regional wastewater handling that reduce bromide discharges can be reflected in receiving waters. A three-year study at water intakes downstream of wastewater discharges on the Monongahela River in western Pennsylvania evaluated water chemistry in the context of flow measurements. The authors concluded that an overall decrease in bromide concentrations at drinking water intakes from 2010 to 2012 was likely associated with shale gas operators voluntarily ceasing the practice of sending high-bromide wastewaters to treatment facilities that discharge to surface waters without adequate TDS removal (Wilson and Van Briesen, 2013).

Elevated TDS and halides need to be interpreted in the context of other inputs into a watershed. An EPA source apportionment study of the Allegheny River in Pennsylvania (U.S. EPA, 2015o) found that CWTs accounted for almost 90% of the bromide at one drinking water treatment plant intake and 37% of the bromide at another intake. Other sources include coal-fired power plants and acid mine drainage. Furthermore, although effluent is diluted when discharged to a water body, this may not always be sufficient to avoid water quality problems if there are existing pollutant loads in the waterbody from other contributors (e.g., such as acid mine drainage or power plant effluent) (Ferrar et al., 2013). Warner et al. (2013a) evaluated effluent from the Josephine Brine Treatment Facility, which treated both conventional and unconventional (as defined by PA DEP) oil and gas wastewater at the time of the study. The authors concluded that even a 500 to 3,000-fold dilution of the wastewater would not reduce bromide levels to background. Modeling by Weaver et al. (2016) suggests that bromide levels in receiving streams can be improved by reducing concentrations in the effluent, discharging during periods of high streamflow, and discharging intermittently (pulsing). (See Appendix F for additional description of modeling studies.)

In addition to concerns about formation of DBPs within downstream drinking water systems, treatment at the upstream CWTs and POTWs themselves can also produce DBPs if the facilities disinfect prior to discharge. The DBPs may then be released into receiving waters and increase concerns about the total loads of brominated and iodinated DBPs at downstream drinking water systems (Hladik et al., 2014). A study by Hladik et al. (2014) documented brominated and iodinated DBPs at the outfalls of CWTs and POTWs treating both conventional and unconventional wastewater and noted that this DBP signature was different than for those plants that did not accept oil and gas wastewater.

8.5.1.3 Other Constituents That Can Affect Downstream DBP Formation

In addition to halogens, organic matter and ammonium can also be present in hydraulic fracturing wastewater (Chapter 7; Appendix E) and can have an influence on the formation of DBPs at downstream drinking water systems (Harkness et al., 2015). Experimental work by Parker et al. (2014) found that a mixture of river water with 1-2% flowback by volume could contribute to DBP formation due to the higher dissolved organic carbon content of the flowback. Harkness et al. (2015) studied the chemical composition of water associated with oil and gas production and found high concentrations of ammonium in the flowback and produced waters. Elevated levels of ammonium can convert chlorine to chloramines at downstream drinking water treatment plants. This could have an impact on the plant's disinfection practices because chloramines are a weaker disinfectant than chlorine (Harkness et al., 2015; Parker et al., 2014).

8.5.1.4 Mitigating Impacts from TDS and Halides on Drinking Water Utilities

High bromide concentrations and low flow conditions in waterways have been shown to increase DBP formation in downstream drinking water systems (States et al., 2013). Most drinking water treatment plants are not designed to address high concentrations of TDS (including bromide and iodide), limiting their options for restricting the formation of brominated and iodinated DBPs when these halides are present.

To mitigate these impacts, one strategy that was implemented in Pennsylvania was to disallow influent of high-TDS wastewaters to POTWs and CWTs that discharged to streams and were not designed to treat for TDS. Wilson and Van Briesen (2013) showed that this strategy was effective for reducing bromide concentrations at drinking water utilities downstream from POTWs and CWTs that had formerly accepted hydraulic fracturing wastewaters (States et al., 2013; Warner et al., 2013a; Wilson and Van Briesen, 2013). Alternatively, advanced treatment processes such as reverse osmosis, distillation, evaporation, and crystallization, can be employed to reduce constituents that contribute to high TDS (e.g., such as chloride, bromide, and iodide), reducing impacts on surface waters and, subsequently, downstream drinking water utilities. Strategies such as discharging during higher streamflow periods and using a pulsing or intermittent discharge could also reduce the frequency and severity of potential impacts on drinking water systems from elevated TDS.

8.5.2 Radionuclides

Potential impacts on drinking water resources from TENORM associated with hydraulic fracturing wastewater can arise through a number of pathways, including: treated wastewater in which radionuclides were not adequately removed; accumulation of radionuclides in surface water sediments downstream of wastewater treatment plant discharge points; migration or mobilization from soils that have accumulated radionuclides from previous activities such as pits or land application; and inadequate management of treatment plant solids (such as filter cake), landfill leachate, or sediments in pits or tanks that have accumulated radionuclides.

An additional concern is the potential for underestimation of radium concentrations in hydraulic fracturing wastewater due to the high TDS content. When using wet chemical techniques, high TDS concentrations can result in poor recovery of some chemical constituents. For radium, recovery may be as low as <1% in a high-salt matrix (Nelson et al., 2014). This may lead to the inability to identify an impact on drinking water resources or an underestimation of the severity of an impact. Research suggests that spectroscopic methods are more appropriate for analysis of radium in high-TDS wastewaters (Nelson et al., 2014).

A recent study by the PA DEP (PA DEP, 2015b) provides information that helps fill a general data gap regarding TENORM content in oil and gas wastes that are treated and discharged to surface waters. The study, although not exclusive to Marcellus wastes, was motivated by concerns over an increase in radionuclides in oil and gas wastes observed during the expansion of Marcellus Shale production. The study began in 2013 and quantified radionuclide (radium-226, radium-228, K-40, gross alpha, and gross beta) levels at CWTs, POTWs, well sites, and landfills and discussed human health and environmental implications. Other relevant studies addressing radionuclides focus on CWTs that have handled Marcellus wastewater, evaluation of solids in storage pits, and analysis of scale on pipes and tanks.

8.5.2.1 Effluent from POTWs

In Pennsylvania between 2007 and 2010, TENORM-bearing wastewaters were sent to POTWs, which are generally not required to monitor for radioactivity (Resnikoff et al., 2010). Although management of Marcellus wastewaters via POTWs has declined, there is still potential for input of radionuclides to surface waters via discharge of CWT effluent either directly to surface water or indirectly through discharge to POTWs. The potential for TENORM to pass through treatment at POTWs is one of the concerns addressed in the EPA's recently promulgated pretreatment standards for unconventional oil and gas wastewaters that discharge to POTWs.

Six of the POTWs in the PA DEP TENORM study received effluent from a CWT along with municipal wastewater. Note that the CWTs in the study are not described as receiving exclusively Marcellus wastewater. The POTWs that receive both CWT effluent and municipal waste had radium in their effluent (overall average effluent radium-226 concentration of 103 pCi/L, with a range of <35 to 340 pCi/L). Those POTWs receiving only municipal wastewater also contained radium, with an average effluent radium-226 concentration of 145 pCi/L.[1] These concentrations are many times higher than the MCL for radium (5 pCi/L) and are also orders of magnitude higher than typical background values; radium-226 in river water generally ranges from 0.014 pCi/L to 0.54 pCi/L (IAEA, 2014).[2]

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[1] These values are for unfiltered samples. In filtered samples, the POTWs that receive both CWT effluent and municipal waste had higher average radium-226 values than those for POTWs only treating municipal waste (497 pCi/L vs. 85 piCi/L). Filtered samples are passed through a filter to remove fine particles; concentrations of constituents in filtered samples are often lower than in unfiltered samples. However, liquid samples in this study were filtered after preservation with acid. Therefore, the difference between unfiltered and filtered samples may not be reliable.

[2] A confounding issue for this study is that it was not clear why the radium-226 concentrations were comparable or higher for those POTWs not receiving oil and gas CWT effluent. However, sample sizes were small and possible alternative sources for the radium were not discussed. The report also did not describe how it was verified that the POTWs did not receive contributions from oil and gas wastewater.

8.5.2.2 Effluent from CWTs

Four of the ten CWTs sampled during the PA DEP TENORM study (PA DEP, 2015b) discharged to surface water under a National Pollution Discharge Elimination System (NDPES) permit, and the other six discharged to POTWs. The average radium-226 concentration in the effluent from the CWTs (1,840 pCi/L for unfiltered samples) was an order of magnitude higher than in effluent from the POTWs. Samples of treated wastewater from zero-discharge facilities contained higher concentrations, averaging 2,610 pCi/L radium-226 and 295 pCi/L radium-228 (PA DEP, 2015b). The treated wastewater from these zero-discharge facilities will likely be reused for subsequent hydraulic fracturing jobs, postponing the need for disposal, but reuse could result in overall increases in some constituents of concern due to repeated passage through the subsurface. In addition, there is also a potential for impacts on drinking water resources from spills and leaks associated with wastewater storage and handling at these facilities.

Sampling done at the Josephine Brine Treatment Plant in western PA from 2010 – 2012 (Warner et al., 2013a) detected radium in the effluent (mean values of 4 pCi/L of radium-226 and 2 pCi/L of radium-228). Treatment at the facility removes radium by coprecipitation with barium sulfate. The authors note that if the activities of radium-226 and radium-228 in Marcellus brine influent at the CWT are similar to those reported by other researchers (Rowan et al., 2011), then the CWT achieved a 1,000-fold reduction in radium content. (This facility also accepted conventional oil and gas wastewater.) The detection of radium in the effluent from this CWT suggests that if the influent concentration is extremely high, radium will still be found in the effluent of a treatment plant even if the treatment process removes a high percentage (see Section 8.4 and Appendix F for additional discussion on constituent removal efficiencies at CWTs).

8.5.2.3 Accumulation in Sediments

In addition to concerns about TENORM in discharges to surface waters, studies have shown the potential for a legacy of radionuclide accumulation in surface water sediments. The PA DEP TENORM study (PA DEP, 2015b) found radium in sediments near the outfalls for CWTs (averages of 84.2 pCi/g and 19.8 pCi/g for radium-226 and -228, respectively) and three POTWs receiving treated oil and gas wastewater from CWTs (radium-226 and radium-228 concentrations ranging from 1.8 to 18.2 pCi/g). Typical background soil levels of radium are approximately 1 to 2 pCi/g (PA DEP, 2015b).

Warner et al. (2013a) measured radium-226 levels in stream sediment samples at the point of discharge of a CWT that had treated both conventional oil and gas wastewater and unconventional Marcellus wastewater. They found concentrations approximately 200 times greater than upstream and background sediments. This indicates the potential for accumulation of contaminants in localized areas near wastewater discharge facilities. Although the CWT studied by Warner et al. (2013a) also accepted conventional oil and gas wastewater, the authors observed that the radium-228/radium-226 ratio in the river sediments near the discharge (0.22 – 0.27) is consistent with ratios in Marcellus wastewater. The authors indicate that the radium likely accumulated in the sediments, originating from the discharge of treated unconventional Marcellus oil and gas wastewater. Accumulation of TENORM can also occur in sediments receiving discharged effluent from landfills that accept oil and gas wastes. In the PA DEP TENORM study (PA DEP, 2015b), samples of impacted soils were collected at three landfill outfalls. Radium-226 and -228 were detected in all samples (2.82 to 4.46 pCi/g and 0.979 to 2.53 pCi/g, respectively).

A study by Skalak et al. (2014), on the other hand, did not find elevated levels of alkali earth metals (including radium) in sediments just downstream of the discharge points of five POTWs that had previously treated Marcellus wastewater. These inconsistencies among studies suggest that accumulation of contaminants in sediment may depend on treatment processes and their removal rates for each constituent as well as stream chemistry and hydrologic characteristics. Contamination with radium-226 would potentially be long lived because of the long half-life of radium.[1]

The association of radium with sediments near discharge points is attributed to adsorption of radium to the sediments, a process governed by factors such as the salinity of the water and sediment characteristics. Increased salinity promotes desorption of radium from sediments, while lower salinity promotes adsorption, with radium adsorbing particularly strongly to sediments high in iron and manganese (hydr)oxides (Porcelli et al., 2014; Gonneea et al., 2008). Warner et al. (2013a) speculate that when saline CWT effluent is discharged into stream water, the lower salinity of the stream environment facilitates sorption of radium onto streambed sediments. The long-term fate of radium sorbed to sediments depends upon changes in water salinity and the sediment properties, including any reduction/oxidation chemical reactions that affect iron and manganese minerals in the sediments. Additionally, the sediment may be physically transported downstream due to high flows or if sediment is disturbed and resuspended.

8.5.2.4 Pits and Tanks

Where pits or impoundments are used, radionuclides may accumulate in the bottom sludges and can also be found in soils once the pit is closed and leveled. A study of three centralized wastewater storage impoundments in southwestern Pennsylvania (Zhang et al., 2015a) showed that radium-226 accumulated in various components of the bottom solids, including through coprecipitation with barium sulfate. Sludge from one pit showed a substantial increase in radium-226 between sampling events 2.5 years apart (from 8.8 pCi/g to 872 pCi/g). The authors attributed the steep increase to enrichment in radium during cycles of wastewater reuse. In Texas, accumulation of radionuclides (potassium, thorium, bismuth, radium, and lead) was documented for two pits that stored fluids associated with hydraulic fracturing (Rich and Crosby, 2013). One pit was decommissioned and used as farmland, and the other was active at the time of sampling. Analyses of soil and sludge samples detected a number of radionuclides, including radium-226, radium-228, thorium-228, strontium-90, and potassium-40 (radium-226 was only found at the former pit). Rich and Crosby (2013) note a total beta radiation value of 1,329 pCi/L in one sample from the active pit. They note that this value exceeded regulatory guidelines even though the values for individual

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[1] The half-life of radium-226 is approximately 1,600 years, while the half-life of radium-228 is 5.76 years. The half-life is the time it takes for half of the nuclei in a sample of a radioactive element to decay. After two half-lives, one fourth of the original sample will be left, and after three half-lives there will be one eighth of the original sample remaining, and so forth.

radionuclides did not exceed regulatory guidelines, suggesting that using a single radionuclide (i.e., radium) as an indication of exposure can underestimate total radioactivity.

Although the sample sizes were small for both the Zhang et al. (2015a) and the Rich and Crosby (2013) studies, the results suggest that radionuclides associated with sediments from some pits could have potential impacts on surface water or groundwater. These studies illustrate the need for appropriate management where wastes have high TENORM content. Rich and Crosby (2013) note that pits are often found in agricultural regions. If pit solids that are incorporated into soils (e.g., during draining and leveling or during land application) contain radionuclides, they may reach surface water in runoff or leach from the solids and migrate to groundwater. In active pits, Rich and Crosby (2013) note that TENORM in the contents may be deposited onto crops and soil through aerosolization or breaching. The Pennsylvania study (Zhang et al., 2015a) suggests that landfill leachate may be affected by receiving sludges from impoundments that store produced water and will need to be managed appropriately.

With radium-226 values of 121 pCi/g and 872 pCi/g, sludges from the pits studied by Zhang et al. (2015a) exceeded the limit for disposal as a nonhazardous solid in a municipal or industrial solid waste landfill but would meet the radium-226 limits for disposal in a hazardous waste landfill. There are currently no federal requirements to test solid residuals for radionuclides before disposal. At landfills studied in the PA DEP TENORM report (PA DEP, 2015b), seven samples of treated effluent from nine facilities that accept oil and gas waste had radium-226 values ranging from 105 pCi/L to 378 pCi/L and radium-228 values ranging from <6 pCi/L to 1,100 pCi/L. Untreated effluent from the nine landfills had radium-226 contents ranging from 70 to <139 pCi/L. The study authors conclude that there is “limited potential” for environmental impacts from spills or discharges of leachate from these facilities.

Where wastewater is stored in tanks, TENORM concentrations can increase through radioactive ingrowth.[1] Radium-226 and radium-228 are generally considered the radionuclides of greatest concern in wastewaters and are the most frequently measured. But recent research indicates that in closed environments such as tanks, where the radium decay product radon cannot escape, total radioactivity may increase due to ingrowth of other decay products of radium such as Pb-210, Po-210, and Th-228 (Nelson et al., 2015). Experimental work by Nelson et al. found that concentrations of these decay products in Marcellus produced water that was stored in a sealed drum started growing immediately. Concentrations started at zero and reached 10.49 pCi/L for Po-210 and 155 pCi/L for Th-228 over the first 50 and 66 days of storage, respectively. The authors note that these decay products are not soluble, would be associated primarily with particulates, and could be bioavailable. This study demonstrates that analyzing for radium will not provide a complete indication of sample radioactivity if the water is stored in a closed environment and that subsequent management decisions would need to take into account possible increases in radioactivity due to ingrowth.

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[1] The ingrowth, or growth within a sample, of radioactive daughter products from radionuclides initially present in the sample can cause greater radioactivity than that resulting from the parent radionuclides alone.

8.5.2.5 Other Solids

Other solid wastes associated with unconventional oil and gas production that may contain radionuclides include solid residuals from POTWs and CWTs and scale in oil and gas equipment. Filter cake samples from POTWs were found by PA DEP (2015b) to have highly variable radium-226 concentrations, with an average of 16 pCi/g, while typical soil concentrations in Pennsylvania have been found to be less than 2.5 pCi/g (Greeman et al., 1999). Filter cake from CWTs had an average radium-226 concentration of 111 pCi/g. The authors conclude that there could be impacts on surface waters through spills or effects on groundwater from landfill leachate containing contaminants originating in residuals sent to landfills.

Accumulation of TENORM-bearing scale in CWTs or POTWs may continue to affect the treatment plant even after discontinuing treatment of wastewaters containing high radionuclide concentrations. Radium can adsorb onto scales in pipes and tanks and can also be removed from water by coprecipitation if sulfate or carbonate is added to hydraulic fracturing wastewater to precipitate calcium, barium, or strontium (Kappel et al., 2013; USGS, 2013a). Pipe scale in oil and gas production facilities has been found to have radium concentrations as high as 154,000 pCi/g, although concentrations of less than about 13,500 pCi/g are more common (Schubert et al., 2014). A similar issue, the potential for accumulation and possible release of radionuclides and other trace inorganic constituents in water distribution systems, has gained attention, with the potential for drinking water concentrations to exceed drinking water standards (Water Research Foundation, 2010). Scale eventually removed from pipes or other oil and gas equipment can end up in landfills and then leach into groundwater or run off to surface water (USGS, 2013a). Also, laboratory research suggests that radium in land-applied barium sulfate scales from conventional oil and gas operations may become mobilized by microbial processes, rendering the radium more mobile and bioavailable (Matthews et al., 2006; Swann et al., 2004); see discussion in Section 8.4.6.1. Monitoring would be needed in order to ascertain the potential for accumulation and release of radionuclides from systems that have treated or continue to treat hydraulic fracturing wastewaters with elevated TENORM concentrations.

8.5.2.6 Road Spreading

Salt and radionuclide accumulation can occur near road spreading sites; one study in Pennsylvania describes a roughly 20% increase in average radium-226 concentrations in soils near five roads where wastewaters from conventional operations had been spread for de-icing (Skalak et al., 2014). However, the standard deviation for the samples was large (24 pCi/g), and background concentrations were approximately 1 pCi/g. Should significant accumulation of radionuclides in soils near roads occur, it would present a vehicle for potential impacts on drinking water resources. The frequency with which hydraulic fracturing wastewater contributes to this type of impact depends on state-level regulations dictating whether the wastewater can be used for road spreading.

8.5.2.7 Potential for Monitoring

Effluent from treatment plants (e.g., CWTs, POTWs) and receiving waters can be monitored for radionuclides. Research suggests that radium-226 and radium-228 are the predominant radionuclides in Marcellus Shale wastewater, and they account for most of the gross alpha and gross beta activity in the waters studied (Rowan et al., 2011). Gross alpha and gross beta measurements may, therefore, serve as an effective screening mechanism for the presence of radionuclides in hydraulic fracturing wastewater. This in turn can help in evaluating management strategies. Portable gamma spectrometers allow rapid screening of wastewater effluent. Sediments can also be measured for radionuclide concentrations at discharge points. If an accurate assessment of total radioactivity is needed rather than a screening, measuring radium content may not be adequate depending upon how wastewater has been stored. Analyses of other radionuclides such as Pb-210, Po-210, and Th-228 may be warranted, especially if the wastewater has been stored in closed loop systems.

8.5.3 Metals

Given the presence in hydraulic fracturing wastewaters of some heavy metals, as well as barium and strontium concentrations that can reach hundreds or even thousands of milligrams per liter (Table 7-5), surface waters may be impacted if discharges from CTWs or POTWs indirectly receiving oil and gas wastewater via CWTs are not managed appropriately or if spills occur.

Common treatment processes, such as chemical precipitation, are effective at removing many metals (Section 8.4). Effluent sampling results collected between October 2011 and February 2013 from seven facilities in Pennsylvania treating oil and gas wastewaters were requested by the EPA. The results revealed low to modest concentrations of copper (0 – 50 μg/L), zinc (14 – 256 μg/L), and nickel (8 – 22 μg/L) (U.S. EPA, 2015f, g). However, metals such as barium and strontium were found to range from low to elevated concentrations in the effluent for some of the facilities. The data showed effluent barium concentrations ranging from 0.35 to 25 mg/L (median of 3.5 mg/L and average of 6.7 mg/L). For results that were greater than 2 mg/L, the drinking water MCL for barium was exceeded. Strontium concentrations ranged from 0.36 to 546 mg/L (median of 297 mg/L and mean of 236 mg/L) (U.S. EPA, 2015g). (See Chapter 9 for information on health effects for barium and strontium.)

Volz et al. (2011) discussed a December 2010 effluent sampling effort at a Pennsylvania CWT that had been treating both conventional and Marcellus wastewater; they measured average barium and strontium concentrations of 27 mg/L and nearly 3,000 mg/L, respectively (eight samples from the one plant) (Volz et al., 2011). NPDES compliance data submitted for 2011 shows that effluent from the same CWT had average barium effluent levels ranging from 26 to 98 mg/L in the months prior to PA DEP's April 2011 request to cease sending hydraulic fracturing wastewater to this and other facilities exempt from the 2010 TDS regulation (U.S. EPA, 2015f, g). After May, 2011, barium effluent concentrations dropped to average values of 9 to 22 mg/L. The facility is scheduled to upgrade its TDS removal capabilities, which should help decrease concentrations of metals in the effluent.

Limited data are available on metal concentrations in wastewater and treated effluent that are directly discharged; additional information would be needed to assess whether there could be downstream effects on drinking water utilities. NPDES discharge permits, which restrict TDS discharge concentrations, would likely reduce metal effluent concentrations due to the additional treatment necessary to minimize TDS.

8.5.4 Volatile Organic Compounds

Benzene is a common constituent in hydraulic fracturing wastewater, and it is of concern due to recognized human health effects. A wide range of concentrations of BTEX compounds occurs in wastewater from the Barnett and Marcellus shales. Natural gas formations generally produce more BTEX than oil formations (Veil et al., 2004), and lower concentrations of BTEX naturally occur in wastewater from CBM production (Appendix Table E-9). The organic chemistry of Marcellus wastewater has been found by Akob et al. (2016) to be more variable than that of inorganic constituents, indicating the need to consider the concentrations of organic compounds when planning wastewater management.

Processes such as air stripping or dissolved air flotation can remove VOCs during treatment, but if treatment is not adequate prior to discharge, the VOCs may reach water resources. For example, the average benzene concentration measured in the discharge from a Pennsylvania CWT in December 2010 was 12 µg/L (Volz et al., 2011) exceeding the MCL for benzene of 5 µg/L.[1] The facility was receiving wastewater from both conventional and unconventional operations at that time. Ferrar et al. (2013) measured for BTEX in effluent from the same facility, and mean concentrations among the four compounds ranged from approximately 2 to 46 µg/L. Concentrations were lower for samples taken after May 19, 2011 (when Marcellus operators voluntarily stopped sending wastewater to POTWs and CWTs exempt from the 2010 TDS regulation), and the difference between pre and post May 2011 sampling was considered statistically significant.

Spills and leakage from pits creates another potential route of entry to drinking water resources, as described in Section 8.4.5. Akob et al. (2016) documented the microbial degradation of organic compounds in Marcellus produced water and note that more research is needed to evaluate how this could mitigate the migration of organic constituents in the event of spills or leaks.

8.5.5 Semi-Volatile Organic Compounds

Little is known about the fate of the SVOC, 2-butoxyethanol (2-BE) (an antifoaming and anti-corrosion agent used in slick-water) (Volz et al., 2011) or its potential impact on surface waters, drinking water resources, or drinking water systems. This compound is very soluble in water and is subject to biodegradation, with an estimated half-life of approximately 1-4 weeks in the environment (Wess et al., 1998). It is classified by the EPA's Integrated Risk Information System (IRIS) as not likely to be carcinogenic to humans, and the International Agency for Research on Cancer (IARC) classifies it as having insufficient evidence to determine carcinogenicity (see Chapter 9 for more information). 2-BE was detected in the discharge of a Pennsylvania CWT at

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[1] Among the BTEX compounds, the MCL for benzene is the lowest at 5 µg/L; the MCL for ethylbenzene is 700 µg/L, the MCL for toluene is 1,000 µg/L, and the MCL for xylenes is 10,000 µg/L.

concentrations of 59 mg/L (Volz et al., 2011). Ferrar et al. (2013) detected 2-BE in the effluent from a CWT in western Pennsylvania at average concentrations of 34 – 45 mg/L; the latter value was measured when the CWT was receiving only conventional oil and gas wastewater. Data are lacking on 2-BE concentrations in surface waters that receive treated effluent from hydraulic fracturing wastewater treatment systems.

Polyaromatic hydrocarbons (PAHs; a group of SVOCs) have been found in hydraulic fracturing wastewater (Section 7.3.4.7, Table 7-6). PAHs detected in an unlined pit containing oil and gas wastewater near the Duncan Oil Field in New Mexico were also detected in soils 82 ft (25 m) downgradient at concentrations ranging from 2,000 to 4,900 µg/kg and 164 ft (50 m) downgradient, with concentrations ranging from 22 to 370 µg/kg (Sumi, 2004; Eiceman, 1986).

8.5.6 Oil and Grease

Oil and grease in oil and gas wastewater can come from the formation or from oil-based drilling fluids. Typically, oil and grease are separated from the wastewater before discharge either by heat treatment or by gravity separation followed by skimming. If these processes are inefficient, oil and grease can be integrated with the discharge to surface waters. For example, in some cases, oil and grease are allowed to separate in pits, and water is then withdrawn from the lower part of the pit. If the oil layer is allowed to drop to the level of the standpipe or if the water is agitated, oil and grease may be discharged along with the water. Oil and grease are also often dispersed in wastewater in the form of small droplets that are 4 to 6 microns in diameter. These droplets can be difficult to remove using typical oil/water separators (Veil et al., 2004).

A study was conducted in Wyoming by the U.S. Fish and Wildlife Service from 1996 to 1999 of sixty five oil and gas sites that discharge to ephemeral streams and subsequently to wetlands. Fifteen percent of the wetlands receiving wastewater contained oil-stained vegetation and had a visible oil sheen on the sediments. In addition, ten of twelve sites that were randomly selected for water sample collection (from oil field separator or skim pit effluent) exceeded the discharge limit of 10 mg/L for oil and grease with one site as high as 54 mg/L (Ramirez, 2002).

8.6 Synthesis

A variety of strategies may be considered for the management of hydraulic fracturing wastewater. Important factors for planning management include cost, logistics, wastewater composition, wastewater volumes, and regulations. Available information suggests that Class IID wells regulated under the UIC Program are the most frequently used wastewater management practice, but reuse, sending to a CWT, and various other methods are also employed.

8.6.1 Summary of Findings

8.6.1.1 Wastewater Volumes

The most current national estimate of the total wastewater volume generated in the oil and gas industry (both onshore and offshore) was 889.59 billion gal (21.18 billion bbls or 3.37 trillion L) in 2012, although this estimate is subject to a number of uncertainties (Veil, 2015). The total amount of wastewater generated may increase if hydrocarbon production increases in a region, although Veil (2015) suggests that this trend may not hold true at the national level. Geographically, a large portion of onshore oil and gas wastewater in the United States is reported to be generated in the western part of the country, consistent with the areas where most oil and gas wells are located and most production takes place.

Obtaining reliable national estimates of the amount of wastewater attributable to hydraulic fracturing is a challenge. State data collection efforts vary, and in many states, production data do not identify which wells have been hydraulically fractured. However, annual estimates compiled from those states where hydraulic fracturing wastewater is identified range from hundreds of millions to billions of gallons of wastewater generated each year. Data from individual states indicate that along with an increase in the numbers of hydraulically fractured wells, associated wastewater volumes have generally increased over the last several years into 2014. However, while there is a general correlation between unconventional oil and gas production and wastewater volume, the relationship is complicated by several factors such as timing of drilling and production. More complete and comparable estimates of local, state, and regional wastewater volumes would facilitate wastewater management on the part of operators as well as planning on the part of agencies that oversee wastewater management.

8.6.1.2 Wastewater Management Practices

Hydraulic fracturing wastewater is managed in a variety of ways, including disposal via Class IID wells; minimal treatment and reuse (in subsequent fracturing operations); more complete treatment followed by reuse; sending to CWTs for treatment followed by direct discharge or transfer to POTWs; evaporation; and other uses such as agriculture and wildlife use (allowed only in the arid west when the wastewater is of good enough quality for such uses). All of these strategies have the potential to affect drinking water resources. Wastewater management practices continue to shift in response to evolving understanding of environmental concerns, emplacement of new regulatory controls, changes in costs, and changes in technology and operator practices. Unauthorized discharges of hydraulic fracturing wastewater have also been documented, and such discharges can potentially impact drinking water resources.

As of 2015, available information suggests that Class IID disposal wells are a primary wastewater management practice for operators in most of the major unconventional reservoirs in the United States, with the notable exception of the Marcellus Shale region in Pennsylvania. Class IID wells tend to be economically favorable, especially if they are located within a reasonable transportation distance from well sites (U.S. GAO, 2012). In particular, large numbers of active injection wells are found in Texas (7,876), Kansas (5,516), Oklahoma (3,837), Louisiana (2,448), and Illinois (1,054) (U.S. EPA, 2016d).

Pennsylvania is somewhat unique in having only nine Class IID wells (as of February 2015), along with having experienced significant growth of shale gas production in the Marcellus and corresponding production of large volumes of wastewater. Operators producing from unconventional formations (as defined by PA DEP) have managed their wastewater through the use of POTWs (a practice that is subject to recently promulgated regulations), CWTs, extensive reuse for hydraulic fracturing operations, and hauling to disposal wells (to a lesser degree). The wastewater management history in Pennsylvania provides an example of evolving strategies to manage the treatment, discharge, storage, and reuse of hydraulic fracturing wastewaters that are high in constituents of concern (e.g., bromide, TDS, and TENORM).

Reuse of hydraulic fracturing wastewater to formulate fluid for subsequent hydraulic fracturing jobs is most prevalent in Pennsylvania (as high as 90%), with much of the reuse happening on-site (PA DEP, 2015b). Reuse is practiced in other regions as well (e.g., Haynesville Shale, the Fayetteville Shale, the Barnett Shale, and the Eagle Ford Shale), but at much lower rates (about 5 – 20%). Reliable estimates are not available for all areas of the United States because waste management practices are not consistently reported across all states. If hydraulic fracturing activity slows, demand for wastewater for reuse will also likely decrease, and other forms of wastewater management will be needed. Potential impacts associated with reuse center on concerns over the storage of untreated or minimally treated wastewater on-site or transport to CWTs.

Treatment of hydraulic fracturing wastewater may be done at CWTs or using mobile or semi-mobile systems designed for on-site use. Treatment at a CWT may be followed by direct discharge by the CWT to surface water, indirect discharge to a POTW in accordance with recently promulgated regulations, or reuse. Most CWTs treating hydraulic fracturing wastewater are located in Pennsylvania (about 40 facilities), with a limited number in other states. CWTs vary widely in treatment capabilities, ranging from producing high-quality effluent to minimal treatment for reuse.

Other wastewater management practices, such as evaporation and agricultural uses, represent a smaller fraction of wastewater management nationally. These practices can, however, be locally significant. Although specific instances of contamination were not identified for this assessment, these practices could lead to impacts on drinking water resources if facilities are not properly constructed and maintained or if water quality is not adequately characterized to ensure that management is appropriate.

8.6.1.3 Treatment and Discharge

Wastewater that is treated and subsequently discharged by CWTs can result in impacts due to inadequate treatment. A frequently cited concern is the high TDS content in wastewaters from unconventional formations, which poses challenges for treatment, discharge, and reuse. Treatment processes such as sedimentation, filtration, flotation, and chemical precipitation are capable of removing constituents such as oil and grease, major cations, metals, and TSS. They do not, however, adequately reduce TDS in high-salinity wastewaters. More advanced processes such as reverse osmosis (RO) or distillation are needed if TDS removal is required (Shaffer et al., 2013; Younos and Tulou, 2005). Most available information on treatment of hydraulic fracturing wastewater is based on practices used in Pennsylvania because that is where most data have been collected.

Hydraulic fracturing wastewater discharged from treatment facilities without advanced TDS removal processes has resulted in elevated TDS concentrations (including bromide, iodide, and chloride levels) in receiving waters. Impacts from these discharges is due largely to the role of bromide and iodide in DBP formation at downstream drinking water systems, potentially causing higher levels of harmful DBPs in finished drinking water.[1] Modeling suggests that very small percentages of hydraulic fracturing wastewater added to a river used as a source for drinking water systems could cause a notable increase in DBP formation.

Radionuclides (i.e., TENORM), which are present in some hydraulic fracturing wastewaters, can cause impacts if the wastewater is discharged without adequate treatment. TENORMs have been measured in effluent from wastewater treatment facilities receiving Marcellus wastewater (which includes effluent sent for reuse and not discharged to surface water). Radium-226, radium-228, gross alpha, and gross beta are most cited as the radioactive constituents of concern, likely due to the availability of test methods for these constituents in wastewater. Radium concentrations can range up to thousands or tens of thousands of pCi/L. Fewer data are available on concentrations of uranium and other radionuclides in hydraulic fracturing wastewaters. Also, fewer data exist on radionuclide concentrations in wastewaters from unconventional formations other than the Marcellus, limiting our ability to assess potential impacts from TENORM on a nationwide basis.

Other constituents posing health or environmental concerns that can be discharged in inadequately treated hydraulic fracturing wastewater include organic compounds, barium, strontium, and other metals. Chemicals used in the fracturing fluid or their degradation products could also be present. A variety of treatment processes can be used for removal of these contaminants, from commonly used methods such as chemical precipitation and filtration to more advanced and more costly techniques, such as reverse osmosis, distillation, and mechanical vapor recompression.

8.6.1.4 Storage and Disposal Pits and Impoundments

Regardless of the wastewater management practices used, some type of temporary storage of fluids is generally required. Storage can be in the form of tanks as well as pits and/or impoundments. Pits encompass a variety of structures, from on-site pits for storage at the well site to larger, centralized facilities (typically referred to as "impoundments" or "ponds"). Some states allow evaporation pit facilities or percolation pits as a means of wastewater disposal. The locations and number of pits are not well documented in most states, nor are pits associated with hydraulic fracturing operations necessarily identified, despite efforts by the U.S. EPA (U.S. EPA, 2003b) and environmental groups such as SkyTruth to identify pits in use. Information that is typically available on state websites includes permitted centralized commercial evaporation facilities (COWDFs) most commonly used in the western United States.

Impacts on both groundwater and surface water resources due to inadequate pit capacities, overfilling, and leaks have been documented. In extreme precipitation events, pits can be overtopped. Leaks can occur if liners are compromised or were not used. With an increased emphasis on reuse in some regions, the need for temporary storage of high-TDS wastewater increases the potential for leaks and spills from pits and during fluid handling.

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[1] Some types of DBPs are regulated under SDWA's Stage 1 and Stage 2 DBP Rules, but a subset of DBPs, including a number of chlorinated, brominated, nitrogenous, and iodinated DBPs, are not regulated. Brominated and iodinated DBPs are more toxic than other species of DBPs.

Unlined pits, in particular, provide a pathway for contaminants to reach groundwater, and impacts on groundwater from historic and current uses of unlined pits in the oil and gas industry have been documented. The resulting contamination can be long-lasting. States have taken measures to phase out the use of unlined disposal and storage pits, but unlined pits that are still in use can provide an ongoing potential source of contamination for groundwater (Grinberg, 2014).

8.6.1.5 Residuals

Solid and liquid residuals associated with hydraulic fracturing wastewater (treatment residuals from CWTs, sludges from tanks and pits, and pipe scale) could have impacts on drinking water resources if not managed and disposed of properly. Liquid residuals are inappropriate for surface water discharge or discharge to a POTW due to high concentrations of salts and other contaminants; they are commonly disposed of in an injection well. Solid residuals may leach a number of constituents, such as alkali metals, alkaline earth metals, and bromide. They can also contain TENORM if radionuclides are present in the wastewater being treated. Given that residuals are commonly disposed of in landfills, TENORM can be problematic due to the possibility of radon emissions and radioactivity in the landfill leachate. Solids from pits or tanks can also contain TENORM if the wastewater contains radionuclides, and one study has shown the potential for radioactivity to increase in the closed environment of tanks.

8.6.2 Factors Affecting the Frequency or Severity of Impacts

The frequency and severity of impacts on drinking water resources from hydraulic fracturing wastewater will depend upon the wastewater composition and volumes, and the mix of wastewater management strategies used.[1] The types of potential impacts (along with frequency and severity) may shift in time as management practices change in response to evolving environmental, regulatory, economic, or logistical drivers. The frequency and severity of impacts can also depend on the size and initial quality of the drinking water resource and its proximity to wastewater management operations.

8.6.2.1 Role of Changing Wastewater Management Practices

The most common disposal option for hydraulic fracturing wastewater is injection into Class II disposal wells. If this option becomes restricted in a given location, the wastewater management options could shift, at least locally, towards other options such as sending wastewater to CWTs for treatment and either discharge or reuse. Although reuse avoids the immediate need to discharge wastewater by directing it to ongoing hydraulic fracturing activities, the practice could concentrate radionuclides or other constituents as fluid moves through cycles of reuse. Whether such concentrations would be significant depends on the ratio of recycled to “fresh” water when the wastewater gets reused. Alternatively, wastewater might need to be transported to more distant

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[1] Both national and state regulations affect the wastewater management practices used. At a national level, although the EPA’s oil and gas ELG regulations generally prohibit the direct discharge of oil and gas wastewater to waters of the U.S., treatment and discharge of hydraulic fracturing wastewater can occur under certain limited circumstances, such as under an exemption authorizing discharge for agricultural and wildlife use in the arid west, or by Centralized Waste Treatment facilities. For additional information on national regulations relevant to hydraulic fracturing wastewater management, see Text Box 8-2.

Class IID wells. This option, while attractive from the perspective of limited disposal impacts, could increase the frequency of impacts from spills and leaks during transportation (see Chapter 7 for discussion of roadway transport of produced water).

8.6.2.2 Treatment and Discharge

Both the frequency and severity of potential impacts on drinking water resources from treated hydraulic fracturing wastewater depend on the influent concentrations of the constituents in the wastewater and the type and adequacy of the treatment processes employed. If treatment and/or blending is inadequate, the resulting quality in a receiving water could, for example, influence formation of DBPs during subsequent drinking water treatment, impair biological treatment processes, and release TENORMs into receiving waters.

The volume of treated effluent discharged relative to the size of the receiving water body is an important local factor affecting the frequency and severity of potential impacts. Because of dilution effects, drinking water systems drawing from smaller rivers will likely face greater challenges in dealing with contaminants in their source water than systems drawing from larger rivers receiving the same volume of effluent. Seasonal changes in streamflow will also affect frequency and severity by affecting the degree of dilution. Existing loadings of pollutants from other sources in a watershed can increase the frequency and severity of potential impacts if the additional contributions from hydraulic fracturing wastewater cause concentrations to exceed thresholds.

Direct discharges of wastewaters with lower TDS concentrations to ephemeral streams are allowed in parts of the country where the wastewater is considered to be “of good enough quality” for livestock watering and wildlife use, and the discharges may constitute a large portion of streamflow. Permits authorizing such discharges may only require monitoring for a limited set of constituents. In particular, they may not necessarily require monitoring for specific constituents associated with hydraulic fracturing. The potential for water quality impacts from such discharges depends upon whether chemicals used for fracturing fluid or maintenance (or their degradation products) are present and at what concentrations. Long-term discharges to these ephemeral streams could result in ongoing impacts if there are unrecognized or unaddressed water quality issues.

Concerns about radionuclides in hydraulic fracturing wastewater have received considerable public attention, especially in the Marcellus region. The severity and frequency of impacts on receiving waters and sediments from TENORM depends upon the TENORM content in the wastewater (highest in regions with NORM-rich formations), temporal variability in the wastewater composition, and the treatment processes used. There are insufficient data to indicate whether radionuclides from these wastewaters have reached drinking water intakes. However, data do suggest that radionuclides can accumulate in sediments at or near discharge points from facilities that treat and discharge oil and gas wastewater. A recent PA DEP study (PA DEP, 2015b) reported radium in the effluent of both CWTs handling oil and gas wastewater and POTWs receiving effluent from such facilities.

Analysis of TENORM concentrations in hydraulic fracturing wastewaters prior to treatment, selection of appropriate treatment processes that adequately address the TENORM levels, and monitoring of TENORM in the treated effluent and receiving waters could help address the frequency and severity of potential impacts on drinking water resources in these areas. However, a confounding issue is underestimation of radium concentrations when using traditional wet chemical methods with high-TDS waters. This could consequently cause underestimation of frequency or severity of impacts. Newer studies have begun to use gamma spectroscopy for better recovery, which could help with more accurate assessment of frequency and severity of impacts (Nelson et al., 2014).

Accumulation of other contaminants such as organic compounds or metals in sediments at or near discharge points is also possible. If the sediments are disturbed or entrained due to dredging or flood events, contaminated sediments could be transported downstream closer to drinking water systems. The fate of such sediments and likelihood of mobilization of contaminants originating from hydraulic fracturing wastewaters have not been explored. The frequency and severity of impacts related to contaminated sediments would depend on a number of site-specific factors such as concentrations in the sediments, effluent quality, volume from the discharging facility, stream water quality, and stream hydrodynamics.

8.6.2.3 Storage and Disposal Pits and Impoundments

Tanks, pits, and impoundments, ever-present at oil and gas operations and CWTs, provide an opportunity for impacts on drinking water resources. Tanks are generally regarded as being safer than pits in terms of containment, although recent research has shown the potential for an increase in radioactivity in tank sediment if the wastewater contains TENORM. For pits and impoundments, the likelihood and severity of impacts due to spills and leaks depends in part on state construction and maintenance requirements for pits and how well these are observed. Frequency and severity of impacts will be lessened by attention to design standards, competent construction, and operational practices.

Liners, in particular, are an important measure to protect groundwater resources and are a common aspect of pit construction requirements. Liner specifications address materials, thickness, and leak detection. If a liner is compromised or nonexistent, the severity of impacts on groundwater will be affected by the volume leaked, the composition of the water in the pit, the depth to the water table, soil permeability, and the capacity of the soil to retain certain pollutants as the water percolates through. If substantial sediment has built up in the bottom of the pit, then in the event of a liner breach, contaminants may leach if the sediments permit water to pass through and into the soil. The fate and transport of wastewater contaminants in the subsurface is governed by a complex set of physical, chemical, and biological processes that dictate interactions between wastewater constituents and soil minerals, degradation or transformation of wastewater constituents, and possible mobilization of constituents in the soil under a pit (see Section 5.8 in Chapter 5 for a thorough discussion of processes affecting movement of constituents in the subsurface). Duration of use is also a consideration; the longer a pit with a faulty or nonexistent liner receives wastewater, the more severe the ultimate impact could be on underlying sediment and groundwater.

In the event of overtopping of a pit due to overfilling or extreme weather, the severity of impacts on surface water or groundwater will depend on the volume that overflows, wastewater composition, distance to surface water (if wastewater flows over land), depth to the water table, and soil properties (if the overflow infiltrates into the soil). If the overflow reaches a stream or river, the size of the spill relative to stream size and flow rate could also affect the severity of the impact. The combined factors that can contribute to overflows include capacity of the pit, the volume of fluid stored in the pit (i.e., freeboard) at the start of the precipitation event, and failure to monitor/ reduce pit fluid levels if needed.

As with concerns over discharges, the potential for impacts will be tied to other, existing stresses within a watershed. If the surface water is already receiving pollutant loadings from other sources, then an additional contribution from a pit-related leak or spill may not be as readily accommodated without causing water quality impairment.

8.6.2.4 Other Management Practices and Management of Residuals

Other management strategies such as irrigation, road spreading, and evaporation are less frequently employed for hydraulic fracturing wastewaters. The severity of impacts on surface waters from irrigation and road spreading will depend on the constituents in the wastewater (e.g., salts, radionuclides, and chemicals used in hydraulic fracturing), the distance to a receiving water, and whether stormwater management measures exist to mitigate runoff. The factors influencing whether constituents will migrate to shallow groundwater include depth to the water table, precipitation, soil permeability, and the soil's ability to retain pollutants that can adsorb to particles. If irrigation and road spreading are long-term management practices, the frequency of impacts will likely be proportional to the frequency with which the practices are employed.

Liquid and solid residuals generated from the treatment, storage, and handling of hydraulic fracturing wastewater have highly concentrated waste constituents. This could increase the potential severity of impacts due to spills that reach surface water resources or leach to groundwater. Potential impacts from management of residuals can be lessened in frequency and severity through careful handling, adequate characterization (including TENORM content), and selecting an appropriate disposal method, including use of a landfill that can accept TENORM waste if needed.

8.6.3 Uncertainties

A full understanding of hydraulic fracturing wastewater management is limited by a lack of available data in several areas. First, it is difficult to assemble a complete national- or regional-level picture of wastewater volumes and the management practices used because the tracking and availability of data vary from state to state. Although some states provide well-organized and relatively thorough data, not all states collect or make such information available. It can be difficult to identify wastewater volumes specifically associated with hydraulic fracturing (as compared to all oil and gas production activities). Such data would be needed to place hydraulic fracturing wastewater in the broader context of all oil and gas wastewaters. It is also generally difficult to determine whether hydraulic fracturing wastewater is being injected under a given disposal well permit because the permit rarely identifies which production wells are contributing to the wastewater stream. Data are also generally difficult to locate for wastewater production volumes, the chemical composition and concentrations in wastewater, and the management and disposal strategies for residuals.

Up-to-date information on the volume of hydraulic fracturing wastewater disposed of via underground injection by state is not uniformly available. Without this information, it is difficult to assess whether disposal well capacity will become an issue in areas where hydraulic fracturing activity is expected to increase or where use of disposal wells may become restricted locally or regionally.

For CWTs permitted to discharge to surface water, the ability to assess the potential effects of these discharges on drinking water resources is limited by the lack of effluent water quality data. Some monitoring data are required by the permit, but the list of monitored constituents may be limited. Selection of the appropriate water quality parameters to be monitored is critical to ensure that potentially problematic constituents are identified (e.g., chemicals associated with hydraulic fracturing fluids, maintenance chemicals, and degradation products of those chemicals). Some chemicals used in fracturing fluids are not disclosed, and analytical methods are lacking for some chemicals of concern and their degradation products.

Pollutant removal capabilities of the treatment facilities would also be valuable information to have, but this would require well-coordinated collection of both influent and effluent samples; this type of data is even less commonly available. In addition, the use of inappropriate analytical methods for the high TDS wastewater associated with hydraulic fracturing operations can complicate the use of available data. Methods used should be suitable for the highly complex matrix of contaminants encountered with oil and gas wastewater to have confidence in the results of chemical analyses.

Monitoring of surface waters downgradient of discharges, such as screening with a TDS proxy (i.e., conductivity), would also help assess the frequency of impacts on receiving waters by hydraulic fracturing activities (including spills and discharges of wastewater). Such data can also give an estimation of the severity of those impacts. Other than a few studies in the Marcellus Shale region, these types of water quality data are lacking. Existing data are also limited regarding legacy effects, such as accumulation of contaminants in sediments at discharge points, soil accumulation due to application of de-icing brines or salts from wastewater treatment, and handling of wastewater treatment residuals.

Assessing longer-term impacts on surface water quality from hydraulic fracturing activities in general is severely hampered by inadequate data. Bowen et al. (2015) state that available national-level databases are inadequate for addressing the question of whether there is evidence of national-level trends in surface water quality (as measured by specific conductivity and chloride) in areas where unconventional oil and gas production is taking place. Work by the Northeast-Midwest Institute and the USGS (Betanzo et al., 2016) was undertaken to explore the types and amounts of data needed to assess whether shale gas development activities contaminate surface water or groundwater in the Susquehanna River Basin. The focus was on longer-term cumulative impacts because detection of such impacts requires water quality monitoring. Detection of impacts (in either surface water or groundwater) requires a systematic monitoring approach that includes sampling at appropriately selected locations at an adequate frequency and duration and for a suite of water quality parameters to detect changes over time. Comparison sites without hydraulic fracturing activity are needed as well. The authors concluded that the data necessary to detect changes in surface water or groundwater due to hydraulic fracturing activities do not currently exist for the Susquehanna River Basin.

8.6.4 Conclusions

Oil and gas operations in the United States generated an estimated 2.43 billion gal of wastewater per day (about 60 million bbls/day) in 2012 (Veil, 2015). This includes wastewater associated with hydraulic fracturing activities, although what portion of this oil and gas wastewater is attributable to hydraulic fracturing operations is difficult to estimate. Available information indicates that the majority of hydraulic fracturing wastewater is injected into Class IID wells regulated under the UIC Program. In the Marcellus Shale region in Pennsylvania, this option is limited, and the majority of wastewater is reused (either with or without treatment) for new hydraulic fracturing jobs. Hydraulic fracturing wastewater may also be treated at a CWT and discharged by the CWT to surface water or to a POTW. In the western United States, wastewater is used in other ways (e.g., livestock watering) if water quality allows. Wastewater is also sent to evaporation ponds for disposal or stored on-site or in centralized pits or impoundments prior to final disposal or reuse.

Impacts on drinking water resources have resulted from discharges of inadequately treated wastewater and from leaks, spills, and percolation associated with pits. Other mechanisms for impacts include improper handling of treatment residuals or pit and tank sludges as well as leaching and runoff associated with other wastewater management practices. The impacts related to pits and residuals/sludges affect both surface water and groundwater; unlined pits or those with compromised liners present a particular concern (see Chapter 7 for additional discussion of spills). The constituents that have received the greatest attention in the literature include TDS, DBP precursors (especially bromide), and radium, although hydraulic fracturing wastewater can contain elevated concentrations of a number of organic and inorganic constituents of concern. Regardless of the management option utilized, if the wastewater is not thoroughly characterized or sampling is not conducted for analytes of concern, the severity and frequency of the impacts will be unknown or unquantified. The nature and volume of wastewater generated through hydraulic fracturing activities necessitate careful consideration of handling, treatment, and ultimate reuse or disposal to ensure that water resources are not adversely impacted. There is also a need for reliable and consistent waste generation data collection and reporting, improved efforts to characterize wastewater quality (both treated and untreated), and systematic monitoring efforts to be able to detect impacts on drinking water resources.

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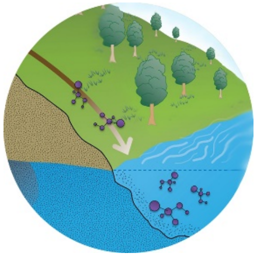

Chapter 9. Identification and Hazard Evaluation of Chemicals across the Hydraulic Fracturing Water Cycle

Abstract

This chapter identifies chemicals associated with hydraulic fracturing and provides an overview of the potential human health effects associated with these chemicals, as well as variables that could affect chemical occurrence in drinking water. The EPA has identified 1,606 chemicals associated with hydraulic fracturing, including 1,084 chemicals that are used in hydraulic fracturing fluid and 599 chemicals that have been detected in produced water. There is some uncertainty surrounding this chemical list, as it does not include a subset of chemicals that are classified as confidential business information, and because understanding of produced water composition is constrained by limitations of analytical chemistry as well as site-specific variations in the geochemistry of hydraulically fractured rock formations.

The EPA used selected federal, state, and international sources of toxicological data to identify toxicity values that can be used to support risk assessment for these chemicals, including chronic oral reference values (RfVs) for noncancer effects and oral slope factors (OSFs) for cancer. Chronic oral RfVs or OSFs were available for 173 (11%) of the total 1,606 chemicals. Health effects associated with chronic oral exposure to these chemicals include carcinogenicity, neurotoxicity, immune system effects, changes in body weight, changes in blood chemistry, liver and kidney toxicity, and reproductive and developmental toxicity.

For the majority of chemicals that lack chronic oral RfVs or OSFs, risk assessors will have to turn towards other sources of toxicological information that may have greater uncertainty than RfVs and OSFs, including quantitative structure-activity relationship (QSAR) models or additional data from the EPA's Aggregated Computational Toxicology Resource (ACToR) database. To understand whether specific chemicals can affect human health through their presence in drinking water, data on chemical concentrations in drinking water are needed. In the absence of these data, a preliminary analysis of relative hazard potential for drinking water resources can be conducted using the multi-criteria decision analysis (MCDA) approach outlined in this chapter. The MCDA combines data on toxicity, occurrence, and physicochemical properties for selected subsets of chemicals and was used in this chapter to highlight several chemicals that may be more likely than others to reach drinking water resources and present a health hazard.

Overall, while evidence suggests that hydraulic fracturing has the potential to impact human health, the actual human health implications are not well understood or well documented. Given that chemicals in hydraulic fracturing fluids and produced water are likely to vary on a regional basis and even between individual wells, the materials presented in this chapter are best applied for risk assessment and risk management decision-making at the local level.

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9. Identification and Hazard Evaluation of Chemicals across the Hydraulic Fracturing Water Cycle

9.1 Introduction

In this chapter, we present and integrate what is known about chemicals in the hydraulic fracturing water cycle, and provide an initial assessment of the potential for these chemicals to impact human health. The discussion is focused on the availability of toxicity values and qualitative assessments that can be used to inform the risk assessment of these chemicals for oral exposure via drinking water—in particular, the available noncancer oral reference values (RfVs), cancer oral slope factors (OSFs), and qualitative cancer classifications.[1,2,3] Public health impacts will depend upon both the inherent toxicity of these chemicals and the potential for human exposure. We highlight several field studies that have detected hydraulic fracturing-related chemicals in drinking water resources, and discuss properties of chemicals related to environmental fate and transport that could affect their potential impact on drinking water resources. To the extent information was available to do so, knowledge of toxicological and chemical properties was combined to illustrate a preliminary analysis of the relative hazard that these chemicals could pose to drinking water resources. The data are presented in this chapter as follows:

Section 9.2 provides a brief background on public health concerns surrounding hydraulic fracturing and unconventional oil and gas extraction, which have been highlighted in several recent studies.

Section 9.3 discusses how information sources were used to create a list of chemicals used in or detected in various stages of the hydraulic fracturing water cycle. The consolidated chemical list includes chemicals reportedly added to hydraulic fracturing fluids in the chemical mixing stage, as well as fracturing fluid chemicals, formation chemicals, or their reaction products that may be carried in produced water.

Section 9.4 provides an overview of the methods that were used for gathering information on toxicity and physicochemical properties for all chemicals identified in Section 9.3, and outlines the number of chemicals that had available data on these properties. For toxicological data, the primary focus is on chronic oral RfVs, OSFs, and qualitative cancer classifications from selected data sources that met the EPA's criteria for inclusion in this assessment. This section also discusses other

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[1] A reference value (RfV) is an estimate of an exposure for a given duration to the human population (including susceptible subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime. RfV is a generic term not specific to a given route of exposure (U.S. EPA, 2011f). In the context of this report, the term RfV refers to reference values for non-cancer effects occurring via the oral route of exposure and for chronic durations, except where noted.

[2] An oral slope factor (OSF) is an upper-bound, approximating a 95% confidence limit, on the increased cancer risk from a lifetime oral exposure to an agent. This estimate, usually expressed in units of proportion (of a population) affected per mg/kg day, is generally reserved for use in the low dose region of the dose response relationship, that is, for exposures corresponding to risks less than 1 in 100 (U.S. EPA, 2011f).

[3] Qualitative cancer classifications are a system used for the hazard identification of probable carcinogens, in which human data, animal data, and other supporting evidence are combined to characterize the weight of evidence (WOE) regarding the potential of an agent to cause cancer in humans.

potential sources of toxicity information: the use of quantitative structure-activity relationship (QSAR) modeling to estimate chemical toxicity, as well as the availability of toxicological information on the EPA's Aggregated Computational Toxicology Resource (ACToR) database. A brief description of other potential tools and approaches that may be used by stakeholders for site-specific evaluation of chemical hazards, but are not used in this report, is provided in Appendix G.

Section 9.5 describes the potential hazards of subsets of chemicals identified as being of interest in previous chapters of this report. This includes chemicals in hydraulic fracturing fluid (Chapter 5); organic chemicals, inorganic chemicals, and pesticides detected in produced water (Chapter 7); stray gas, such as methane (Chapter 6); and disinfection byproducts (DBPs) formed from constituents of hydraulic fracturing fluid wastewaters (Chapter 8). We discuss instances in which these chemicals have been detected in drinking water resources in areas of hydraulic fracturing activity, and provide an overview of the available toxicological information for these chemicals.

Section 9.6 uses a multi-criteria decision analysis (MCDA) framework to provide a preliminary analysis of the potential hazards of chemicals used in hydraulic fracturing fluids or detected in produced water. The MCDA framework is used to integrate data on chemical toxicity, occurrence, and physicochemical properties. In this context, occurrence and physicochemical properties are used as metrics to estimate the likelihood that a chemical will reach and impact drinking water resources. Chemicals considered in these hazard evaluations include a subset of chemicals identified in the EPA FracFocus 1.0 project database, as well as a subset of organic chemicals that have been detected in produced water.

This chapter is not a human health risk assessment. As shown in Text Box 9-1, risk assessment consists of four basic steps: hazard identification, dose-response assessment, exposure assessment, and risk characterization. This chapter provides an overview of hazard identification and dose-response assessment for these chemicals, but lacks information to fully characterize exposure and risk. In Section 9.5, we highlight instances in which these chemicals have been detected in drinking water resources, but these data are only available for a small number of chemicals. The MCDA approach in Section 9.6 provides a method for integrating data on toxicity and exposure potential, but should be considered only as a preliminary analysis, and should not be used in place of local data on chemical exposure.

This chapter is focused on potential human health hazards of chemicals for the oral route of exposure (drinking water); therefore, the toxicological properties and physicochemical ranking metrics described herein do not necessarily apply to other routes of exposure that may occur with these chemicals, such as inhalation or dermal exposure. We additionally note that this analysis is focused on individual chemicals, rather than mixtures of chemicals used as additives.

In general, characterizing chemicals and their properties on a national scale is challenging and the use and occurrence of chemicals is likely to differ between geological basins and possibly on a well-to-well basis (Chapters 5 and 7). Therefore, for the protection of human health at the local level, chemical hazard evaluations are best conducted on a regional or site-specific scale. This level of analysis is outside the scope of this report; however, the methods of hazard evaluation presented here can also be applied on a regional or site-specific scale in order to identify chemicals that may present a potential human health hazard.

Text Box 9-1. Applying Toxicological Data for Human Health Risk Assessment.

Understanding potential human health impacts requires knowledge not only of the inherent toxicity of the chemicals found in contaminated environmental media, but also of the potential for exposure to these chemicals. The process of evaluating the nature and probability of such impacts is known as human health risk assessment. Overall, human health risk assessment includes four basic steps (U.S. EPA, 2016a):

1. Hazard identification: Examining whether a chemical has the potential to cause harm to humans and/or ecological systems, and if so, under what circumstances.

2. Dose-response assessment: Examining the numerical relationship between exposure and effects.

3. Exposure assessment: Examining what is known about the frequency, timing, and levels of contact with a chemical.

4. Risk characterization: Examining how well the data support conclusions about the nature and extent of risk from exposure to a chemical. Information from the hazard identification, dose-response assessment, and exposure assessment are summarized and integrated into quantitative and qualitative expressions of risk.

The RfVs and OSFs compiled by the EPA in this study pertain to the first two steps of human health risk assessment: identifying chemicals that have the potential to affect human health (hazard identification), and characterizing the exposure levels at which those effects occur (dose-response assessment). These toxicity values may be used in combination with site-specific chemical exposure information (exposure assessment) in order to evaluate potential human health risks (risk characterization). Qualitative cancer classifications characterize the weight of evidence regarding the potential for a chemical to cause cancer, and therefore provide additional information that can be used for hazard identification.

Toxicity information spans a wide range with respect to extent, quality and reliability. The RfVs, OSFs, and qualitative cancer classifications compiled in this study are those identified by the EPA as being of the highest quality and reliability, per the criteria discussed in this chapter. The QSAR-based toxicity estimates discussed in this chapter are considered to be lower on the continuum of quality and reliability, but may provide useful information pertaining to hazard identification and dose-response assessment when a chemical does not have an RfV or OSF available. The EPA's ACToR database provides an aggregation of a wide range of toxicological data that may also be useful for supporting the risk assessment of these chemicals. This chapter provides information on whether a chemical has data available from ACToR; however, it is beyond the scope of this report to evaluate the quality and reliability of data for these chemicals within ACToR, or to provide guidance on how the data within ACToR should be used to support human health risk assessment.

9.2 Overview: Hydraulic Fracturing and Potential Impacts on Human Health

As discussed in the previous chapters of this assessment, a variety of chemicals are associated with the hydraulic fracturing water cycle. Chemicals are added to hydraulic fracturing fluids at the chemical mixing stage (Chapter 5), and then injected into the well (Chapter 6). These chemical additives may return to the surface in produced water, along with chemicals from the formation (Chapter 7). The chemicals in produced water may persist in wastewater effluents, with some constituents contributing to the formation of disinfection byproducts in treated wastewater (Chapter 8). Through events such as large volume spills (Figure 9-1), mechanical integrity failures, hydraulic fracturing directly into groundwater resources, or discharge of inadequately treated hydraulic fracturing wastewater, there are specific instances in which these chemicals have been demonstrated to enter drinking water resources. Thus, there is potential for human exposure to these chemicals, and the potential for adverse human health effects resulting from exposure.

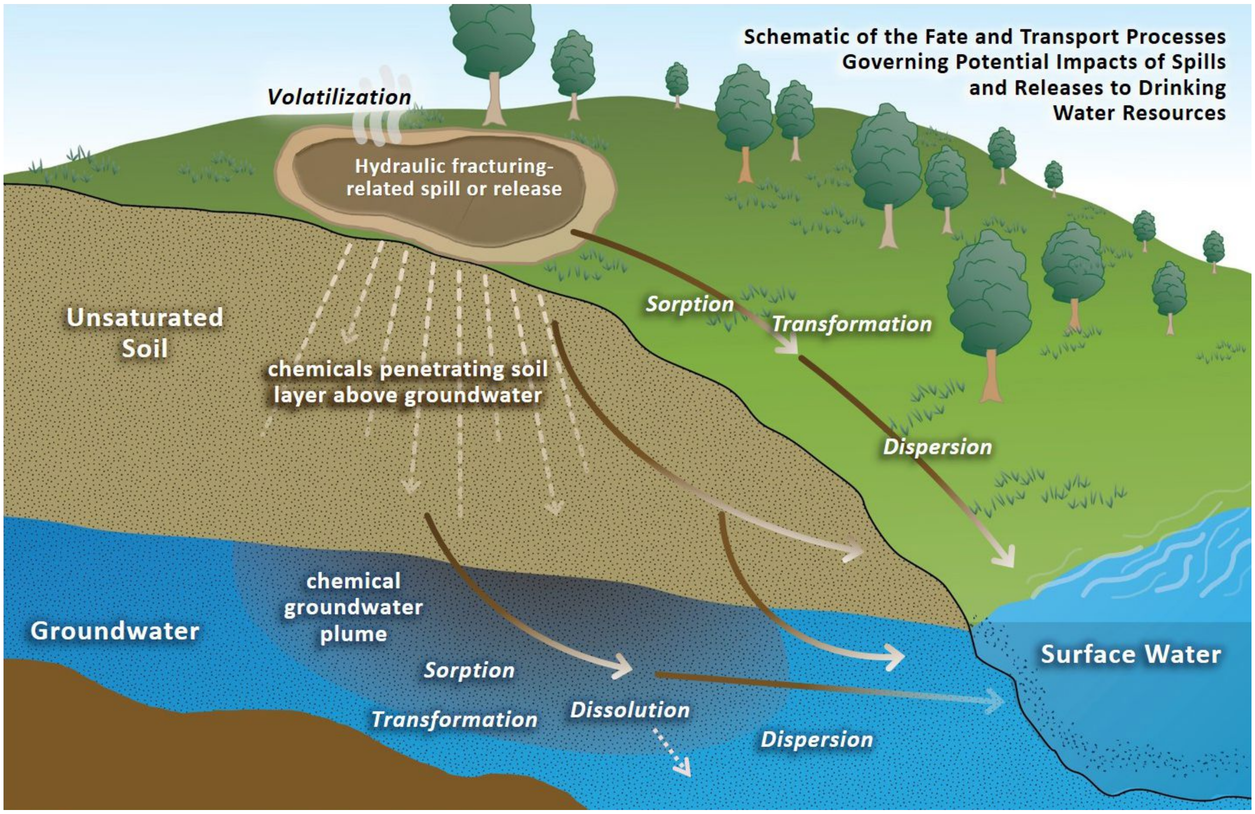

Figure 9-1. Fate and transport schematic for a hydraulic fracturing-related spill or release.

Multiple authors have noted with the recent increase in hydraulic fracturing operations there may be an increasing potential for significant public health and environmental impacts (Goldstein et al., 2014; Finkel et al., 2013; Korfmacher et al., 2013; Weinhold, 2012). These concerns have been highlighted in several recent studies. An epidemiological study in Colorado demonstrated residential proximity of pregnant mothers to natural gas wells is associated with an increased incidence of congenital heart defects, and, to a lesser extent, neural tube malformations (Mckenzie et al., 2014). A similar study in Pennsylvania found pregnant mothers living closer to unconventional natural gas wells were more likely to have infants that were small for gestational age, with lower birth weights compared to infants from mothers living farther from wells (Stacy et al., 2015). Residential proximity to natural gas wells in the Marcellus Shale is associated with an increase the number of self-reported health symptoms, particularly upper respiratory and dermal symptoms (Rabinowitz et al., 2015), chronic rhinosinusitis, migraine headache, and fatigue symptoms (Tustin et al., 2016). Laboratory studies have found that endocrine disrupting activity measured using in vitro bioassays may be elevated in surface and groundwater at known hydraulic fracturing spill sites (Kassotis et al., 2014) and in surface water downstream from a hydraulic fracturing wastewater injection facility (Kassotis et al., 2016). Although none of these studies demonstrate a direct effect of hydraulic fracturing activity on human health, and none of the epidemiological studies provided measures of individual or population level exposures or differentiated between drinking water contamination and other potential routes of exposure (e.g., air pollution), all are suggestive of a relationship between unconventional oil and gas development and adverse health outcomes.

Previous chapters of this report have identified cases in which contamination of drinking water resources could clearly be linked to hydraulic fracturing activity. For example, equipment failure and human error have led to spills of hydraulic fracturing fluids across the country and have affected the quality of drinking water resources (U.S. EPA, 2015m; Brantley et al., 2014; COGCC, 2014; Gradient, 2013). Other studies highlighted in previous chapters provide indirect evidence hydraulic fracturing activity has contaminated surface water or groundwater. For example, two recent studies in the Marcellus Shale detected known hydraulic fracturing-related chemicals in nearby groundwater wells, and used multiple lines of evidence to link the origin of these chemicals to hydraulic fracturing activity (Drollette et al., 2015; Llewellyn et al., 2015).

There have also been documented impacts on ecological receptors. In Knox County, Kentucky, retention pits holding hydraulic fracturing flowback fluids overflowed into Acorn Fork Creek during the development of four natural gas wells, causing a decrease in pH and increase in conductivity.[1] Organics and metals including iron and aluminum formed precipitates in the stream, and fish and aquatic invertebrates were killed or displaced in a 2.7 km length of the stream affected by the release (Papoulias and Velasco, 2013). A field report from the Pennsylvania Department of Environmental Protection (PADEP) described a leak in an overland pipe carrying a mixture of flowback and freshwater between two impoundments that impacted a 0.6 km length of a stream, in which 168 fish and 6 salamanders were killed (PA DEP, 2009b).

In some instances, chemical concentrations in drinking water resources impacted or potentially impacted by hydraulic fracturing activity exceeded their respective primary or secondary maximum contaminant level (MCL), or health advisory levels provided by the EPA's National Primary Drinking Water Regulations (NPDWRs) and Drinking Water Standards and Health Advisories (DWSHA) tables (U.S. EPA, 2012b), indicating that these chemicals are present at levels that may impact human health.[2] Examples will be discussed in Section 9.5. These studies generally did not indicate the contaminated water was used directly for human consumption, so it is not clear that people are being exposed to these chemicals at these levels. Nevertheless, these studies indicate that hydraulic fracturing activity may contribute to the entry of chemicals into drinking water resources at potentially harmful levels.

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[1] "Flowback" refers to fluids containing predominantly hydraulic fracturing fluid that return from a well to the surface. Flowback is a type of produced water. See Chapter 7 for more details.

[2] Maximum contaminant level (MCL): The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to the maximum contaminant level goal (MCLG) as feasible using the best available analytical and treatment technologies and taking cost into consideration. MCLs are enforceable standards. The MCLG is a non-enforceable health benchmark goal which is set at a level at which no known or anticipated adverse effect on the health of persons is expected to occur and which allows an adequate margin of safety (U.S. EPA, 2012b).

Risk assessment and risk management decisions will be informed by scientific information on the toxicity of chemicals in hydraulic fracturing fluid and wastewater. The U.S. House of Representatives' Committee on Energy and Commerce Minority Staff released a report in 2011 noting that more than 650 products (i.e., chemical mixtures) used in hydraulic fracturing contain 29 chemicals that are either known or possible human carcinogens or are currently regulated under the Safe Drinking Water Act (House of Representatives, 2011). More recently, several studies have performed a reconnaissance of toxicity and/or physicochemical property data for specific subsets of chemicals used in hydraulic fracturing fluids (Elliott et al., 2016; Wattenberg et al., 2015; Stringfellow et al., 2014; Colborn et al., 2011), and have provided discussion on the hazards inherent to these chemicals. In all cases, authors reported toxicity data was not available for many of the chemicals assessed in these studies, with some studies indicating significant data gaps. For instance, Wattenberg et al. (2015) evaluated 168 chemicals commonly used in hydraulic fracturing fluids in North Dakota, and reported that 59% did not have chronic toxicity data available, and 35% did not have acute toxicity data available. Elliott et al. (2016) performed a systematic evaluation of reproductive and developmental toxicity for 1021 chemicals used in hydraulic fracturing fluids or detected in wastewater, and found this toxicity information was lacking for 76% of these chemicals.

Overall, while combined evidence suggests hydraulic fracturing has the potential to impact human health via contamination of drinking water resources, the actual public health impacts are not well understood and not well documented. Available information indicates there are many chemicals within the hydraulic fracturing water cycle that are known to be hazardous to human health, as well as hundreds of chemicals for which toxicological data is limited or unavailable.

In this chapter, our primary goal is to evaluate the availability of toxicity data for a list of chemicals used in hydraulic fracturing fluids or present in produced water, focusing primarily on toxicity values from sources that meet the criteria for inclusion in this assessment, and to highlight chemicals that may pose human health hazards.

9.3 Identification of Chemicals Associated with the Hydraulic Fracturing Water Cycle

As the initial step towards evaluating the hazards of chemicals in the hydraulic fracturing water cycle, the EPA compiled a list of chemicals used in or released by hydraulic fracturing operations across the country.[1] This section describes the compilation of that list. This consolidated list includes a total of 1,606 chemicals, and can be broken down into two sublists: (1) a list of chemicals used in hydraulic fracturing fluids, and (2) a list of chemicals detected in produced water from hydraulically fractured wells (Text Box 9-2).

This list demonstrates the range and variety of chemicals that are associated with the hydraulic fracturing industry. These chemicals should not be considered unique to the hydraulic fracturing

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[1] We use the word "chemical" to refer to any individual chemical or chemical substance that has been assigned a CASRN (Chemical Abstracts Service Registry Number). A CASRN is a unique identifier for a chemical substance, which can be a single chemical (e.g., hydrochloric acid, CASRN 7647-01-0) or a mixture of chemicals (e.g., hydrotreated light petroleum distillates (CASRN 64742-47-8), a complex mixtures of C9 to C16 hydrocarbons). For simplicity, we refer to both pure chemicals and chemical substances that are mixtures, which have a single CASRN, as "chemicals."

industry; many of the chemicals used in hydraulic fracturing fluids are widely used industrial chemicals, and many of the chemicals in produced water are naturally occurring. Although this list represents the best information available to the EPA at the time of the assessment, it should not be considered comprehensive. It is likely that, as industry practices change, chemicals may be used or detected that are not included on these lists. Some additional limitations to this chemical list are described in the subsections below.

Text Box 9-2. The EPA's List of Chemicals Identified in Hydraulic Fracturing Fluids and/or Produced Water.

This chemical list progressed through multiple iterations as the EPA's hydraulic fracturing study was developed, culminating in the list of 1,606 chemicals presented in this report.

The first iteration of this chemical list was published in the interim progress report (U.S. EPA, 2012h), and included 1,026 chemicals that were identified from ten sources of information. Seven of these information sources were documents from federal and state governmental units—including the EPA (U.S. EPA, 2011a, e, 2004a; Material Safety Data Sheets), the U.S. House of Representatives (House of Representatives, 2011), the New York State Department of Environmental Conservation (NYSDEC, 2011), and the Pennsylvania Department of Environmental Protection (PA DEP, 2010a)—which obtained data directly from industry. This includes a list of chemicals provided directly to the EPA by nine well operating companies, representing chemicals used in hydraulic fracturing fluids between 2005 and 2009, and a list of chemicals detected by these companies in produced water from 81 wells. The remaining three sources are as follows: a technical report prepared by the Gas Technology Institute for the Marcellus Shale Coalition, which is a drilling industry trade group (Hayes, 2009); a peer-reviewed journal article by Colborn et al. (2011); and the FracFocus Chemical Disclosure Registry, which is a national hydraulic fracturing chemical registry developed by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission (GWPC, 2012).

In the external review draft of the EPA's hydraulic fracturing study report (U.S. EPA, 2015d), this chemical list was updated to 1,173 chemicals. The updated chemical list includes the 1,026 chemicals published in the progress report, along with additional chemicals that were identified in the EPA FracFocus 1.0 report (U.S. EPA, 2015a).

For the final version of this assessment, the list has again been updated to include additional chemicals in produced water, which were identified from 18 additional literature sources. The final list includes a total of 1,606 chemicals that have been reported as used in hydraulic fracturing fluids or detected in produced water. The complete list of sources used to compile the final chemical list is provided in Appendix Table H-1. To the extent possible, after chemicals were identified from the sources in Table H-1, the EPA verified the identity of the chemicals used in hydraulic fracturing fluids and detected in produced water of hydraulically fractured wells as described in Appendix Section H.1.

9.3.1 Chemicals Used in Hydraulic Fracturing Fluids

Of the 1,606 total chemicals, the EPA identified 1,084 chemicals as being used in hydraulic fracturing fluids. This list was originally introduced in Chapter 5 of this assessment (Section 5.4), which describes some of the chemical classes and their purpose, and identifies the most frequently used chemicals. This list of 1,084 chemicals is shown in Appendix Table H-2.

Although a total of 8 sources were used to identify the list of chemicals used in hydraulic fracturing fluids, only one source—the EPA analyses based on disclosures submitted to FracFocus—had sufficient information for estimating the frequency with which these chemicals were used (Section 5.4, Text Box 5-1).[1] Of the 1,084 chemicals, 688 were identified in the EPA FracFocus 1.0 report (U.S. EPA, 2015a).[2] Frequency of use for individual chemicals ranged from low (480 chemicals on the list were reported in less than 1% of disclosures nationally) to very high (methanol was reported in 73% of disclosures nationally).

As discussed in Chapter 5, this list provides valuable information on the chemicals used in hydraulic fracturing fluids, but should not be considered complete. For example, in the analysis of the disclosures submitted to the FracFocus 1.0 registry, the EPA was only able to assign standardized chemical names to 65% of ingredient records. The remaining 35% of ingredient records did not have valid CASRNs and were excluded from the analysis because they could not be assigned a standardized chemical name (U.S. EPA, 2015a). In a more recent analysis of data reported to the FracFocus registry through April 2015, Konschnik and Dayalu (2016) found that 80% of chemicals had valid CASRN. That analysis identified an additional 263 CASRNs that are not on the EPA's list of chemicals used in hydraulic fracturing fluids (Dayalu and Konschnik, 2016).

Industry use of CBI is another factor that likely limits the completeness of this chemical list and introduces uncertainty. For example, companies submitting to FracFocus 1.0 were not required to disclose chemicals claimed as CBI. EPA determined that approximately 70% of the disclosures submitted to FracFocus 1.0 contain at least one CBI chemical, and for those disclosures, the average number of CBI chemicals per disclosure was five. Overall, 11% of ingredients were reported to FracFocus 1.0 as CBI (U.S. EPA, 2015a). Konschnik and Dayalu (2016) report a 5.6% increase in the number of CBI ingredients, as well as an increase in the number of disclosures reporting the use of at least one CBI ingredient (Section 5.4; Text Box 5-2).

Although FracFocus disclosures do not provide the name or CASRN of CBI chemicals, the chemical family is sometimes provided. The EPA determined that 79% of CBI ingredient records submitted to FracFocus 1.0 had enough information to partially define the chemical and assign it to a chemical family (U.S. EPA, 2015a). This resulted in the designation of 448 standardized chemical families to which these chemicals could be assigned. The most common standardized chemical families for CBI ingredients were oxyalkylated alcohol (4.7% of CBI ingredient records), petroleum distillates (4.0% of CBI ingredient records), and quaternary ammonium compounds (3.6% of CBI ingredient records) (U.S. EPA, 2015a) (Appendix Table B-1). These standardized chemical family designations are not discussed further in this chapter, but may be useful for site-specific risk assessment, as they

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[1] The FracFocus frequency of use data presented in this chapter is based on 35,957 FracFocus disclosures that were deduplicated, within the study time period (January 1, 2011 to February 28, 2013), and with ingredients that have a valid CASRN. In the interest of including as many chemicals as possible, this analysis includes chemicals that do not have valid concentration data. The 692 chemicals includes 16 chemicals that are listed as being used as proppants.

[2] EPA analyses based on disclosures submitted to FracFocus identified 692 unique CASRN. Of these 692, we determined that 4 chemicals are listed under two different CASRN (indicated in the footnote of Appendix Table H-2). Frequency of use data is therefore available for 688 chemicals that were included on EPA's list of chemicals in hydraulic fracturing fluids.

may provide insight into potential physicochemical properties and toxicity of CBI chemicals used at a particular site.

9.3.2 Chemicals Detected in Produced Water

Of the 1,606 total chemicals, the EPA identified 599 as having been detected in produced water. Included among these chemicals are naturally occurring organic compounds, metals, radionuclides, industrial chemicals, and pesticides. These chemicals were originally introduced in Chapter 7 of this assessment, and were compiled from a total of 21 sources. Seventy-seven of the total 599 chemicals in produced water were also identified by at least one of the sources in Appendix H as being used in hydraulic fracturing fluid. However, the EPA used different sets of sources to identify chemicals used in hydraulic fracturing fluids versus those detected in produced water, and there is not a matched comparison between the chemicals used in hydraulic fracturing fluids and returned in produced water at each particular well. Therefore, it is difficult to draw direct comparisons between these two chemical lists, or to use these lists to draw conclusions on the persistence of chemicals in produced water from hydraulically fractured wells. The list of 599 chemicals identified in produced water is shown in Appendix Table H-4.

Although this list provides useful information on the chemical composition of produced water, it is not likely that the data sources were able to capture all of the chemicals present. Chemicals and their metabolites may go undetected in produced water because they were not targeted in the analytical protocols, they were below the limit of detection, or because no standard analytical method exists. Additionally, as discussed in Chapter 7, the composition and concentration of chemicals in produced water will differ depending upon factors like the geology of the formation, the chemicals used for hydraulic fracturing, and the amount of time that has elapsed since hydraulic fracturing. There is therefore expected to be a high degree of local and temporal variation in these chemicals, and there was not sufficient information to determine the frequency with which these chemicals were detected on a national basis.

Concentration data in produced water are available for 175 of these 599 chemicals (Appendix E), including inorganic contributors to salinity (Appendix Tables E-4 and E-5), metals (Appendix Tables E-6 and E-7), radioactive constituents (Appendix Table E-8), and organic constituents (Appendix Tables E-9, E-11, E-12, and E-13). The remaining chemicals were detected in produced water, but concentration was not reported. For these chemicals with concentration data, the measured concentrations spanned several orders of magnitude. For instance, for organic chemicals in produced water from the Marcellus shale formation (Appendix Table E-11), average or median measured concentrations ranged from 2.7 μg/L for N-nitrosodiphenylamine to 400 μg/L for carbon disulfide.

9.4 Toxicological and Physicochemical Properties of Hydraulic Fracturing Chemicals

As the next step towards evaluating the hazards of chemicals in the hydraulic fracturing water cycle, toxicological and physicochemical data were collected as available for each of the chemicals identified in Appendix H. This section describes the compilation of these data, and discusses the extent to which toxicological and physicochemical property data are available for this list of chemicals.

The primary focus of the toxicological analysis in this chapter is on the availability of chronic oral RfVs and OSFs from sources that met the EPA's criteria for inclusion in this study. Qualitative cancer classifications were also identified from these sources when available. This is not intended to be an exhaustive compilation of toxicity values for this chemical list. Rather, it is intended to be a reconnaissance of high-quality toxicological information that met the EPA's criteria for inclusion in this study. If a source of RfVs, OSFs, or qualitative cancer classifications was not included here, that only means that it did not meet the criteria for the purposes of the EPA's study, which are described in this chapter in Section 9.4.1.

Section 9.4.1 describes the criteria used to identify and select RfVs, OSFs, and qualitative cancer classifications, and describes the availability of these toxicological data for the chemicals on the EPA's list of hydraulic fracturing-related chemicals. The next two sections describe additional sources of toxicological information, which may be useful for hazard evaluation when chronic oral RfVs and OSFs are not available: Section 9.4.2 describes the use of a QSAR model to estimate chronic oral toxicity, and Section 9.4.3 describes the availability of additional toxicological information on the EPA's ACToR database. Section 9.4.4 describes other available software tools and approaches that may be used by stakeholders for site-specific risk assessment, but are not utilized in this report. Section 9.4.5 discusses the methods used in this report to generate physicochemical property data, and presents the availability of physicochemical property data for the chemicals on the EPA's list. A brief overview of the toxicity values discussed in the chapter is presented in Text Box 9-3.

As a resource that can be used to support risk assessment at hydraulic fracturing sites, all of the selected RfVs, OSFs, qualitative cancer classifications, QSAR-based toxicity estimates, and physicochemical property data described in this chapter will be compiled into an electronic database that will be publicly accessible via the EPA's website. Additionally, the EPA's compilation of toxicity data for this chemical list has been discussed in two recent manuscripts, both of which focused on the list of 1,173 chemicals that was presented in the external review draft of the EPA's hydraulic fracturing study report (U.S. EPA, 2015d). Yost et al. (2016b) describes the compilation of RfVs and OSFs for the list of 1,173 chemicals. Yost et al. (2016a) describes the use of a QSAR model to estimate toxicity for the list of 1,173 chemicals.

Text Box 9-3. Toxicity Values for Hydraulic Fracturing-Related Chemicals.

Here we provide a brief description of the toxicity values that are presented in this chapter, and how they should be interpreted and used to evaluate chemical hazards. Formal definitions of these terms are footnoted in the chapter and can also be found in the glossary (Appendix J).

Reference value (RfV): RfVs are health-protective values, which describe the dose of a chemical that is likely to be without an appreciable risk of adverse health effects. In general, lower RfVs indicate greater toxicity; however, comparison of RfVs among a set of chemicals requires careful consideration. RfVs are developed by considering the full database of epidemiological and experimental studies available for a particular chemical.

(Text Box 9-3 is continued on the following page.)

Text Box 9-3 (continued). Toxicity Values for Hydraulic Fracturing-Related Chemicals.

These data are used to identify the critical effect, which is the first adverse effect, or its known precursor, that occurs as the dose rate increases (U.S. EPA, 2011f). An RfV is then derived by starting with a quantitative point of departure (POD), which is the toxicological dose-response point that marks the beginning of a low-dose extrapolation for the critical effect, and applying uncertainty factors (UFs) to derive a value for the protection of human health. UFs are applied to account for 5 areas of uncertainty: (1) intraspecies variability; (2) interspecies uncertainty; (3) extrapolation from a subchronic study; (4) extrapolating from a no-observed-adverse-effect level (NOAEL); and (5) deficiencies in the database. A UF of 1, 3, or 10 can be applied for any of these areas of uncertainty depending upon the amount and/or type data available, up to a maximum total UF of 3,000 (U.S. EPA, 2002). Thus, a chemical with a low RfV may reflect high uncertainty in the value, and not necessarily the toxicity of the chemical. Chemicals with a lower total UF generally have more reliable and robust health effect information.

Oral slope factor (OSF): An OSF is a measure of the increased cancer risk from a lifetime oral exposure to an agent. Higher OSFs indicate greater carcinogenic potency. As with RfVs, OSFs are developed by considering the full database of epidemiological and experimental studies for a particular chemical, and evaluating the increase in cancer incidence as dose rate increases. OSFs should be considered in conjunction with qualitative cancer classifications, which characterize the weight of evidence regarding the agent's potential to cause cancer in humans.

No-observed-adverse-effect level (NOAEL): NOAEL is defined as the highest exposure level at which there are no biologically significant increases in the frequency or severity of adverse effect between the exposed population and its appropriate control; some effects may be produced at this level, but they are not considered adverse or precursors of adverse effects (U.S. EPA, 2011f).

Lowest-observed-adverse-effect level (LOAEL): LOAEL is defined as the lowest exposure level at which there are biologically significant increases in the frequency or severity of adverse effects between the exposed population and its appropriate control group (U.S. EPA, 2011f). Lower LOAELs indicate greater toxicity.

Maximum contaminant level (MCL): MCLs are the highest level of a contaminant that is allowed in drinking water. MCLs are set as close to the maximum contaminant level goal (MCLG) as feasible using the best available analytical and treatment technologies and taking cost into consideration. MCLs are enforceable standards. The MCLG is a non-enforceable health benchmark goal which is set at a level at which no known or anticipated adverse effect on the health of persons is expected to occur and which allows an adequate margin of safety (U.S. EPA, 2012b). Whereas RfVs, LOAELs, and NOAELs are expressed in terms of dose (mg/kg-day), MCLs are expressed in terms of the concentration of an agent in water (μg/L).

9.4.1 Reference Values (RfVs), Oral Slope Factors (OSFs), and Qualitative Cancer Classifications

For the purpose of this study, the EPA's primary goal was to identify high quality toxicity values that met the criteria for inclusion in this study, and that could be used by stakeholders to support the risk assessment of hydraulic fracturing chemicals (Text Box 9-1). Briefly, the sources of RfVs, OSFs, and qualitative cancer classifications selected by the EPA for the purposes of this chapter met the following key criteria:

1. The body or organization generating or producing the peer-reviewed RfVs, peer-reviewed OSFs, or peer-reviewed qualitative assessment must be a governmental or intergovernmental body.
2. The data source must include peer-reviewed RfVs, peer-reviewed OSFs, or peer reviewed qualitative assessments.
3. The RfVs, OSFs, or qualitative assessments must be based on peer-reviewed scientific data.
4. The RfVs, OSFs, or qualitative assessments must be focused on protection of the general public.
5. The body generating the RfVs, OSFs, or qualitative assessments must be free of conflicts of interest with respect to the chemicals for which it derives reference values or qualitative assessments.

These five criteria were developed by the EPA specifically for the purpose of this assessment, and are similar to the EPA Office of Solid Waste and Emergency Response (OSWER) recommendations for selecting toxicity values in conducting site-specific risk assessments (Regional Tier 3 Toxicity Value Workgroup, 2013; U.S. EPA, 2003a, 1989).[1] The OSWER directives provide recommendations on the appropriate sources of toxicity values and toxicological information that should be considered in risk assessments, and were designed to recognize toxicity values that were developed using the best available scientific information. In addition, these directives outline references to various resources that provide guidance on the approaches and issues considered in deriving toxicity values. This type of information can be especially important in cases in which multiple sources of toxicity values need to be considered or evaluated, or in which a value needs to be developed. More detail on these criteria for selection and inclusion of data sources, as well as the full list of data sources that were considered for this study, are available in Appendix G.

Table 9-1 shows the data sources that met these five criteria for the selection of toxicological information. The federal databases of RfVs or OSFs that met these criteria are the EPA's Integrated Risk Information System (IRIS) database, the EPA's Provisional Peer-Reviewed Toxicity Value (PPRTV) database, the EPA's Human Health Benchmarks for Pesticides (HHBP) database, and the Agency for Toxic Substances and Disease Registry (ATSDR) database. IRIS and PPRTV also provide qualitative cancer classifications. One state source of RfVs and OSFs, the California Environmental Protection Agency (CalEPA) Toxicity Criteria Database, met the criteria for inclusion.[2] One intergovernmental source of RfVs, the World Health Organization (WHO) International Programme on Chemical Safety (IPCS) Concise International Chemical Assessment Documents (CICAD), met the criteria for inclusion. The International Agency for Research on Cancer (IARC) and U.S. National Toxicology Program (NTP) Report on Carcinogens (RoC) also met the criteria and were used as additional sources for qualitative cancer classifications.

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[1] OSWER changed its name to the Office of Land and Emergency Management (OLEM), effective December 15, 2015.

[2] State RfVs and OSFs are also publicly available from Alabama, Texas, Hawaii, and Florida, but they did not meet the criteria for consideration as sources for RfVs and OSFs in this report. See Appendix G for details.

Table 9-1. Sources of selected RfVs, OSFs, and qualitative cancer classifications.

Type of toxicological Information	Data source	Website
RfVs, OSFs, and qualitative cancer classifications	EPA Integrated Risk Information System (IRIS) database	http://cfpub.epa.gov/ncea/iris/index.cfm?fuseaction=iris.showSubstanceList
RfVs, OSFs, and qualitative cancer classifications	EPA Provisional Peer-Reviewed Toxicity Value (PPRTV) database	http://hhpprtv.ornl.gov/index.html
RfVs, OSFs	EPA Human Health Benchmarks for Pesticides (HHBP) database	http://iaspub.epa.gov/apex/pesticides/f?p=HHBP:home
RfVs	Agency for Toxic Substances and Disease Registry (ATSDR) Minimum Risk Levels	http://www.atsdr.cdc.gov/toxprofiles/index.asp#bookmark05
RfVs, OSFs	California Environmental Protection Agency (CalEPA) Toxicity Criteria Database	http://oehha.ca.gov/tcdb/index.asp
RfVs	World Health Organization (WHO) International Programme on Chemical Safety (IPCS) Concise International Chemical Assessment Documents (CICAD)	http://www.who.int/ipcs/publications/cicad/en/
Qualitative cancer classifications	National Toxicology Program (NTP) 13th Report on Carcinogens (RoC)	https://ntp.niehs.nih.gov/pubhealth/roc/
Qualitative cancer classifications	International Agency for Research on Cancer (IARC) Monographs	http://monographs.iarc.fr/

In addition to the sources in Table 9-1, we also consulted the NPDWRs and DWSHA tables (U.S. EPA, 2014a) to determine whether the chemicals on this list are regulated as drinking water contaminants. NPDWRs provide a list of MCLs, which are legally enforceable standards on the concentration of a substance that is allowed in drinking water under the Safe Drinking Water Act. In this chapter, MCL values are referenced as a means of comparison with reported concentration data where appropriate, and are reported in Appendix G and are compiled on the EPA's electronic database for the hydraulic fracturing study.

As noted above, this chapter focuses on the presentation and use of chronic RfVs. Chronic RfVs account for the potential that chemical exposure may be continuous, in low concentration, and over a longer duration. In the absence of reliable information on the potential duration of chemical exposure, this is a conservative assumption for the protection of human health. Chronic RfVs are also lower than less-than-chronic RfVs (e.g., acute, intermediate, or subchronic toxicity values), and are therefore more health protective. For these reasons, chronic RfVs are generally preferred as the default by risk assessors when conducting site-specific risk assessments (U.S. EPA, 1989) and when developing regional screening levels (U.S. EPA, 2016b). In contrast, acute RfVs are more applicable for single exposures and/or exposures of limited frequency to high concentration and shorter durations (e.g., emergencies). However, the availability of less-than chronic RfVs are also presented for the sake of completeness.

Some chemicals had chronic oral RfVs or OSFs available from more than one of the sources in Table 9-1. For these chemicals, we selected a single value for use in this chapter by applying a modification of the EPA OSWER Directives 9285.7-53 and 9285.7-86 tiered hierarchy of toxicity values (U.S. EPA, 2003a). A single RfV and/or OSF was selected from the sources in this order: HHBP (pesticides only), IRIS, PPRTV, ATSDR, and then other available values. The RfVs considered from these sources included chronic oral reference doses (RfDs) from the IRIS, PPRTV, and HHBP programs; chronic oral minimal risk levels (MRLs) from ATSDR; oral maximum allowable daily levels (MADLs) from CalEPA; and tolerable daily intakes (TDIs) from CICAD.[1,2,3,4,5]

Of the 1,606 chemicals identified by the EPA, 173 (11%) have federal, state, or international chronic oral RfVs and/or OSFs from sources listed in Table 9-1. Chronic oral RfVs and/or OSFs from the selected sources are lacking for the remaining 1,433 (89%) chemicals that the EPA has identified as associated with hydraulic fracturing. All available chronic oral RfVs and OSFs from the sources listed in Table 9-1 are tabulated in Appendix G. Chronic oral RfVs and OSFs for chemicals used in hydraulic fracturing fluids are listed in Appendix Tables G-1a through G-1c, and chronic oral RfVs and OSFs for chemicals reported in hydraulic fracturing flowback or produced water are listed in Appendix Tables G-2a through G-2c. The EPA's IRIS database was the most abundant source of these toxicity values.

Overall, when chemicals in hydraulic fracturing fluid and chemicals in produced water are considered separately, the availability of chronic RfVs and OSFs can be summarized as follows:

- For the 1,084 chemicals used in hydraulic fracturing fluid, chronic oral RfVs or OSFs from at least one of the selected federal, state, and international sources were available for 98 chemicals (9%). From the US federal sources alone, chronic oral RfVs were available for 81 chemicals (7%), and OSFs were available for 15 chemicals (1%).

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[1] The OSWER hierarchy indicates that sources should be used in this order: IRIS, PPRTV, and then other values. In this report, this hierarchy was followed, but HHBP values were used in lieu of an IRIS value for a few chemicals that are pesticides.

[2] An RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. It can be derived from a NOAEL, LOAEL, or benchmark dose, with uncertainty factors generally applied to reflect limitations of the data used. Generally used in the EPA's non-cancer health assessments (U.S. EPA, 2011f). This estimate is expressed in terms of mg/kg-day.

[3] An MRL is an estimate of daily human exposure to a hazardous substance at or below which the substance is unlikely to pose a measurable risk of harmful (adverse), non-cancerous effects. MRLs are calculated for a route of exposure (inhalation or oral) over a specified time period (acute, intermediate, or chronic). MRLs should not be used as predictors of harmful (adverse) health effects (ATSDR, 2016). Chronic MRL: Duration of exposure is 365 days or longer. This estimate is expressed in terms of mg/kg-day.

[4] An MADL is the maximum allowable daily level of a reproductive toxicant at which the chemical would have no observable adverse reproductive effect, assuming exposure at 1,000 times that level (OEHHA, 2012). This estimate is expressed in terms of µg/day.

[5] A TDI is an estimate of the intake of a substance, expressed on a body mass basis, to which an individual in a (sub) population may be exposed daily over its lifetime without appreciable health risk (WHO, 2015). This estimate is expressed in terms of mg/kg-day.

- For the 599 chemicals reported in produced water, chronic oral RfVs or OSFs from at least one of the selected federal, state, and international sources were available for 120 chemicals (20%). From the US federal sources alone, chronic oral RfVs were available for 97 chemicals (16%), and OSFs were available for 30 chemicals (5%).

In addition to these chronic values, some of the chemicals also have less-than-chronic oral RfVs available from the sources listed in Table 9-1. Subchronic, acute, or intermediate oral RfVs were identified for 103 chemicals on the consolidated list, including 60 chemicals used in hydraulic fracturing fluid (Appendix Table G-1d), and 73 chemicals reported in produced water (Appendix Table G-2d). The majority of these chemicals also had chronic oral RfVs available, although there were 10 chemicals that had less-than-chronic oral RfVs but lacked a chronic oral RfV. All of these less-than-chronic RfVs were found on the PPRTV, ATSDR, or HHBP databases. As stated above, chronic values more protective of human health than less-than-chronic values, and are generally preferred for risk assessment. These less-than-chronic values are therefore not discussed further in this report, but are provided in Appendix G as supporting information.

Of the 1,606 chemicals identified by EPA, 207 (13%) had a qualitative cancer classification available from at least one of the sources listed in Table 9-1, which include IRIS, PPRTV, IARC, and RoC. These classifications are based on the weight-of-evidence (WOE) that a chemical causes cancer in humans. Of these 207 chemicals:

- 21 were reported by at least one source to be a known carcinogen in humans.
- 66 were reported by at least one source to be a probable or possible carcinogen in humans. These chemicals have been demonstrated to be carcinogenic in animal models, but have limited or insufficient data to adequately assess carcinogenicity in humans.
- 117 were reported to be not classifiable as to carcinogenicity in humans. These chemicals have been evaluated by at least one of these sources for their potential to cause cancer, but had inadequate evidence from human exposure and animal studies to assess carcinogenic potential.
- 3 were reported as not likely to be a human carcinogen.

The complete list of chemicals with qualitative cancer classifications are shown in Appendix Table G-1e (chemicals in hydraulic fracturing fluids) and Appendix Table G-2e (chemicals in produced water).

9.4.2 Estimating Toxicity Using Quantitative Structure Activity Relationship (QSAR) Modeling

Because the majority of chemicals identified in this report do not have RfVs and/or OSFs from the selected sources, it is likely that risk assessors at the local and regional level may turn to alternative sources of toxicological information. One potential resource is QSAR modeling software, which is able to provide estimates or predictions of toxicity based on chemical structure. A key advantage to QSAR models is that they are able to rapidly and inexpensively estimate toxicity values for chemicals. A disadvantage is that QSAR estimates may be of higher uncertainty and less reliable than values generated using traditional toxicological methods. However, because they increase the available pool of toxicity information, QSAR estimates may be a useful resource for risk assessors that are faced with evaluating potential exposures to data-poor chemicals.

A recent study by Yost et al. (2016a) used TOPKAT (Toxicity Prediction by Komputer Assisted Technology) QSAR software to estimate toxicity for the EPA's list of chemicals used in hydraulic fracturing fluids or detected in produced water, and evaluated how effectively these toxicity estimates could be used to rank chemicals based on toxicity. The chemical list examined in this study is the list of 1,173 chemicals published in the external review draft of the EPA's hydraulic fracturing study report (U.S. EPA, 2015d) (Text Box 9-2), so the full list of 1,606 chemicals was not assessed using the QSAR model. TOPKAT is commercially available QSAR software that is able to estimate the rat chronic oral lowest-observed-adverse-effect level (LOAEL), which is the LOAEL measured in a rat model following chronic oral exposure to a chemical.[1]

The authors of this study used TOPKAT to generate rat chronic oral LOAEL estimates for EPA's list of chemicals, and assigned qualitative confidence scores (high, medium, or low) to each estimate based on parameters reported by the model. The authors then examined a list of 48 chemicals that had both a high-confidence TOPKAT LOAEL estimate and a chronic oral reference dose (RfD) from EPA's IRIS database. The authors ranked these 48 chemicals from most toxic to least toxic based on either TOPKAT LOAEL estimate or on IRIS chronic oral RfD, and then used Spearman rank correlation to examine the similarity between these chemical rankings.

Of the 1,173 hydraulic fracturing chemicals, TOPKAT was able to generate toxicity estimates for 515 (44%) of the chemicals, including 453 chemicals that are used in hydraulic fracturing fluids, and 86 chemicals that have been detected in produced water. The authors found a strong and statistically significant correlation between chemical rankings based on high-confidence TOPKAT LOAEL estimates and on IRIS chronic oral RfDs, indicating that high-confidence TOPKAT LOAEL estimates can effectively be used to rank chemicals based on toxicity when experimentally derived toxicity values are not available. Overall, TOPKAT LOAEL estimates were available for 417 chemicals in this study that lack chronic oral RfVs or OSFs from the sources identified by EPA. Of these, 389 were found to be high-confidence estimates.

When available, the high-confidence TOPKAT LOAEL estimates from Yost et al. (2016b) are discussed in this chapter as an additional resource that can be used to rank chemicals based on toxicity. Low- or medium-confidence TOPKAT LOAEL estimates are not shown in this chapter, as the use of these values for chemical ranking has not been validated.

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[1] LOAEL is defined as the lowest exposure level at which there are biologically significant increases in the frequency or severity of adverse effects between the exposed population and its appropriate control group following chronic (lifetime) exposure.

9.4.3 Chemical Data Available from EPA's Aggregated Computations Toxicology Resource (ACToR) Database

An additional tool for obtaining information focused on toxicology and risk assessment is the EPA's ACToR database.[1] ACToR is a large data warehouse developed by the EPA to consolidate large and disparate amounts of public data on chemicals, including data on chemical identity, structure, physicochemical properties, in vitro assay results, and in vitro toxicology data. The primary goals of ACToR are to make information on chemical health effects and exposure potential readily accessible, to characterize chemical toxicological data gaps, and to provide a resource for model building to address data gaps in environmental risk information (Judson et al., 2012).

ACToR contains data on over 500,000 chemicals from over 2,500 data sources, covering many domains including hazard, exposure, risk assessment, risk management, and use. Data sources and collections in ACToR include the US EPA, National Institutes of Health (NIH), the Centers for Disease Control and Prevention (CDC), US Food and Drug Administration (FDA), State Agencies, the European Chemicals Agency (ECHA), corresponding government agencies in Canada (e.g., Health Canada), Europe and Japan, the World Health Organization (WHO), and non-governmental organizations (NGOs). Data within ACToR ranges from the federal RfVs and OSFs discussed in Section 9.3.1, which have undergone extensive peer review, to other toxicity values and study and test results that have undergone little to no peer review.

ACToR organizes these data into several levels of "assays" and "assay categories," which serve to classify data sets according to the nature of the data. For instance, the "Hazard" assay category includes all data that are associated directly or indirectly with toxicology experiments. The "Risk Management" assay category includes regulatory and non-regulatory risk management benchmarks. Considering the diversity and overlapping nature of the data resources within ACToR, a single data set may fall into multiple assay categories (Judson et al., 2012).

We searched the ACToR database for information related to the list of 1,606 hydraulic fracturing-related chemicals. Specifically, we searched within the "Hazard" and "Risk Management" assay categories of ACToR. Results of the query were then filtered to include the assays that are most relevant to chemical exposure via drinking water. These assays were assigned into the following nine data classes: carcinogenicity, dose response values, drinking water criteria, genotoxicity or mutagenicity, hazard identification, LOAEL/NOAEL, RfV, OSF, and water quality criteria.[2]

Of the 1,606 chemicals, it was found that 735 (46%) have some data available within these data classes on ACToR, with the total number of data points found for individual chemicals ranging from 1 to 243. Figure 9-2 shows the percentage of the total 1,606 chemicals that had data available in each of the nine ACToR data classes, and indicates the fraction of those chemicals that also had a chronic oral RfV or OSF available from at least one of the selected sources in Table 9-1. As can be seen in Figure 9-2, 37% of the chemicals had some information on hazard identification, 25% had

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[1] The ACToR database, including the full list of data collections and assays, is available at: http://actor.epa.gov.

[2] NOAEL is defined as the highest exposure level at which there are no biologically significant increases in the frequency or severity of adverse effect between the exposed population and its appropriate control; some effects may be produced at this level, but they are not considered adverse or precursors of adverse effects. Source: U.S. EPA (2011f).

information on carcinogenicity, and 24% had a LOAEL or NOAEL identified. A LOAEL and/or NOAEL identified from a well conducted dose-response study are often considered the minimum data needed for RfV derivation (U.S. EPA, 2002).

Focusing on the 1,433 chemicals that lacked a chronic RfV and/or OSF from the selected sources described in Section 9.3.1, 567 (40%) had available data within at least one of these data classes on ACToR. Thus, ACToR has a significant amount of potentially useful data on chemical hazards, including for some data-poor chemicals, and might help to fill data gaps in the ongoing effort to understand potential hazards of hydraulic fracturing chemicals.

It is outside the scope of this assessment to evaluate the quality and reliability of data within ACToR that has not already undergone peer review. Therefore, with the exception of data from the sources listed in Table 9-1, data from ACToR was not considered in the hazard evaluation presented in this chapter. However, as a potential resource for risk assessors, the tables in this chapter indicate whether a chemical had data available on ACToR.

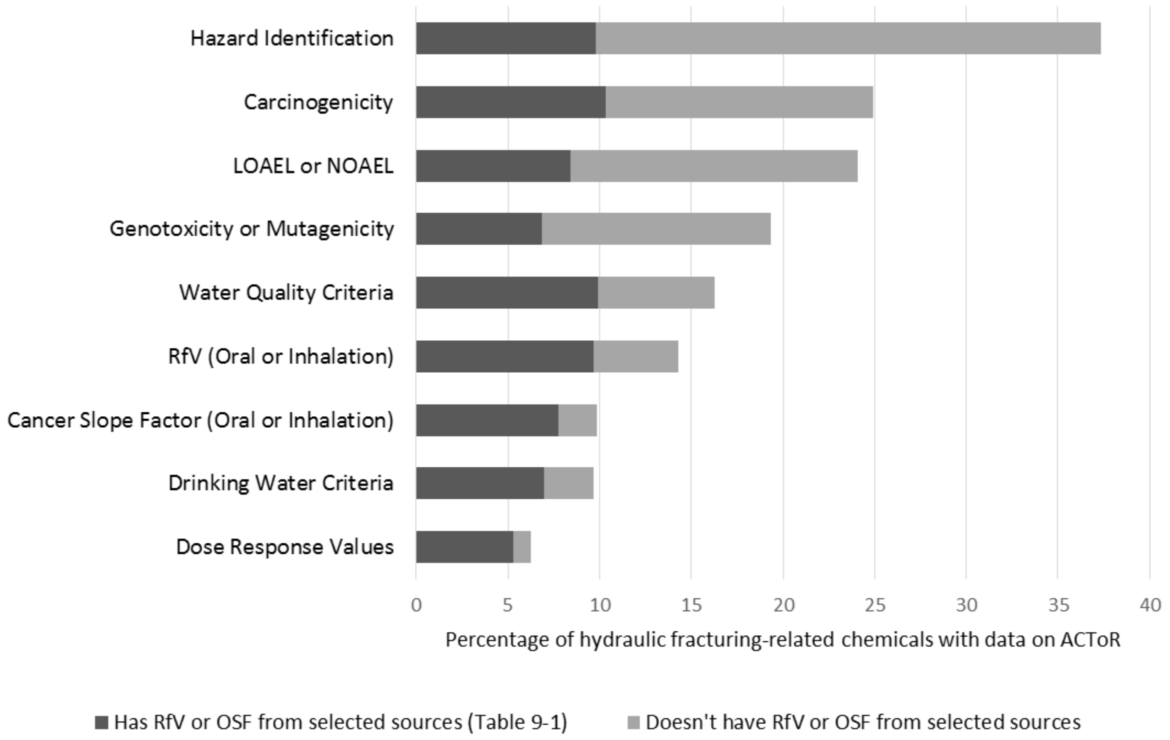

Figure 9-2. Percentage of hydraulic fracturing-related chemicals (out of 1,606 total) with at least one data point in each ACToR data class.

9.4.4 Additional Tools for Hazard Evaluation

In addition to the methods and approaches utilized in this chapter, there are other potential tools and approaches that could be used by stakeholders to prioritize and estimate toxicity of chemicals that have a limited toxicity database. We briefly describe three such approaches in Appendix G (Section G.4): the Threshold of Toxicological Concern (TTC) approach, the Organisation for

Economic Co-operation and Development (OECD) QSAR Toolbox, and the application of data from high throughput screening (HTS) assays. Toxicity predictions from these additional data sources can be either quantitative or qualitative, and may be used to fill and address gaps related to risk assessment.

Although these additional tools may be potentially useful for the evaluation of chemical hazards, they currently have limited utility in this chapter, and are not discussed further. The TTC approach requires an estimate of human intake, which is challenging for hydraulic fracturing-related chemicals, since the potential for human exposure is generally not clear. The OECD QSAR Toolbox is potentially useful for qualitative assessment, and may be useful for quantitative toxicity assessment as its human health hazard and repeated dose toxicity databases expand. HTS assays are an emerging technology, and the potential application of these data for human health risk assessment is not well understood. These tools would be more appropriately applied by stakeholders on a site-specific basis, as preliminary steps to identify potential chemicals of concern.

9.4.5 Physicochemical Properties

As presented in Chapter 5, EPI Suite™ software was used to generate data on the physicochemical properties of the hydraulic fracturing-related chemicals identified by EPA. EPI Suite provides an estimation of physicochemical properties based upon chemical structure, and will additionally provide experimentally measured values for these properties when they are available for a given chemical. For more details on this software and on the use of physicochemical properties for fate and transport estimation, see Chapter 5.

From the total list of 1,606 chemicals associated with hydraulic fracturing, EPI Suite was able to generate data on physicochemical properties for 917 (57%) of the chemicals (Appendix H). This includes 455 chemicals that are reported in hydraulic fracturing fluids, 521 chemicals that have been reported in produced water, and 59 chemicals that were both used in hydraulic fracturing fluids and reported in produced water. The remaining 689 chemicals on EPA's total list lacked the structural information necessary to generate estimates.

In addition to EPI Suite, two other software programs were consulted to generate physicochemical property data for EPA's list of hydraulic fracturing-related chemicals. QikProp (Schrodinger, 2012) and LeadScope (Leadscope Inc., 2012) are commercial products designed primarily as drug development and screening tools, which are able to estimate properties related to chemical fate and transport as well as pharmacokinetics. Properties generated by QikProp and LeadScope are generally more relevant to drug development than to environmental assessment. The properties generated by QikProp and LeadScope were not used in the analysis presented in this report, but will be compiled on the electronic database for EPA's hydraulic fracturing study.

9.4.6 Summary of Available Toxicological and Physicochemical Information for Hydraulic Fracturing Chemicals

Figure 9-3 summarizes the toxicological and physicochemical information that is available for the list of hydraulic fracturing chemicals identified by EPA in this study. This figure also summarizes the availability of data on the occurrence of these chemicals in hydraulic fracturing fluids (frequency of use) or in produced water (measured concentrations).

Availability of toxicological, physicochemical, and occurrence data for 1,606 chemicals

1,084 chemicals used in hydraulic fracturing fluids		599 chemicals detected in produced water
98 chemicals (9%)	**RfVs and OSFs**	120 chemicals (20%)
454 chemicals (42%)	**TOPKAT LOAELs**	119 chemicals (20%)
550 chemicals (51%)	**ACToR database**	259 chemicals (43%)
455 chemicals (42%)	**EPI Suite**	521 chemicals (87%)
688 chemicals (63%) with frequency of use data (FracFocus 1.0)	**Occurrence data**	175 chemicals (29%) with measured concentration data

Figure 9-3. Overall representation of the selected toxicological, physicochemical, and occurrence data available for the 1,606 hydraulic fracturing-related chemicals identified by the EPA.

Overall, there is a clear paucity of chronic oral RfVs and OSFs for this list of chemicals, indicating that the majority of chemicals associated with hydraulic fracturing activity have not undergone significant toxicological assessment. QSAR-based toxicity estimates (TOPKAT LOAELs) were available for a larger number of these chemicals, and were often available for chemicals that lack chronic oral RfVs and OSFs. EPA's ACToR database offers additional toxicological data that may be useful for the hazard evaluation of these chemicals, although the quality and reliability of the data for these chemicals within ACToR was not evaluated here.

9.5 Hazard Identification of Hydraulic Fracturing Chemicals

This section focuses on the hazard identification of subsets of chemicals that were identified as being of particular interest in previous chapters of this report, or which otherwise may be of particular interest to risk assessors. For these chemicals, we summarize what is known about events that may lead to the entry of these chemicals into drinking water resources. We provide examples of recent studies that have reported these chemicals in drinking water resources, including examples in which these chemicals have been reported at concentrations exceeding MCLs. We then summarize the available toxicological data for these chemicals, including chronic oral RfVs, OSFs, cancer classifications, QSAR-based toxicity estimates (TOPKAT LOAELs), and the availability of relevant toxicological information from EPA's ACToR database—and indicate which chemicals are regulated by EPA as drinking water contaminates.

We focused on the following subsets of chemicals:

1. Chemicals used in hydraulic fracturing fluids (Chapter 5)
6. Organic chemicals that may be returned to the surface in produced water, including naturally occurring hydrocarbons such as BTEX (Chapter 7)
7. Inorganic chemicals that may be returned to the surface in produced water, including metals, inorganic ions, and technologically enhanced naturally occurring radioactive material (TENORM) (Chapter 7)
8. Methane in stray gas, which has been reported in drinking water resources in areas of hydraulic fracturing activity (Chapter 6)
9. Disinfection byproducts (DBPs) that may be formed from wastewater constituents (Chapter 8)
10. Banned chemicals reported in produced water, specifically organochlorine pesticides and polychlorinated biphenyls (PCBs).
11. Chemicals on EPA's consolidated list that were reported in both hydraulic fracturing fluids and produced water

The hazard identification for these subsets of chemicals is presented below.

9.5.1 Chemicals Used in Hydraulic Fracturing Fluids

Chapter 5 provided an overview of chemicals that are used in hydraulic fracturing fluids. These chemicals have the potential to enter drinking water resources through events such as spills of hydraulic fracturing fluids, injection of hydraulic fracturing fluids directly into groundwater, and leakoff of fluids into the formation. These chemicals may also persist in produced water, and may enter drinking water resources through spills or releases of produced water or inadequately treated wastewater.

Several recent field studies have detected chemicals that are commonly used in hydraulic fracturing fluids in groundwater near hydraulically fractured wells. In some cases, the origin of the chemicals could be clearly linked to hydraulic fracturing activity. For example, in Killdeer, North Dakota (Section 6.2.2.1), evidence strongly suggests a well blowout during hydraulic fracturing led to the contamination of a drinking water aquifer with tert-butyl alcohol, a degradation product of tert-butyl hydroperoxide used in hydraulic fracturing fluids at that site (U.S. EPA, 2015i). In groundwater monitoring wells in the Pavillion Field in Wyoming, Digiulio and Jackson (2016) reported detections of organic chemicals used in hydraulic fracturing fluids at that site, including 2-

butoxyethanol, naphthalene, 1,2,4-trimethylbenzene, diethylene glycol, methanol, ethanol, and isopropanol, likely as a result of shallow hydraulic fracturing in that region.

Other studies provide indirect evidence that chemical contaminants originated from hydraulic fracturing activity. For example, in the Marcellus Shale in Pennsylvania, Llewellyn et al. (2015) detected trace levels of 2-butoxyethanol in water wells near several hydraulically fractured wells, with multiple lines of evidence suggesting that the chemical originated from a surface spill or leak related to hydraulic fracturing activity. In northeastern Pennsylvania, Drollette et al. (2015) found trace concentrations of known constituents of hydraulic fracturing fluid in private residential groundwater wells, including di(2-ethylhexyl) phthalate, with evidence suggesting that the chemicals originated from known surface spills of hydraulic fracturing fluids. In the Barnett Shale, Texas, a survey of water quality in public and residential wells reported chemicals that are known to be used in hydraulic fracturing fluids, including methanol, ethanol, isopropanol, and propargyl alcohol, but it was not clear whether these chemicals originated from hydraulic fracturing activity or from other potential sources (Hildenbrand et al., 2015).

Table 9-2 shows the list of chemicals that were reported in at least 10% of disclosures nationally in the EPA FracFocus 1.0 project database (excluding water, quartz, and sodium chloride), and shows the noncancer toxicity data (chronic oral RfVs and TOPKAT LOAEL estimates) and ACToR data available for these chemicals.[1] Cancer information is provided in Table 9-3. Nine (26%) of these 34 chemicals have a chronic oral RfV available from at least one of the sources in Table 9-1. Chronic oral RfVs ranged from 0.002 mg/kg-day (propargyl alcohol) to 2 mg/kg-day (methanol and ethylene glycol). Critical effects for these chemicals include kidney/renal toxicity, hepatotoxicity, developmental toxicity (extra cervical ribs), reproductive toxicity, neurotoxicity, and decreased terminal body weight. Only one of these chemicals, sodium chlorite, is regulated in drinking water under the NPDWRs.

Of the 25 chemicals that lack chronic oral RfVs, 11 have high-confidence TOPKAT LOAEL estimates available. Of these, methenamine (~14% of disclosures) had the lowest TOPKAT LOAEL estimate, and choline chloride (~15% of disclosures) had the second lowest. All but five of these chemicals had at least some relevant toxicological data available on EPA's ACToR database.

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[1] The analysis of the FracFocus 1.0 project database presented in this chapter did not exclude chemicals that lacked valid concentration data, in order to present a more inclusive analysis of the potential toxicity of chemicals used in hydraulic fracturing fluids. The chemical list and percent disclosures listed for each chemical is therefore slightly different that those shown in Chapter 5 (Table 5-3), which excluded chemicals lacking valid concentration data.

Table 9-2. Chemicals reported to FracFocus 1.0 from January 1, 2011 to February 28, 2013 in 10% or more disclosures, with the percent of disclosures for which each chemical is reported. Chronic oral RfVs, TOPKAT LOAEL estimates, and availability of ACToR data are shown when available.

Chemicals are ordered in the table, from high to low, based on their number of disclosures in the EPA FracFocus 1.0 project database. Water, quartz, and sodium chloride are excluded from this analysis. Asterisk (*) indicates chemicals that are regulated as drinking water contaminants under the NPDWRs.

			Chronic oral RfV[b]			QSAR	ACToR
Chemical Name	**CASRN**	**% of Disclo-sures[a]**	**RfV (mg/kg-day)**	**Source of RfV**	**Critical effect[c]**	**TOPKAT LOAEL[d] (mg/kg)**	**# of data points[e]**
Methanol	67-56-1	73%	2	IRIS	Extra cervical ribs		122
Distillates, petroleum, hydrotreated light	64742-47-8	67%					4
Hydrochloric acid	7647-01-0	66%					50
Ethylene glycol	107-21-1	47%	2	IRIS	Kidney toxicity	130	102
Isopropanol	67-63-0	46%				81.4	26
Diammonium peroxydisulfate	7727-54-0	44%					11
Guar gum	9000-30-0	39%					2
Sodium hydroxide	1310-73-2	39%					26
Propargyl alcohol	107-19-7	33%	0.002	IRIS	Renal and hepatotoxicity		42
Glutaraldehyde	111-30-8	33%				398	13
Ethanol	64-17-5	31%				59.2	182
Potassium hydroxide	1310-58-3	31%					21
Acetic acid	64-19-7	25%				183	35
Citric acid	77-92-9	24%				55.8	25
2-Butoxyethanol	111-76-2	23%	0.1	IRIS	Hemosiderin deposition in the liver	707	44
Solvent naphtha, petroleum, heavy arom.	64742-94-5	21%					5
Naphthalene	91-20-3	19%	0.02	IRIS	Decreased terminal body weight	67.5	157

			Chronic oral RfV[b]			QSAR	ACToR
Chemical Name	**CASRN**	**% of Disclo-sures[a]**	**RfV (mg/kg -day)**	**Source of RfV**	**Critical effect[c]**	**TOPKAT LOAEL[d] (mg/kg)**	**# of data points[e]**
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	16%				52.4	
Choline chloride	67-48-1	15%				20.8	24
Phenol-formaldehyde resin	9003-35-4	14%					
Carbonic acid, dipotassium salt	584-08-7	14%				137	3
Methenamine	100-97-0	14%				12.3	15
Thiourea, polymer with formaldehyde and 1-phenylethanone	68527-49-1	13%					
1,2,4-Trimethylbenzene	95-63-6	13%	0.01	IRIS	Decreased pain sensitivity	91.5	71
Polyethylene glycol	25322-68-3	13%					5
Polyethylene glycol nonylphenyl ether	9016-45-9	13%					4
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides	68424-85-1	12%	0.44	HHBP	Decreased body weight and weight gain		3
Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy branched	127087-87-0	12%					
Ammonium chloride	12125-02-9	12%					18
Formic acid	64-18-6	11%	0.9	PPRTV	Reproductive toxicity		72
Tetrakis(hydroxy-methyl) phosphonium sulfate	55566-30-8	11%				148	3
Sodium chlorite*	7758-19-2	11%	0.03	IRIS	Neuro-developmental effects		66

			Chronic oral RfV[b]			QSAR	ACToR
Chemical Name	**CASRN**	**% of Disclo-sures[a]**	**RfV (mg/kg-day)**	**Source of RfV**	**Critical effect[c]**	**TOPKAT LOAEL[d] (mg/kg)**	**# of data points[e]**
Alcohols, C12-14, ethoxylated propoxylated	68439-51-0	11%				1450	
Sodium persulfate	7775-27-1	10%					6

CASRN = Chemical Abstract Service Registry Number; RfV = Reference value; IRIS = Integrated Risk Information System; PPRTV = Provisional Peer-Reviewed Toxicity Value; HHBP = Human Health Benchmarks for Pesticides; QSAR = Quantitative structure-activity relationship; TOPKAT = Toxicity Prediction by Komputer Assisted Technology; ACToR = EPA's Aggregated Computational Toxicology Online Resource

[a] The FracFocus frequency of use data presented in this chapter is based on 35,957 FracFocus disclosures that were deduplicated, within the study time period (January 1, 2011 to February 28, 2013), and with ingredients that have a valid CASRN.

[b] Reference value (RfV): An estimate of an exposure for a given duration to the human population (including susceptible subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime. RfVs considered in this analysis include chronic oral reference doses (RfDs) from IRIS, PPRTV, and HHBP; chronic oral minimal risk levels (MRLs) from ATSDR; maximum allowable daily levels (MADLs) from CalEPA; and tolerable daily intake (TDI) from CICAD. See Section 9.4.1.

[c] Critical effect: The first adverse effect, or its known precursor, that occurs to the most sensitive species as the dose rate of an agent increases.

[d] TOPKAT LOAEL: The LOAEL is the lowest exposure level at which there are biologically significant increases in frequency or severity of adverse effects between the exposed population and its appropriate control group. TOPKAT LOAELs were predicted using a QSAR-based software model, as described in Section 9.4.2. Values are rounded to 3 significant figures.

[e] Indicates the total number of data points available for a chemical in the relevant data classes on EPA's ACToR database, as described in Section 9.4.3.

Table 9-3 shows the chemicals reported in at least 10% of disclosures nationally in the EPA FracFocus 1.0 project database that are considered by at least one of the sources in Table 9-1 to be known, probable, or possible human carcinogens. Ethanol is classified as a "carcinogenic to humans" (Group 1) by IARC. Naphthalene is classified by IARC as "possibly carcinogenic to humans" (Group 2B), and is classified by RoC as "reasonably anticipated to be a human carcinogen," while IRIS classifies naphthalene as having inadequate data to assess carcinogenic potential. Neither chemical has an available OSF.

Table 9-3. List of OSFs and qualitative cancer classifications available for all carcinogenic chemicals reported to FracFocus 1.0 from January 1, 2011 to February 28, 2013 in 10% or more disclosures.

Includes all chemicals from Table 9-2 that are classified as known, probable, or possible human carcinogens by at least one of the sources in Table 9-1.

		OSF[a]		Qualitative cancer classification			
Chemical Name	**CASRN**	**OSF (per mg/kg-day)**	**Source of OSF**	**IRIS[b]**	**PPRTV[c]**	**IARC[d]**	**RoC[e]**
Ethanol	64-17-5					1	
Naphthalene	91-20-3			"Data are inadequate to assess human carcinogenic potential"		2B	RAHC

CASRN = Chemical Abstract Service Registry Number; IRIS = Integrated Risk Information System; PPRTV = Provisional Peer Reviewed Toxicity Values; IARC = International Agency for Research on Cancer Monographs; RoC = National Toxicology Program 13th Report on Carcinogens

[a] Oral slope factor (OSF): An upper-bound, approximating a 95% confidence limit, on the increased cancer risk from a lifetime oral exposure to an agent. This estimate, usually expressed in units of proportion (of a population) affected per mg/kg-day, is generally reserved for use in the low dose region of the dose response relationship, that is, for exposures corresponding to risks less than 1 in 100. OSFs considered in this analysis include values from IRIS, PPRTV, HHBP, and CalEPA. See Section 9.4.1.

[b] IRIS assessments use EPA's 1986, 1996, 1999, or 2005 guidelines to establish descriptors for summarizing the weight of evidence as to whether a contaminant is or may be carcinogenic. See glossary in Appendix G for details.

[c] PPRTV assessments use EPA's 1999 guidelines to establish descriptors for summarizing the weight of evidence as to whether a contaminant is or may be carcinogenic. See glossary in Appendix G for details.

[d] The IARC summarizes the weight of evidence as to whether a contaminant is or may be carcinogenic using five weight of evidence classifications: Group 1: Carcinogenic to humans; Group 2A: Probably carcinogenic to humans; Group 2B: Possibly carcinogenic to humans; Group 3: Not classifiable as to its carcinogenicity to humans; Group 4: Probably not carcinogenic to humans. See glossary in Appendix G for details.

[e] The listing criteria in the 13th RoC Document are: Known = Known to be a human carcinogen; RAHC = Reasonably anticipated to be a human carcinogen.

In addition to evaluating chemicals that are frequently used in hydraulic fracturing fluids, we also evaluated the availability of toxicological data for subsets of chemicals that are used less frequently on a national basis (Figure 9-4). For this analysis, we binned the chemicals according to frequency of use as identified from the EPA FracFocus 1.0 project database (>10% of disclosures, 5-10% of disclosures, 1-5% of disclosures, <1% of disclosures, or unknown frequency of use), and evaluated the percentage of chemicals within each bin that have available chronic oral RfVs or OSFs, TOPKAT LOAEL estimates, and relevant data on ACToR. This analysis demonstrates that the availability of chronic oral RfVs and OSFs is low across all of these subsets of chemicals. Proportionately, the availability of chronic oral RfVs, OSFs, and data on ACToR is slightly higher for chemicals that are used in >10% of disclosures, compared to chemicals that are used less frequently.

Of the chemicals on the EPA's list that had frequency of use data available from the EPA FracFocus 1.0 project database, the majority were used in <1% of disclosures (n=480), suggesting that potential exposure to these chemicals is more likely to be a local issue rather than a national issue. Given that the analysis of the EPA FracFocus 1.0 project database presented in this chapter was based on 35,957 disclosures, a chemical used in <1% of wells nationally could still be used in several hundred wells. Chemicals used infrequently on a national basis could still be used more frequently within certain areas or counties, increasing the potential for local exposure to that chemical.

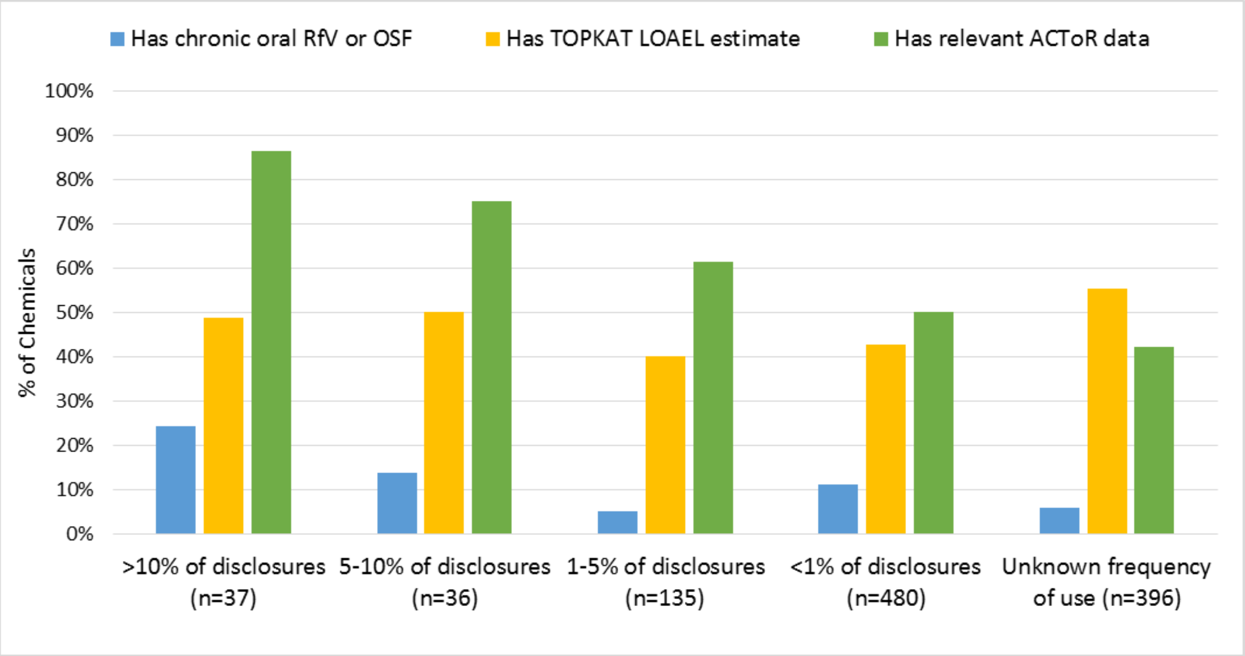

Figure 9-4. Availability of toxicity data (chronic oral RfVs/OSFs, TOPKAT LOAEL estimates, and relevant data on ACToR) for subsets of chemicals used at various frequencies in hydraulic fracturing fluids, as determined based on the number of disclosures in the EPA FracFocus 1.0 project database.

As described in Chapter 5, many of the chemicals used in hydraulic fracturing fluids can be classified as chemical mixtures. Among the most common chemical mixtures on EPA's list of chemicals are petroleum distillates (i.e., hydrocarbon solvents), which are complex mixtures of petroleum hydrocarbons.[1] Two of the most frequently used chemicals in Table 9-2 are petroleum distillates. (Petroleum) hydrotreated light distillates is a mixture of hydrocarbons having carbon numbers predominantly in the range of C9 through C16, and was reported as used in 67% of disclosures in the EPA FracFocus 1.0 project database. Heavy aromatic (petroleum) solvent naphtha is a mixture consisting predominantly of aromatic hydrocarbons in carbon fraction range of C9 through C16, and was reported as used in 21% of disclosures in the EPA FracFocus 1.0 project database. These petroleum distillates lack chronic oral RfVs or OSFs, and have little information available in ACToR. However, a methodology that describes the toxicity and derivation of surrogate

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[1] Total petroleum hydrocarbons (TPH) is a term used to describe a large family of several hundred chemical compounds that originally come from crude oil. TPH is a mixture of chemicals, but they are all made mainly from hydrogen and carbon, called hydrocarbons. TPH are divided into groups of petroleum hydrocarbons that act alike in soil or water. These groups are called petroleum hydrocarbon fractions. Each hydrocarbon fraction contains many individual chemicals. Some chemicals that may be found in TPH are hexane, jet fuels, mineral oils, benzene, toluene, xylenes, naphthalene, and fluorene, as well as other petroleum products and gasoline components. Source: ATSDR (2011).

toxicity values for such mixtures was developed by the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) (Edwards et al., 1997). This indicator/surrogate approach uses a combination of toxicity data and existing RfVs on individual compounds and fraction-specific mixtures. Examples of compounds present in each fraction include: toluene, ethylbenzene, and styrene (C5-C8) and isopropylbenzene (cumene), naphthalene, fluorene, pyrene, and methylnaphthalene (C9-C16). No data was available for consideration for C>16. Applying their methodology, the TPHCWG derived surrogate aliphatic and aromatic oral toxicity values for fractions in the C5-C8, C9-C16, and C17-C35 ranges. For aromatics, the toxicity ranking was C9-C16 and C17-C35 > C5-C8; and for aliphatics, the toxicity ranking was C9-C16 > C17-C35 > C5-C8. As reviewed by the TPHCWG, compounds above C20 are likely not volatile or soluble in groundwater and will remain at the release site and compounds above C35 are typically not likely to be bioavailable by the oral route of exposure. These surrogate toxicity values are not included in EPA's analysis in this report, but this methodology might be useful for risk assessors at sites where these petroleum distillates are used.

We additionally note that several of the frequently used chemicals in Table 9-2 are designated as being "generally recognized as safe" (GRAS) for use in food additives or food contact substances by the U.S. Food and Drug Administration (FDA). This includes hydrochloric acid, guar gum, sodium hydroxide, sodium chloride, potassium hydroxide, acetic acid, citric acid, choline chloride, carbonic acid dipotassium salt, ammonium chloride, and formic acid. Overall, 103 chemicals on EPA's list of chemicals used in hydraulic fracturing fluids have GRAS designations by the FDA. GRAS chemicals may be used by hydraulic fracturing industry operators in an effort to avoid more hazardous chemicals and minimizes concern in the public perception (Loveless et al., 2011). However, GRAS determinations are often specific to certain conditions as expressed in the FDA GRAS Notification Database and therefore do not indicate that the same chemical is safe for use in hydraulic fracturing fluids. For instance, formic acid is considered GRAS for specific use in paper food packaging materials (U.S. FDA, 2016), but has a chronic oral RfD of 0.9 mg/kg-day based on reproductive effects (U.S. EPA, 2010b). For human health risk assessment in areas of hydraulic fracturing activity, hazard and dose-response relations for these chemicals need to be assessed in the context of the use and levels that are likely to be encountered in an appropriate exposure scenario.

9.5.2 Organic Chemicals in Produced Water

Chapter 7 discussed the detection of volatile and semi-volatile organic chemicals in produced water. Many of these chemicals, including the BTEX chemicals and related hydrocarbons, occur naturally in hydrocarbon formations and are characteristic of produced water from oil and gas production wells in both conventional and unconventional reservoirs. Some of these chemicals have anthropogenic origins, such as di(2-ethylhexyl) phthalate, which does not occur naturally but has known use in hydraulic fracturing fluids. Naphthalene is an example of a chemical that may occur naturally in hydrocarbon formations but is also used frequently in hydraulic fracturing fluids (19% of disclosures in the EPA FracFocus 1.0 project database; Table 9-2). These chemicals have the potential to enter drinking water resources through events such as spills of produced water, mechanical integrity failures, infiltration into groundwater from produced water storage pits, and persistence in inadequately treated wastewater.

Several recent field studies have reported these organic constituents in surface water and groundwater in areas of hydraulic fracturing activity. For example, the BTEX chemicals, diesel-range organics, gasoline-range organics, and naphthalene were detected in groundwater monitoring wells in Pavillion Field, Wyoming, likely as a result of legacy contamination from leaking unlined production fluid storage pits (Digiulio and Jackson, 2016). BTEX chemicals were also found to be elevated above their respective MCLs following spills by the oil and gas industry in Colorado, and were reduced to lower concentrations following remediation (Gross et al., 2013). Ferrar et al. (2013) reported mean concentrations of the BTEX chemicals in effluent from a centralized waste treatment (CWT) facility in Pennsylvania ranged from about 2 to 46 µg/L, with significantly lower concentrations observed after oil and gas well operators were asked to stop discharging waste at this facility (Text Box 8-1). In a survey of 500 private and public water supply wells overlying and adjacent to the Barnett Shale in Texas, Hildenbrand et al. (2015) reported that benzene concentrations exceeded their MCL in all 34 wells where benzene was detected, while toluene, ethylbenzene, and xylenes were prevalent at trace levels; the authors noted that BTEX detections occurred at a high rate in an area that houses a large number of underground injection wells for drilling waste disposal, but it was not clear that these chemicals originated from hydraulic fracturing activity or from another potential source.

As there were a large number of organic chemicals identified on EPA's list, this section focuses on the toxicological evaluation of those organic chemicals that had measured concentration data available in Appendix E and had at least some toxicity data available from the sources in Table 9-1, TOPKAT, or ACToR (69 chemicals total).[1] There were an additional 46 organic chemicals that had measured concentration data in Chapter 7 or Appendix E that did not have any toxicity data available. Organic chemicals that lacked concentration data and are not discussed here.

For this subset of 69 organic chemicals, noncancer toxicity values (chronic oral RfVs and high confidence TOPKAT LOAEL estimates) and ACToR data availability are shown in Table 9-4, and cancer information (OSFs and qualitative cancer classifications) are shown in Table 9-5. Chronic oral RfVs were available for 31 of these chemicals, and ranged from 0.001 mg/kg-day (pyridine) to 0.9 mg/kg-day (acetone). Critical effects for these chemicals include kidney/renal toxicity, hepatotoxicity, neurotoxicity, reproductive toxicity (decreased maternal weight gain), developmental toxicity (decreased offspring body weight, fetal toxicity), and decreased terminal body weight. Six of the chemicals in Table 9-4 are regulated as drinking water contaminants under the NPDWRs: the BTEX chemicals (benzene, ethylbenzene, toluene, xylenes), benzo(a)pyrene, and di(2-ethylhexyl) phthalate.

Of the 38 chemicals in Table 9-4 that lack chronic oral RfVs, 10 have high-confidence TOPKAT LOAEL estimates available. Several of these had similarly low LOAEL estimates: benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, and N-nitrosodiphenylamine. Notably, 33 of the chemicals

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[1] Note that chemical names presented in this chapter and in Appendix H sometimes differ from the chemical names presented with the concentration data in Appendix E. This is because Appendix E uses the chemical names provided by the original sources of chemical data, while this chapter and Appendix H use chemical names that were verified by EPA during the curation of the chemical list. See Appendix H for details on the curation of the chemical list.

in Table 9-4 were added to EPA's chemical list after the release of the external review draft (Text Box 9-2), and therefore were not included in the QSAR analysis (Section 9.4.2).

Table 9-4. List of a subset of organic chemicals that have been detected in produced water, with respective chronic oral RfVs, TOPKAT LOAEL estimates, and availability of ACToR data shown when available.

Includes organic chemicals that were identified on the EPA's list of chemicals in produced water (Appendix H) that have measured concentration data available in Appendix E and have at least some toxicity data available from the sources consulted by the EPA. Chemicals are ordered in the table from most toxic to least toxic based on chronic oral RfV. Chemicals without RfVs were ordered based on TOPKAT LOAEL, and then by number of data points on ACToR. *Indicates chemicals that are regulated as drinking water contaminants under the NPDWRs.

		Chronic oral RfV[a]			QSAR estimate	ACToR
Chemical Name	**CASRN**	**RfV (mg/kg-day)**	**Source of RfV**	**Critical Effect[b]**	**TOPKAT LOAEL[c] (mg/day)**	**# of data points[d]**
Pyridine	110-86-1	0.001	IRIS	Increased liver weight	69.5	114
Benzidine	92-87-5	0.003	IRIS	Brain cell vacuolization; liver cell alterations in females		127
2,4-Dichlorophenol	120-83-2	0.003	IRIS	Decreased delayed hypersensitivity response		122
Benzene*	71-43-2	0.004	IRIS	Decreased lymphocyte count	77.6	238
2-Methylnaphthalene	91-57-6	0.004	IRIS	Pulmonary alveolar proteinosis	103	52
1,3,5-Trimethylbenzene	108-67-8	0.01	IRIS	Decreased pain sensitivity	63	76
1,2,4-Trimethylbenzene	95-63-6	0.01	IRIS	Decreased pain sensitivity	91.5	71
Chloroform	67-66-3	0.01	IRIS	Moderate/marked fatty cyst formation in the liver and elevated serum glutamic pyruvic transaminase (SGPT)	47.1	221
Naphthalene	91-20-3	0.02	IRIS	Decreased mean terminal body weight in males	67.5	157
2,4-Dimethylphenol	105-67-9	0.02	IRIS	Clinical signs (lethargy, prostration, and ataxia) and hematological changes	112	88
Di(2-ethylhexyl) phthalate*	117-81-7	0.02	IRIS	Increased relative liver weight	4040	229

		Chronic oral RfV[a]			QSAR estimate	ACToR
Chemical Name	**CASRN**	**RfV (mg/kg-day)**	**Source of RfV**	**Critical Effect[b]**	**TOPKAT LOAEL[c] (mg/day)**	**# of data points[d]**
Pyrene	129-00-0	0.03	IRIS	Kidney effects (renal tubular pathology, decreased kidney weights)	36.1	129
1,4-Dioxane	123-91-1	0.03	IRIS	Liver and kidney toxicity	207	148
Fluoranthene	206-44-0	0.04	IRIS	Nephropathy, increased liver weights, hematological alterations, and clinical effects	44.6	103
Fluorene	86-73-7	0.04	IRIS	Decreased RBC, packed cell volume and hemoglobin	95.1	120
m-Cresol	108-39-4	0.05	IRIS	Decreased body weights and neurotoxicity	123	103
o-Cresol	95-48-7	0.05	IRIS	Decreased body weights and neurotoxicity	229	94
Toluene*	108-88-3	0.08	IRIS	Increased kidney weight	163	188
Diphenylamine	122-39-4	0.1	HHBP	Alterations in clinical chemistry; increased kidney. liver, and spleen weights	30.8	86
Carbon disulfide	75-15-0	0.1	IRIS	Fetal toxicity/ malformations	126	89
Benzyl alcohol	100-51-6	0.1	PPRTV	Effects on survival, growth, and tissue histopathology	210	45
Ethylbenzene*	100-41-4	0.1	IRIS	Liver and kidney toxicity	226	207
Cumene	98-82-8	0.1	IRIS	Increased average kidney weight in female rats	246	101
Acetophenone	98-86-2	0.1	IRIS	General toxicity	274	58
Dibutyl phthalate	84-74-2	0.1	IRIS	Increased mortality	2090	143
Xylenes*	1330-20-7	0.2	IRIS	Decreased body weight, increased mortality	110	174
Benzyl butyl phthalate	85-68-7	0.2	IRIS	Significantly increased liver-to-body weight and liver-to-brain weight ratios		194
Phenol	108-95-2	0.3	IRIS	Decreased maternal weight gain	134	170

		Chronic oral RfV[a]			**QSAR estimate**	**ACToR**
Chemical Name	**CASRN**	**RfV (mg/kg-day)**	**Source of RfV**	**Critical Effect[b]**	**TOPKAT LOAEL[c] (mg/day)**	**# of data points[d]**
Biphenyl	92-52-4	0.5	IRIS	Renal papillary mineralization in male F344 rats		103
Caprolactam	105-60-2	0.5	IRIS	Reduced offspring body weight		39
Acetone	67-64-1	0.9	IRIS	Nephropathy	119	79
Benzo(g,h,i)perylene	191-24-2				29.1	68
Indeno(1,2,3-cd)pyrene	193-39-5				38.6	111
Dibenz(a,h)anthracene	53-70-3				38.9	96
Benzo(b)fluoranthene	205-99-2				39	121
Benzo(k)fluoranthene	207-08-9				39	118
N-Nitrosodiphenylamine	86-30-6				39.4	99
Benzo(a)pyrene*	50-32-8				43	184
Phenanthrene	85-01-8				61.3	69
p-Cresol	106-44-5				95.5	98
Dioctyl phthalate	117-84-0				4740	61
Caffeine	58-08-2					134
Benz(a)anthracene	56-55-3					122
Chrysene	218-01-9					114
2-Mercaptobenzothiazole	149-30-4					95
1,2-Diphenylhydrazine	122-66-7					83
Dimethyl phthalate	131-11-3					79
N-Nitroso-N-methylethylamine	10595-95-6					42
4-(1,1,3,3-Tetramethylbutyl)phenol	140-66-9					30
p-Tert-butylphenol	98-54-4					27
2,6-Di-tert-butylphenol	128-39-2					22
Dimethylphenol	1300-71-6					17
2-Ethylhexyl diphenyl phosphate (Octicizer)	1241-94-7					14
2,5-Cyclohexadiene-1,4-dione	106-51-4					12
Cholesterol	57-88-5					11

Chemical Name	CASRN	Chronic oral RfV[a]			QSAR estimate	ACToR
		RfV (mg/kg-day)	Source of RfV	Critical Effect[b]	TOPKAT LOAEL[c] (mg/day)	# of data points[d]
Benzothiazole	95-16-9					10
Octadecanoic acid	57-11-4					9
Butanoic acid, butyl ester	109-21-7					9
Tetradecanoic acid	544-63-8					7
Triphenyl phosphate	115-86-6					7
Dodecanoic acid	143-07-7					6
Drometrizole	2440-22-4					6
3-(4-Methoxyphenyl)-2-ethylhexylester-2-propenoic acid	5466-77-3					6
2,6-Bis(dimethylethyl)-2,5-cyclohexadiene-1,4-dione	719-22-2					3
Diphenylmethane	101-81-5					3
Isopropyl myristate	110-27-0					2
2-[2-[4-(1,1,3,3-tetramethylbutyl)phen-oxy]ethoxy]-ethanol	2315-61-9					2
Sterane	50-24-8					1
3-(4-Methoxyphenyl)-2-propenoic acid	830-09-1					1

CASRN = Chemical Abstract Service Registry Number; RfV = Reference value; IRIS = Integrated Risk Information System; PPRTV = Provisional Peer-Reviewed Toxicity Value; HHBP = Human Health Benchmarks for Pesticides; QSAR = Quantitative structure-activity relationship; TOPKAT = Toxicity Prediction by Komputer Assisted Technology; ACToR = EPA's Aggregated Computational Toxicology Online Resource

[a] Reference value (RfV): An estimate of an exposure for a given duration to the human population (including susceptible subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime. RfVs considered in this analysis include chronic oral reference doses (RfDs) from IRIS, PPRTV, and HHBP; chronic oral minimal risk levels (MRLs) from ATSDR; maximum allowable daily levels (MADLs) from CalEPA; and tolerable daily intake (TDI) from CICAD. See Section 9.4.1.

[b] Critical effect: The first adverse effect, or its known precursor, that occurs to the most sensitive species as the dose rate of an agent increases.

[c] TOPKAT LOAEL: The LOAEL is the lowest exposure level at which there are biologically significant increases in frequency or severity of adverse effects between the exposed population and its appropriate control group. TOPKAT LOAELs were predicted using a QSAR-based software model, as described in Section 9.4.2. Values are rounded to 3 significant figures.

[d] Indicates the total number of data points available for a chemical in the relevant data classes on EPA's ACToR database, as described in Section 9.4.3.

Of the organic chemicals in produced water listed in Table 9-4, 17 have available OSFs and 23 are classified as known, probable, or possible carcinogens (Table 9-5). Benzidine and benzene were both classified as human carcinogens by IRIS, IARC, and RoC, with benzidine being the most potent carcinogen listed in Table 9-5 (OSF of 230 per mg/kg-day). Benzo(a)pyrine is classified as a human carcinogen by IARC, and as a probable human carcinogen by IRIS. The remaining chemicals were classified as probable or possible human carcinogens.

Table 9-5. List of OSFs and qualitative cancer classifications available for a subset of organic chemicals that have been reported in produced water.

Includes organic chemicals that were identified on EPA's list of chemicals in produced water (Appendix H) that have measured concentration data available in Chapter 7 or Appendix E (Table 9-4) and are classified as known, probable, or possible carcinogens. Chemicals that had OSFs available are ordered in this table from most potent (highest OSF) to least potent (lowest OSF).

		OSFs[a]		**Qualitative Cancer Classifications**			
Chemical Name	**CASRN**	**OSF (per mg/kg-day)**	**Source of OSF**	**IRIS [b]**	**PPRTV [c]**	**IARC [d]**	**RoC [e]**
Benzidine	92-87-5	230	IRIS	A (Human carcinogen)		1	Known
N-Nitroso-N-methylethylamine	10595-95-6	22	IRIS	B2 (Probable human carcinogen)		2B	
Benzo(a)pyrene	50-32-8	7.3	IRIS	B2 (Probable human carcinogen)		1	RAHC
Dibenz(a,h)anthracene	53-70-3	4.1	CalEPA			2A	RAHC
Indeno(1,2,3-cd)pyrene	193-39-5	1.2	CalEPA			2B	RAHC
Benzo(b)fluoranthene	205-99-2	1.2	CalEPA			2B	RAHC
Benzo(k)fluoranthene	207-08-9	1.2	CalEPA			2B	RAHC
1,2-Diphenylhydrazine	122-66-7	0.8	IRIS	B2 (Probable human carcinogen)			RAHC
Benz(a)anthracene	56-55-3	0.7	PPRTV	B2 (Probable human carcinogen)		2B	RAHC
Chrysene	218-01-9	0.12	CalEPA	B2 (Probable human carcinogen)		2B	
1,4-Dioxane	123-91-1	0.1	IRIS	"Likely to be carcinogenic to humans"		2B	RAHC

		OSFs[a]		Qualitative Cancer Classifications			
Chemical Name	**CASRN**	**OSF (per mg/kg-day)**	**Source of OSF**	**IRIS [b]**	**PPRTV [c]**	**IARC [d]**	**RoC [e]**
Benzene	71-43-2	0.015-0.055	IRIS	A (Human carcinogen)		1	Known
Chloroform	67-66-3	0.019	CalEPA	B2 (Probable human carcinogen)		2B	RAHC
Di(2-ethylhexyl) phthalate	117-81-7	0.014	IRIS	B2 (Probable human carcinogen)		2B	RAHC
Ethylbenzene	100-41-4	0.011	CalEPA	D (Not classifiable as to human carcinogenicity)		2B	
Biphenyl	92-52-4	0.008	IRIS	"Suggestive evidence of carcinogenic potential"			
N-Nitrosodiphenyl-amine	86-30-6	0.0049	IRIS	B2 (Probable human carcinogen)		3	
Naphthalene	91-20-3			“Data are inadequate to assess human carcinogenic potential”		2B	RAHC
Cumene	98-82-8			D (Not classifiable as to human carcinogenicity)		2B	RAHC
2-Mercaptobenzo-thiazole	149-30-4					2A	
m-Cresol	108-39-4			C (Possible human carcinogen)			
o-Cresol	95-48-7			C (Possible human carcinogen)	“Data are inadequate for the assessment of human carcinogenic potential”		

Chemical Name	CASRN	OSFs[a]		Qualitative Cancer Classifications			
		OSF (per mg/kg-day)	Source of OSF	IRIS [b]	PPRTV [c]	IARC [d]	RoC [e]
Benzyl butyl phthalate	85-68-7			C (Possible human carcinogen)		3	

CASRN = Chemical Abstract Service Registry Number; IRIS = Integrated Risk Information System; PPRTV = Provisional Peer Reviewed Toxicity Values; HHBP = Human Health Benchmarks for Pesticides; CalEPA = California Environmental Protection Agency; IARC = International Agency for Research on Cancer Monographs; RoC = National Toxicology Program 13th Report on Carcinogens

[a] Oral slope factor (OSF): An upper-bound, approximating a 95% confidence limit, on the increased cancer risk from a lifetime oral exposure to an agent. This estimate, usually expressed in units of proportion (of a population) affected per mg/kg-day, is generally reserved for use in the low dose region of the dose response relationship, that is, for exposures corresponding to risks less than 1 in 100. OSFs considered in this analysis include values from IRIS, PPRTV, HHBP, and CalEPA. See Section 9.4.1.

[b] IRIS assessments use EPA's 1986, 1996, 1999, or 2005 guidelines to establish descriptors for summarizing the weight of evidence as to whether a contaminant is or may be carcinogenic. See glossary in Appendix G for details.

[c] PPRTV assessments use EPA's 1999 guidelines to establish descriptors for summarizing the weight of evidence as to whether a contaminant is or may be carcinogenic. See glossary in Appendix G for details.

[d] The IARC summarizes the weight of evidence as to whether a contaminant is or may be carcinogenic using five weight of evidence classifications: Group 1: Carcinogenic to humans; Group 2A: Probably carcinogenic to humans; Group 2B: Possibly carcinogenic to humans; Group 3: Not classifiable as to its carcinogenicity to humans; Group 4: Probably not carcinogenic to humans. See glossary in Appendix G for details.

[e] The listing criteria in the 13th RoC Document are: Known = Known to be a human carcinogen; RAHC = Reasonably anticipated to be a human carcinogen.

9.5.3 Inorganic Chemicals and TENORM in Produced Water

Chapter 7 discussed the detection of inorganic constituents such as metals, inorganic ions, and TENORM in produced water. Examples include barium, cadmium, chromium, copper, lead, manganese, nickel, zinc, and radium. In general, these chemicals are naturally occurring, and are characteristic of produced water from both conventional and unconventional reservoirs. These chemicals have the potential to enter drinking water resources through events such as spills of produced water, mechanical integrity failures, infiltration into groundwater from produced water storage pits, and persistence in inadequately treated wastewater.

The entry of inorganic constituents of produced water into drinking water resources has been documented in numerous studies. In Pennsylvania, elevated levels of barium and strontium have been observed in CWT effluent (PA DEP, 2015a), with effluent concentrations dropping after oil and gas well operators were asked to stop discharging waste at this facility (see Text Box 8-1 for details on temporal trends in wastewater management in Pennsylvania). Likewise, effluent concentrations at two publicly owned treatment words (POTWs) that had accepted Marcellus wastewater were found to have lower concentrations of bromide, chloride, barium, strontium, and sulfate after oil and gas well operators were asked to stop discharging waste at this facility in May 2011 (Ferrar et al., 2013). Effluents from POTWs and CWTs that handle Marcellus Shale wastewater have been found to have levels of radium-226 and radium-228 that exceed the MCL for radium and are significantly higher than typical background levels of radium in river water (PA DEP, 2015b). Radium-226 and radium-228 have been demonstrated to accumulate in sediments near the outfalls of CWTs and of POTWs that handle oil and gas wastewater from CWTs (PA DEP, 2015b; Warner et al., 2013a), and in sediments receiving effluent from landfills that accept oil and gas wastes (PA DEP, 2015b). In West Virginia, water samples collected downstream of a hydraulic fracturing wastewater injection facility had elevated specific conductance and total dissolved solids, elevated bromide, chloride, sodium, barium, strontium, and lithium concentrations, and different strontium isotope ratios compared to those found in upstream, background waters (Akob et al., 2016). In a survey of 500 groundwater wells overlying and adjacent to the Barnett Shale in Texas, Hildenbrand et al. (2015) reported a variety of metals and anions that are known produced water constituents at concentrations that sometimes exceeded primary or secondary MCLs, health advisory levels, or other suggested levels as provided in the EPA Drinking Water Standards, although it was not clear that these chemicals originated from nearby hydraulic fracturing activity or from other potential sources.

For the inorganic chemicals that were identified in produced water on EPA's chemical list, noncancer toxicity values (chronic oral RfVs) and ACToR data availability for these chemicals are shown in Table 9-6, and cancer information (OSFs and qualitative cancer classifications) are shown in Table 9-7. As shown in Table 9-6, chronic oral RfVs were available for 26 of these chemicals, ranging from 0.00002 mg/kg-day (phosphorus) to 1.6 mg/kg-day (nitrate). Critical effects for these metals include neurotoxicity, developmental and liver toxicity, hyperpigmentation and keratosis of the skin, and decrements in blood copper status and enzyme activity. Nineteen of the inorganic chemicals in Table 9-6 are regulated as drinking water contaminants under the NPDWR.

All but one of these inorganic chemicals had at least some relevant data available on EPA's ACToR database. However, none of the inorganic chemicals have TOPKAT LOAEL estimates available, as this QSAR model is only able to generate estimates for organic chemicals (Section 9.4.2).

Table 9-6. List of inorganics and TENORM reported in produced water, and respective chronic oral RfVs and OSFs when available.

Includes inorganic chemicals that were identified on EPA's list of chemicals in produced water (Appendix H). Chemicals are ordered from most toxic to least toxic based on chronic oral RfV. Chemicals without chronic oral RfVs were ordered in terms of the number of data points on ACToR. *Indicates chemicals are regulated as drinking water contaminants under the NPDWR.

		Chronic oral RfVs[a]			ACToR
Chemical Name	CASRN	RfV (mg/kg-day)	Source of RfV	Critical effect[b]	# of data points[c]
Phosphorus	7723-14-0	0.00002	IRIS	Parturition mortality; forelimb hair loss	113
Vanadium	7440-62-2	0.00007	PPRTV	Kidney histopathology	76
Arsenic*	7440-38-2	0.0003	IRIS	Hyperpigmentation and vascular complications	243

Chemical Name	CASRN	Chronic oral RfVs[a]			ACToR
		RfV (mg/kg-day)	Source of RfV	Critical effect[b]	# of data points[c]
Cobalt	7440-48-4	0.0003	PPRTV	Decreased iodine uptake	76
Antimony*	7440-36-0	0.0004	IRIS	Hematological; alterations in glucose and cholesterol	163
Cadmium*	7440-43-9	0.0005	IRIS	Proteinuria	230
Beryllium*	7440-41-7	0.002	IRIS	Intestinal lesions	186
Mercury	7439-97-6	0.002	CICAD	Renal toxicity	177
Lithium	7439-93-2	0.002	PPRTV	Adverse effects in multiple organ systems	43
Chromium (VI)	18540-29-9	0.003	IRIS	None reported	120
Selenium*	7782-49-2	0.005	IRIS	Clinical selenosis	232
Silver	7440-22-4	0.005	IRIS	Argyria	120
Molybdenum	7439-98-7	0.005	IRIS	Increased uric acid levels	73
Iodine	7553-56-2	0.01	CICAD		27
Nitrite*	14797-65-0	0.1	IRIS	Methemoglobinemia	109
Chlorine	7782-50-5	0.1	IRIS	No adverse effect level	116
Manganese	7439-96-5	0.14	IRIS	Central nervous system (CNS) effects	128
Barium*	7440-39-3	0.2	IRIS	Nephropathy	167
Boron	7440-42-8	0.2	IRIS	Decreased fetal weight (developmental)	93
Zinc	7440-66-6	0.3	IRIS	Decreases in erythrocyte Cu, Zn-superoxide dismutase (ESOD) activity in humans	163
Lead*	7439-92-1	0.5 µg/day [d]	CalEPA	Reproductive Toxicity	168
Strontium	7440-24-6	0.6	IRIS	Rachitic bone	67
Iron	7439-89-6	0.7	PPRTV	Adverse gastrointestinal effects	73
Aluminum	7429-90-5	1	PPRTV	Neurotoxicity	88
Chromium (III)	16065-83-1	1.5	IRIS	No effects observed	71

		Chronic oral RfVs[a]			ACToR
Chemical Name	**CASRN**	**RfV (mg/kg-day)**	**Source of RfV**	**Critical effect[b]**	**# of data points[c]**
Nitrate*	14797-55-8	1.6	IRIS	Clinical signs of methemoglobinemia in excess of 10%	130
Nickel	7440-02-0				181
Copper*	7440-50-8				163
Thallium*	7440-28-0				136
Chromium	7440-47-3				125
Uranium-238*	7440-61-1				100
Ammonia	7664-41-7				90
Zirconium	7440-67-7				55
Alpha particle*	12587-46-1				55
Fluoride*	16984-48-8				53
Radium*	7440-14-4				52
Beta particle*	12587-47-2				51
Magnesium	7439-95-4				40
Tin	7440-31-5				40
Chloride	16887-00-6				32
Sodium	7440-23-5				31
Sulfate	14808-79-8				27
Potassium	7440-09-7				25
Titanium	7440-32-6				25
Calcium	7440-70-2				24
Radium-226*	13982-63-3				13
Radium-228*	15262-20-1				11
Sulfide	18496-25-8				11
Caesium	7440-46-2				7
Caesium-137	10045-97-3				6
Silicon	7440-21-3				5
Rubidium	7440-17-7				5

Chemical Name	CASRN	Chronic oral RfVs[a]			ACToR
		RfV (mg/kg-day)	Source of RfV	Critical effect[b]	# of data points[c]
Bromide	24959-67-9				2
Sulfite	14265-45-3				1
Uranium-235*	15117-96-1				1
Octasulfur	10544-50-0				

CASRN = Chemical Abstract Service Registry Number; RfV = Reference value; IRIS = Integrated Risk Information System; PPRTV = Provisional Peer-Reviewed Toxicity Value; CalEPA = California Environmental Protection Agency; CICAD = Concise International Chemical Assessment Documents; ACToR = EPA's Aggregated Computational Toxicology Online Resource

[a] Reference value (RfV): An estimate of an exposure for a given duration to the human population (including susceptible subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime. RfVs considered in this analysis include chronic oral reference doses (RfDs) from IRIS, PPRTV, and HHBP; chronic oral minimal risk levels (MRLs) from ATSDR; maximum allowable daily levels (MADLs) from CalEPA; and tolerable daily intake (TDI) from CICAD. See Section 9.4.1.

[b] Critical effect: The first adverse effect, or its known precursor, that occurs to the most sensitive species as the dose rate of an agent increases.

[c] Indicates the total number of data points available for a chemical in the relevant data classes on EPA's ACToR database, as described in Section 9.4.3.

[d] CalEPA MADLs are in units of μg/day, while all other chronic oral RfVs in this table are in units of mg/kg-day.

OSFs were available for 4 of the inorganic chemicals reported in produced water, and 14 are classified as known or probable carcinogens (Table 9-7). OSFs ranged from 15 per mg/kg-day for cadmium to 0.0085 mg/kg-day for lead. Chromium (VI), arsenic, alpha particle, beta particle, radium-226, and radium-288 are all classified as known human carcinogens by all sources reporting in this table. Beryllium and cadmium are both classified as known human carcinogens by IARC and NTP, and as probable human carcinogens by EPA. Lead, cobalt, nickel, nitrate, and nitrite are classified by these sources as possible or probable human carcinogens.

Table 9-7. List of qualitative cancer classifications available for inorganics and NORM that were reported in produced water.

Includes inorganic chemicals that were identified on EPA's list of chemicals in produced water (Appendix H) that classified as known, probable, or possible carcinogens by at least one of the sources in Table 9-1. Chemicals that had OSFs available are ordered in this table from most potent (highest OSF) to least potent (lowest OSF).

Chemical Name	CASRN	OSF[a]		Qualitative Cancer Classifications			
		OSF (per mg/kg-day)	Source of OSF	IRIS[b]	PPRTV[c]	IARC[d]	RoC[e]
Cadmium	7440-43-9	15	CalEPA	B1 (Probable human carcinogen)		1	Known
Arsenic	7440-38-2	1.5	IRIS	A (Human carcinogen)		1	Known

		OSF[a]		Qualitative Cancer Classifications			
Chemical Name	**CASRN**	**OSF (per mg/kg-day)**	**Source of OSF**	**IRIS[b]**	**PPRTV[c]**	**IARC[d]**	**RoC[e]**
Chromium (VI)	18540-29-9	0.5	CalEPA	Inhaled: A (Human carcinogen) Oral: D (Not classifiable as to human carcinogenicity)		1	Known
Lead	7439-92-1	0.0085	CalEPA	B2 (Probable human carcinogen)		2B	RAHC
Alpha particle	12587-46-1					1	
Beryllium	7440-41-7			B1 (Probable human carcinogen)		1	Known
Beta particle	12587-47-2					1	
Radium	7440-14-4					1	
Radium-226	13982-63-3					1	
Radium-228	15262-20-1					1	
Cobalt	7440-48-4				Likely to be carcinogenic to humans	2B	
Nickel	7440-02-0					2B	RAHC
Nitrate	14797-55-8					2A	
Nitrite	14797-65-0					2A	

CASRN = Chemical Abstract Service Registry Number; IRIS = Integrated Risk Information System; PPRTV = Provisional Peer Reviewed Toxicity Values; HHBP = Human Health Benchmarks for Pesticides; CalEPA = California Environmental Protection Agency; IARC = International Agency for Research on Cancer Monographs; RoC = National Toxicology Program 13th Report on Carcinogens

[a] Oral slope factor (OSF): An upper-bound, approximating a 95% confidence limit, on the increased cancer risk from a lifetime oral exposure to an agent. This estimate, usually expressed in units of proportion (of a population) affected per mg/kg-day, is generally reserved for use in the low dose region of the dose response relationship, that is, for exposures corresponding to risks less than 1 in 100. OSFs considered in this analysis include values from IRIS, PPRTV, HHBP, and CalEPA. See Section 9.4.1.

[b] IRIS assessments use EPA's 1986, 1996, 1999, or 2005 guidelines to establish descriptors for summarizing the weight of evidence as to whether a contaminant is or may be carcinogenic. See glossary in Appendix G for details.

[c] PPRTV assessments use EPA's 1999 guidelines to establish descriptors for summarizing the weight of evidence as to whether a contaminant is or may be carcinogenic. See glossary in Appendix G for details.

[d] The IARC summarizes the weight of evidence as to whether a contaminant is or may be carcinogenic using five weight of evidence classifications: Group 1: Carcinogenic to humans; Group 2A: Probably carcinogenic to humans; Group 2B: Possibly carcinogenic to humans; Group 3: Not classifiable as to its carcinogenicity to humans; Group 4: Probably not carcinogenic to humans. See glossary in Appendix G for details.

[e] The listing criteria in the 13th RoC Document are: Known = Known to be a human carcinogen; RAHC = Reasonably anticipated to be a human carcinogen.

9.5.4 Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs) in Produced Water

EPA's list of chemicals detected in produced water includes several chemicals that have been banned from commercial use: specifically, organochlorine pesticides and Aroclor 1248, which is a commercial PCB mixture. These chemicals were reported by two of the sources used to compile EPA's chemical list (Appendix H): a technical report prepared by the Gas Technology Institute for the Marcellus Shale Coalition (MSC), which is a drilling industry trade group (Hayes, 2009); and a report by the New York State Department of Environmental Conservation (NYSDEC), which referenced the results of the MSC study (NYSDEC, 2011). These chemicals are listed in Table 9-8 along with their respective noncancer toxicity values (chronic oral RfVs and TOPKAT LOAELs) and availability of relevant toxicological information on ACToR. Cancer information (OSF or qualitative cancer classification) for these chemicals is listed in Table 9-9.

There is uncertainty about why organochlorine pesticides and PCBs were detected, as they are not used in hydraulic fracturing fluids and are not naturally occurring. The MSC study stated the banned substances were detected sporadically and at low concentrations, and suggested they may have originated from laboratory contamination. The NYSDEC report suggested that the banned substances may have been introduced to the shale or the water as a result of drilling or fracturing operations. It is possible that these chemicals were present as legacy contaminants in the source water used for hydraulic fracturing fluid formulation, or were mobilized from the environment near the well. Although these chemicals are notable for their high toxicity, the extent to which these chemicals may be detected in produced water from other hydraulic fracturing sites is not clear.

Chronic oral RfVs for these organochlorine pesticides ranged from 0.000013 mg/kg-day (Heptachlor epoxide) to 0.0005 mg/kg-day (heptachlor), and were all based on liver toxicity. All of these pesticides had TOPKAT LOAEL estimates, and all have relevant data available within EPA's ACToR database.). Heptachlor epoxide, heptachlor, and lindane are regulated as drinking water contaminants under the NPDWR.

Table 9-8. List of organochlorine pesticides and PCBs that were reported in produced water, and their respective chronic oral RfVs, TOPKAT LOAEL estimates, and availability of data in EPA's ACToR database.

Includes banned chemicals that were identified on EPA's list of chemicals in produced water (Appendix H). Chemicals are ordered from most toxic to least toxic based on chronic oral RfV. Chemicals without chronic oral RfVs were ordered in terms of the number of data points on ACToR. *Indicates chemicals that are regulated as drinking water contaminants under the NPDWRs.

		Chronic oral RfV[a]			QSAR	ACToR
Chemical Name	**CASRN**	**RfV (mg/kg-day)**	**Source of RfV**	**Critical effect[b]**	**TOPKAT LOAEL[c] (mg/kg)**	**# of data points[d]**
Heptachlor epoxide*	1024-57-3	0.000013	IRIS	Increased liver-to-body weight ratio in both males and females	0.595	168
Aldrin	309-00-2	0.00003	IRIS	Liver toxicity	0.743	166

		Chronic oral RfV[a]			QSAR	ACToR
Chemical Name	**CASRN**	**RfV (mg/kg-day)**	**Source of RfV**	**Critical effect[b]**	**TOPKAT LOAEL[c] (mg/kg)**	**# of data points[d]**
Dieldrin	60-57-1	0.00005	IRIS	Liver lesions	0.442	167
Lindane*	58-89-9	0.0003	IRIS	Liver and kidney toxicity	23.9	238
Heptachlor*	76-44-8	0.0005	IRIS	Liver weight increases in males	0.927	203
beta-Hexachlorocyclohexane	319-85-7				23.9	88
delta-Hexachlorocyclohexane	319-86-8				23.9	22
Aroclor 1248	12672-29-6				21.87	35
p,p'-DDE	72-55-9				14.6	103
Endrin aldehyde	7421-93-4				4.09	27
Endosulfan I	959-98-8				2.27	32
Endosulfan II	33213-65-9				2.27	32

CASRN = Chemical Abstract Service Registry Number; RfV = Reference value; IRIS = Integrated Risk Information System; QSAR = Quantitative structure-activity relationship; TOPKAT = Toxicity Prediction by Komputer Assisted Technology; ACToR = EPA's Aggregated Computational Toxicology Online Resource

[a] Reference value (RfV): An estimate of an exposure for a given duration to the human population (including susceptible subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime. RfVs considered in this analysis include chronic oral reference doses (RfDs) from IRIS, PPRTV, and HHBP; chronic oral minimal risk levels (MRLs) from ATSDR; maximum allowable daily levels (MADLs) from CalEPA; and tolerable daily intake (TDI) from CICAD. See Section 9.4.1.

[b] Critical effect: The first adverse effect, or its known precursor, that occurs to the most sensitive species as the dose rate of an agent increases.

[c] TOPKAT lowest-observed-adverse-effect level (LOAEL): The LOAEL is the lowest exposure level at which there are biologically significant increases in frequency or severity of adverse effects between the exposed population and its appropriate control group. TOPKAT LOAELs were predicted using a QSAR-based software model, as described in Section 9.4.2.

[d] Indicates the total number of data points available for a chemical in the relevant data classes on EPA's ACToR database, as described in Section 9.4.3.

OSFs were available for 7 of the organochlorine pesticides that are classified as known, probable, or possible human carcinogens (Table 9-9). OSFs ranged from 17 per mg/kg-day (aldrin) to 0.34 per mg/kg-day (p,p'-DDE). Aldrin, dieldrin, heptachlor epoxide, heptachlor, beta-hexachlorocyclohexane, and p,p'-DDE are classified as probable or possible carcinogens. Lindane is classified as a known carcinogen by IARC, and as "reasonably anticipated to be a human carcinogen" by RoC.

Table 9-9. List of OSFs and qualitative cancer classifications available for organochlorine pesticides reported in produced water.

Includes banned chemicals that were identified on EPA's list of chemicals in produced water (Appendix H) that are classified as known, probable, or possible carcinogens by at least one of the sources in Table 9-1. Chemicals are ordered in this table from most potent (highest OSF) to least potent (lowest OSF).

		OSF[a]		Qualitative cancer classifications			
Chemical Name	**CASRN**	**OSF (per mg/kg-day)**	**Source of OSF**	**IRIS[b]**	**PPRTV[c]**	**IARC[d]**	**RoC[e]**
Aldrin	309-00-2	17	IRIS	B2 (Probable human carcinogen)		3	
Dieldrin	60-57-1	16	IRIS	B2 (Probable human carcinogen)		3	
Heptachlor epoxide	1024-57-3	9.1	IRIS	B2 (Probable human carcinogen)			
Heptachlor	76-44-8	4.5	IRIS	B2 (Probable human carcinogen)		2B	
beta-Hexachlorocyclohexane	319-85-7	1.8	IRIS	C (Possible human carcinogen)			
Lindane	58-89-9	1.1	CalEPA			1	RAHC
p,p'-DDE	72-55-9	0.34	IRIS	B2 (Probable human carcinogen)			

CASRN = Chemical Abstract Service Registry Number; IRIS = Integrated Risk Information System; CalEPA = California Environmental Protection Agency; IARC = International Agency for Research on Cancer Monographs; RoC = National Toxicology Program 13th Report on Carcinogens

[a] Oral slope factor (OSF): An upper-bound, approximating a 95% confidence limit, on the increased cancer risk from a lifetime oral exposure to an agent. This estimate, usually expressed in units of proportion (of a population) affected per mg/kg-day, is generally reserved for use in the low dose region of the dose response relationship, that is, for exposures corresponding to risks less than 1 in 100. OSFs considered in this analysis include values from IRIS, PPRTV, HHBP, and CalEPA. See Section 9.4.1.

[b] IRIS assessments use EPA's 1986, 1996, 1999, or 2005 guidelines to establish descriptors for summarizing the weight of evidence as to whether a contaminant is or may be carcinogenic. See glossary in Appendix G for details.

[c] PPRTV assessments use EPA's 1999 guidelines to establish descriptors for summarizing the weight of evidence as to whether a contaminant is or may be carcinogenic. See glossary in Appendix G for details.

[d] The IARC summarizes the weight of evidence as to whether a contaminant is or may be carcinogenic using five weight of evidence classifications: Group 1: Carcinogenic to humans; Group 2A: Probably carcinogenic to humans; Group 2B: Possibly carcinogenic to humans; Group 3: Not classifiable as to its carcinogenicity to humans; Group 4: Probably not carcinogenic to humans. See glossary in Appendix G for details.

[e] The listing criteria in the 13th RoC Document are: Known = Known to be a human carcinogen; RAHC = Reasonably anticipated to be a human carcinogen.

9.5.5 Methane in Stray Gas

Chapter 6 discussed stray gas as a potential hazard in areas of hydraulic fracturing activity (Text Box 6-3). Stray gas refers to the phenomenon of natural gas (primarily methane, plus lesser amounts of ethane) migrating into shallow groundwater, into water wells, or to the surface (e.g., cellars, streams, or springs). As discussed in Chapter 6, some studies indicate an association between hydraulic fracturing activity and elevated methane concentrations in drinking water, while other studies did not find such a correlation. Potential pathways for migration of stray gas into aquifers include pathways along production wells with casing and/or cement issues, through naturally existing fractures, through induced fractures, or via a route that is some combination of these pathways.

Although ingestion of methane is not considered to be toxic, it has the potential to pose a physical hazard. Methane can accumulate to explosive levels when allowed to exsolve (degas) from groundwater in closed environments. High concentrations of methane may also displace oxygen and act as an asphyxiant (NIOSH, 2000), potentially causing suffocation, loss of consciousness, or symptoms such as headache and nausea. Methane is not a regulated drinking water contaminant. Methane does not have an RfV, OSF, or qualitative cancer classification available from any of the sources consulted by EPA, and did not have a high-confidence TOPKAT LOAEL estimate. Information on methane is available within the ACToR database.

9.5.6 Disinfection Byproducts (DBPs) Formed from Wastewater Constituents

Some of the inorganic constituents of hydraulic fracturing produced water, including chloride, bromine, iodine, and ammonium, can contribute to the formation of DBPs during wastewater treatment (Harkness et al., 2015; Parker et al., 2014). The entry of these constituents into drinking water resources—e.g., as a result of wastewater spills or from the discharge of inadequately treated hydraulic fracturing wastewater—can result in DBPs in finished drinking water from downstream drinking water treatment plants (States et al., 2013). DBPs may also be formed when hydraulic fracturing produced water is treated at a centralized or publicly owned treatment works, and may reach drinking water resources when the treated wastewater is discharged to surface water (Hladik et al., 2014). Currently, there are no data available on the concentrations of DBPs in finished drinking water as related to contributions of DBP precursors from hydraulic fracturing wastewater.

Regulated DBPs such as bromate, chlorite, haloacetic acids, and trihalomethanes are a small subset of the full spectrum of DBPs that include other chlorinated and brominated DBPs as well as nitrogenous and iodated DBPs. Long term exposure to these DBPs can result in an increased risk of cancer, anemia, liver and kidney effects, and central nervous system effects. Some of the unregulated DBPs may be more toxic than their regulated counterparts (Harkness et al., 2015; McGuire et al., 2014; Parker et al., 2014). In addition, brominated forms of DBPs are considered to be more cytotoxic, genotoxic, and carcinogenic than chlorinated species based on studies using rodents, various types of human cells, and a salmonella strain containing human P450 genes (McGuire et al., 2014; Parker et al., 2014; States et al., 2013; Krasner, 2009; Richardson et al., 2007). As with brominated DBPs, there is concern that some iodinated forms of DBPs are more cytotoxic and genotoxic than chlorinated species (McGuire et al., 2014; Parker et al., 2014; Krasner, 2009; Richardson et al., 2007), as evidenced by studies involving rodent research and human cell research (Plewa et al., 2010; Plewa and Wagner, 2009; Richardson et al., 2007). The MCLs (mg/L) for the regulated DBPs are: 0.01 for bromate, 1.0 for chlorite, 0.06 for haloacetic acid, and 0.08 for total trihalomethanes.

9.5.7 Chemicals Detected in Multiple Stages of the Hydraulic Fracturing Water Cycle

As mentioned in Section 9.3 above, there were a total of 77 chemicals on EPA's list that were identified as being used in hydraulic fracturing fluids and detected in produced water. The presence of these chemicals within both of these stages of the hydraulic fracturing water cycle may indicate that these chemicals persist after they are injected into the well. However, this is not necessarily the case, as some of these chemicals (e.g., BTEX, naphthalene, metals) also occur naturally in oil and gas reservoirs. Additionally, the EPA's list of chemicals used in hydraulic fracturing fluids and list of chemicals in produced water were compiled from different sets of sources, and does not provide a matched comparison between the chemicals used in hydraulic fracturing fluid and the chemicals present in produced water at a particular site. There may have been other chemicals in present in produced water that were not detected by these studies due to limitations of analytical chemistry. Thus, the EPA's composited chemical list cannot reliably be used to draw conclusions on the persistence of hydraulic fracturing chemicals following well injection.

Of the 77 chemicals identified in both hydraulic fracturing fluids and produced water, 45 have a chronic oral RfV or OSF available from at least one of the sources in Table 9-1. These 45 chemicals and their respective toxicity values are shown in Table 9-10, with frequency of use data from the EPA FracFocus 1.0 project database provided when available. Eleven of these chemicals are regulated as drinking water contaminants.

Table 9-10. List of 45 chemicals on EPA's list that were used in hydraulic fracturing fluids and detected in produced water and have an RfV or OSF available.

Frequency of use data from the EPA FracFocus 1.0 project database is provided when available. Chemicals with available data from the FracFocus 1.0 project database are ordered from high to low based on frequency of use. Chemicals without frequency of use data are ordered from most toxic to least toxic based on chronic oral RfV. *Indicates chemicals that are regulated as drinking water contaminants under the NPDWRs.

			Chronic oral RfVs[b]			OSFs[d]	
Chemical Name	**CASRN**	**% of Disclo-sures[a]**	**RfV (mg/kg-day)**	**Source of RfV**	**Critical Effect[c]**	**OSF (per mg/kg-day)**	**Source of OSF**
Methanol	67-56-1	73%	2	IRIS	Extra cervical ribs		
Ethylene glycol	107-21-1	47%	2	IRIS	Kidney toxicity		
Propargyl alcohol	107-19-7	33%	0.002	IRIS	Renal and hepatotoxicity		
2-Butoxyethanol	111-76-2	23%	0.1	IRIS	Hemosiderin deposition in liver (inhalation study)		
Naphthalene	91-20-3	19%	0.02	IRIS	Decreased mean terminal body weight in males		

Chemical Name	**CASRN**	**% of Disclo-sures**[a]	**Chronic oral RfVs**[b]			**OSFs**[d]	
			RfV (mg/kg-day)	**Source of RfV**	**Critical Effect**[c]	**OSF (per mg/kg-day)**	**Source of OSF**
1,2,4-Trimethylbenzene	95-63-6	13%	0.01	IRIS	Decreased pain sensitivity		
Formic acid	64-18-6	11%	0.9	PPRTV	Reproductive Toxicity		
N,N-Dimethylformamide	68-12-2	9%	0.1	PPRTV	Increase in ALT enzyme and liver weight		
Benzyl chloride	100-44-7	6%	0.002	PPRTV	Cardiotoxicity	0.17	IRIS
1,2-Propylene glycol	57-55-6	4%	20	PPRTV	Reduced RBC counts and hyperglycemia		
Xylenes*	1330-20-7	2%	0.2	IRIS	Decreased body weight, increased mortality		
D-Limonene	5989-27-5	2%	0.1	CICAD	Increased liver weight		
1-Butanol	71-36-3	1%	0.1	IRIS	Hypoactivity and ataxia		
Toluene*	108-88-3	0.7%	0.08	IRIS	Increased kidney weight		
Bis(2-chloroethyl) ether	111-44-4	0.7%				1.1	IRIS
2-(2-Butoxyethoxy)ethanol	112-34-5	0.6%	0.03	PPRTV	Changes in red blood cells (RBC)		
1,3,5-Trimethylbenzene	108-67-8	0.5%	0.01	IRIS	Decreased pain sensitivity		
Cumene	98-82-8	0.5%	0.1	IRIS	Increased average kidney weight in female rats		
Iron	7439-89-6	0.4%	0.7	PPRTV	Adverse gastrointestinal effects		
1,2,3-Trimethylbenzene	526-73-8	0.4%	0.01	IRIS	Decreased pain sensitivity		

Chemical Name	CASRN	% of Disclo-sures[a]	Chronic oral RfVs[b]			OSFs[d]	
			RfV (mg/kg-day)	Source of RfV	Critical Effect[c]	OSF (per mg/kg-day)	Source of OSF
Phenol	108-95-2	0.4%	0.3	IRIS	Decreased maternal weight gain		
Ethylbenzene*	100-41-4	0.4%	0.1	IRIS	Liver and kidney toxicity	0.011	CalEPA
1,4-Dioxane	123-91-1	0.3%	0.03	IRIS	Liver and kidney toxicity	0.1	IRIS
Acetone	67-64-1	0.2%	0.9	IRIS	Nephropathy		
Boron	7440-42-8	0.05%	0.2	IRIS	Decreased fetal weight		
o-Xylene*	95-47-6	0.05%	0.2	ATSDR	Neurotoxicity		
Acetophenone	98-86-2	0.04%	0.1	IRIS	General toxicity		
Quinoline	91-22-5	0.02%				3	IRIS
Dichloromethane*	75-09-2	0.02%	0.006	IRIS	Hepatic effects (hepatic vacuolation, liver foci)	0.002	IRIS
Trimethylbenzene	25551-13-7	0.01%	0.01	IRIS	Decreased pain sensitivity		
Benzene*	71-43-2	0.01%	0.004	IRIS	Decreased lymphocyte count	0.015-0.055	IRIS
Bisphenol A	80-05-7	0.01%	0.05	IRIS	Reduced mean body weight		
Aluminum	7429-90-5	0.003%	1	PPRTV	Neurotoxicity		
Hydrazine	302-01-2	0.003%				3	IRIS
Chlorobenzene*	108-90-7	0.003%	0.02	IRIS	Histopathologic changes in liver		
Arsenic*	7440-38-2		0.0003	IRIS	Hyperpigmentation and vascular complications	1.5	IRIS
Acrolein	107-02-8		0.0005	IRIS	Decreased survival		
Chromium (VI)	18540-29-9		0.003	IRIS	None reported	0.5	CalEPA
Tributyl phosphate	126-73-8		0.01	PPRTV	Occasional salivation	0.009	PPRTV

			Chronic oral RfVs[b]			OSFs[d]	
Chemical Name	**CASRN**	**% of Disclo-sures[a]**	**RfV (mg/kg-day)**	**Source of RfV**	**Critical Effect[c]**	**OSF (per mg/kg-day)**	**Source of OSF**
Di(2-ethylhexyl) phthalate*	117-81-7		0.02	IRIS	Increased relative liver weight	0.014	IRIS
Chlorine	7782-50-5		0.1	IRIS	No adverse effect level		
p-Xylene*	106-42-3		0.2	ATSDR	Neurotoxicity		
Zinc	7440-66-6		0.3	IRIS	Decreases in erythrocyte Cu, Zn-superoxide dismutase (ESOD) activity in humans		
Lead*	7439-92-1		0.5 µg/day [e]	CalEPA	Reproductive toxicity	0.0085	CalEPA
Chromium (III)	16065-83-1		1.5	IRIS			

CASRN = Chemical Abstract Service Registry Number; RfV = Reference value; IRIS = Integrated Risk Information System; PPRTV = Provisional Peer-Reviewed Toxicity Value; HHBP = Human Health Benchmarks for Pesticides; ATSDR = Agency for Toxic Substances and Disease Registry; CalEPA = California Environmental Protection Agency; CICAD = Concise International Chemical Assessment Documents; QSAR = Quantitative structure-activity relationship; TOPKAT = Toxicity Prediction by Komputer Assisted Technology; ACToR = EPA's Aggregated Computational Toxicology Online Resource

[a] The FracFocus frequency of use data presented in this chapter is based on 35,957 FracFocus disclosures that were deduplicated, within the study time period (January 1, 2011 to February 28, 2013), and with ingredients that have a valid CASRN.

[b] Reference value (RfV): An estimate of an exposure for a given duration to the human population (including susceptible subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime. RfVs considered in this analysis include chronic oral reference doses (RfDs) from IRIS, PPRTV, and HHBP; chronic oral minimal risk levels (MRLs) from ATSDR; maximum allowable daily levels (MADLs) from CalEPA; and tolerable daily intake (TDI) from CICAD. See Section 9.4.1.

[c] Critical effect: The first adverse effect, or its known precursor, that occurs to the most sensitive species as the dose rate of an agent increases.

[d] Oral slope factor (OSF): An upper-bound, approximating a 95% confidence limit, on the increased cancer risk from a lifetime oral exposure to an agent. This estimate, usually expressed in units of proportion (of a population) affected per mg/kg-day, is generally reserved for use in the low dose region of the dose response relationship, that is, for exposures corresponding to risks less than 1 in 100. OSFs considered in this analysis include values from IRIS, PPRTV, HHBP, and CalEPA. See Section 9.4.1.

[e] CalEPA MADLs are in units of µg/day, while all other chronic oral RfVs in this table are in units of mg/kg-day.

9.6 Hazard Evaluation of Selected Subsets of Hydraulic Fracturing Chemicals Using Multi-Criteria Decision Analysis (MCDA): Integrating Toxicity, Occurrence, and Physicochemical Data

Based on the information presented in Section 9.5, it is clear that there are a variety of chemicals used in hydraulic fracturing fluids or detected in produced water that are known to be hazardous to human health. However, there are gaps in our understanding of the potential for human exposure to these chemicals. Although there are subsurface and surface pathways by which these chemicals may be introduced into drinking water resources—including spills, leaks, mechanical integrity failures, intersection of the fracture network with groundwater, or discharge of wastewater, as described in previous chapters of this report—there are significant limitations associated with the publicly available data on these potential impacts, and the potential for human exposure has not been systematically characterized. This makes it difficult to determine which chemicals are of the greatest concern for human exposure in drinking water, and creates a challenge for hazard evaluation.

Although exposure assessment data are limited, some of the chemicals identified by EPA have other data available that might provide preliminary insight into relative hazard potential. This includes data on toxicity, frequency of use in hydraulic fracturing fluids, detected concentrations in produced water, and data on physicochemical properties. By integrating these types of data, we can place the severity of potential impacts (i.e., the toxicity of specific chemicals) into the context of factors that affect the likelihood of impacts (i.e., frequency of use, environmental fate and transport).

Multi-criteria decision analysis (MCDA) is one possible approach that can be used to facilitate data integration. MCDA is a well-established decision support tool, which is used to integrate multiple lines of evidence to develop an overall ranking or classification (Hristozov et al., 2014; Mitchell et al., 2013b; Huang et al., 2011; Linkov et al., 2011). Using MCDA, a problem is approached by dividing it into smaller criteria that need to be evaluated; the criteria are each analyzed individually, and then combined to provide an integrated evaluation. This approach is structured yet flexible, and offers a transparent means of combining information to provide weight of evidence and insight into a complex problem. MCDA has gained increasing popularity as an environmental decision-making tool (Huang et al., 2011). A recent publication by Yost et al. (In Press) described the use of an MCDA framework to evaluate the hazard potential of chemicals associated with hydraulic fracturing.

Here, to demonstrate one possible method for exploring the potential hazards of these chemicals, we use an adaptation of the MCDA framework developed by Yost et al. (In Press) to analyze and rank selected subsets of chemicals that have data available.[1] Chemicals were assigned scores based on toxicity, occurrence, and physicochemical properties that describe transport in water. These scores were then combined to develop a relative ranking of chemicals based on hazard potential.

The MCDA scores provide a preliminary evaluation of hazard potential, and serve as a qualitative metric for making comparison between chemicals when exposure assessment data is limited or unavailable. This analysis is not intended to define whether or not a chemical will present a human health hazard or indicate that one chemical is safer than another, and should not be used in place of

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[1] Yost et al. (In Press) used the MCDA framework to analyze and rank the hazards of chemicals used in hydraulic fracturing fluids, using data from the FracFocus 1.0 project database as the metric of occurrence. This chapter uses that same framework for the analysis of chemicals used in hydraulic fracturing fluids. For chemicals detected in produced water, this chapter modifies the MCDA framework by using measured concentration in produced water as the metric of occurrence.

site-specific data on chemical exposures. An overview of the MCDA framework and selection of chemicals for inclusion in the MCDA is described below.

9.6.1 Overview of the MCDA Framework for Hazard Evaluation

The MCDA framework employed in this chapter was designed specifically to fit the scope of EPA's hydraulic fracturing study (Yost et al., In Press). A basic schematic of the model is shown in Figure 9-5, and the methods for assigning scores are outlined below. Under the MCDA framework, each chemical was assigned three scores:

1. A Toxicity Score;
2. An Occurrence Score; and
3. A Physicochemical Properties score.

The three scores were each standardized based on the highest and lowest respective score within the given subset of chemicals, and then summed to develop a Total Hazard Potential Score for each chemical. The Total Hazard Potential Scores reflect a relative ranking of each chemical within the given subset of chemicals, and offer a means of making comparisons between chemicals.

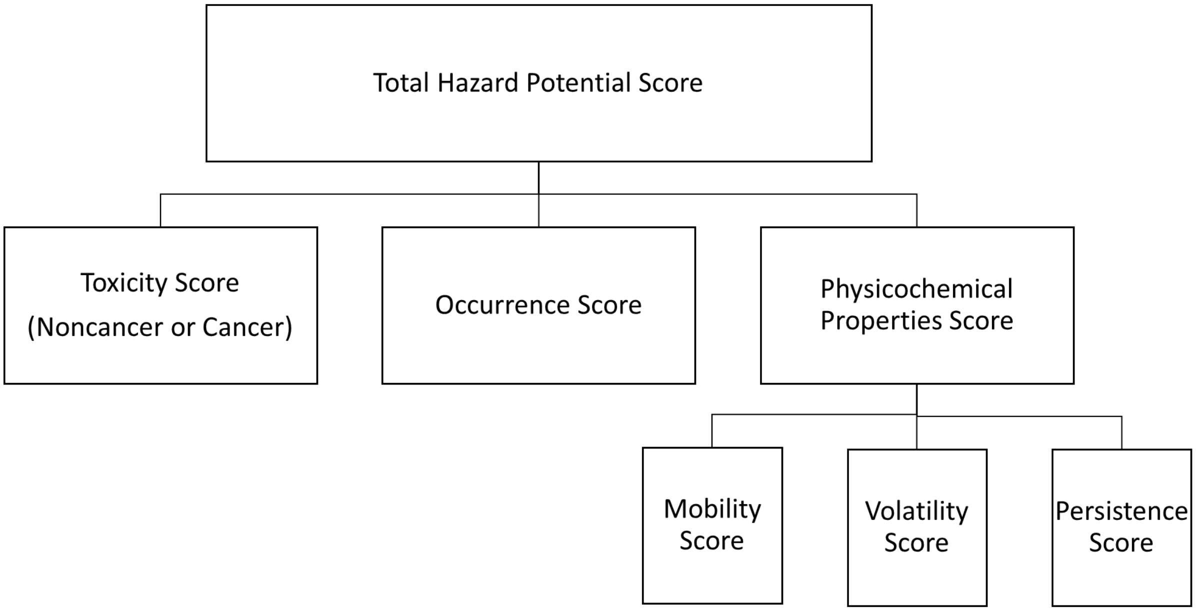

Figure 9-5. Overview of the MCDA framework for hazard evaluation.
Source: Yost et al. (In Press).

9.6.2 Selection of Chemicals for Hazard Evaluation in the MCDA Framework

From the overall list of 1,606 chemicals identified in this assessment, subsets of chemicals were selected for hazard evaluation in the MCDA framework if they had sufficient data for inclusion, using an adaptation of the criteria outlined by Yost et al. (In Press). Specifically, chemicals were selected if they had the following information available:

1. Had a chronic oral RfV or OSF from a US federal source (IRIS, PPRTV, ATSDR, HHBP);
2. Had available data on frequency of use in hydraulic fracturing fluids (data available from the EPA FracFocus 1.0 project database) or measured concentrations in produced water (data available from Appendix E)[1]; and
3. Had data on physicochemical properties available from EPI Suite.

The rationale for applying these criteria is as follows:

1. Federal toxicity values generally undergo more extensive peer review compared to other sources of toxicity values, and are based on the best available scientific information. For this reason, EPA generally prefers to apply RfVs and OSFs from US federal sources for human health risk assessment.
2. Data on frequency of use (in hydraulic fracturing fluids) or measured concentration (in produced water) provide a metric to help assess the likelihood of chemical occurrence in the hydraulic fracturing water cycle.
3. Information on physicochemical properties enables estimation of the likelihood a chemical will be transported in water.

Chemicals used in hydraulic fracturing fluids and chemicals detected in produced water were evaluated separately using the MCDA framework. To explore the different types of toxicity values identified by EPA, two versions of the MCDA were performed on each of these subsets of chemicals: a noncancer MCDA, in which the Toxicity Score is calculated using chronic oral RfVs; and a cancer MCDA, in which the Toxicity Score is calculated using OSFs. For chemicals used in hydraulic fracturing fluids, the noncancer MCDA was repeated for specific subsets of chemicals used in three states that have a significant amount of hydraulic fracturing activity: Texas, Pennsylvania, and North Dakota. Thus, seven iterations of the MCDA were performed: 1-4) noncancer MCDAs for chemicals used in hydraulic fracturing fluids on a national or state-specific basis, 5) a cancer MCDA for chemicals used in hydraulic fracturing fluids, 6) a noncancer MCDA for chemicals detected in produced water, and 7) a cancer MCDA for chemicals detected in produced water.

In total, 42 chemicals used in hydraulic fracturing fluid and 29 chemicals detected in produced water had sufficient information available for inclusion in noncancer MCDAs (Figure 9-6), while 10 chemicals used in hydraulic fracturing fluid and 7 chemicals detected in produced water had sufficient information available for inclusion in cancer MCDAs (Figure 9-7).

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[1] Chemicals in produced water were considered for the MCDA if they had average or median measured concentrations from any of the tables in Appendix E. Chemicals with only a maximum or minimum concentration listed in Appendix E were not considered for the MCDA.

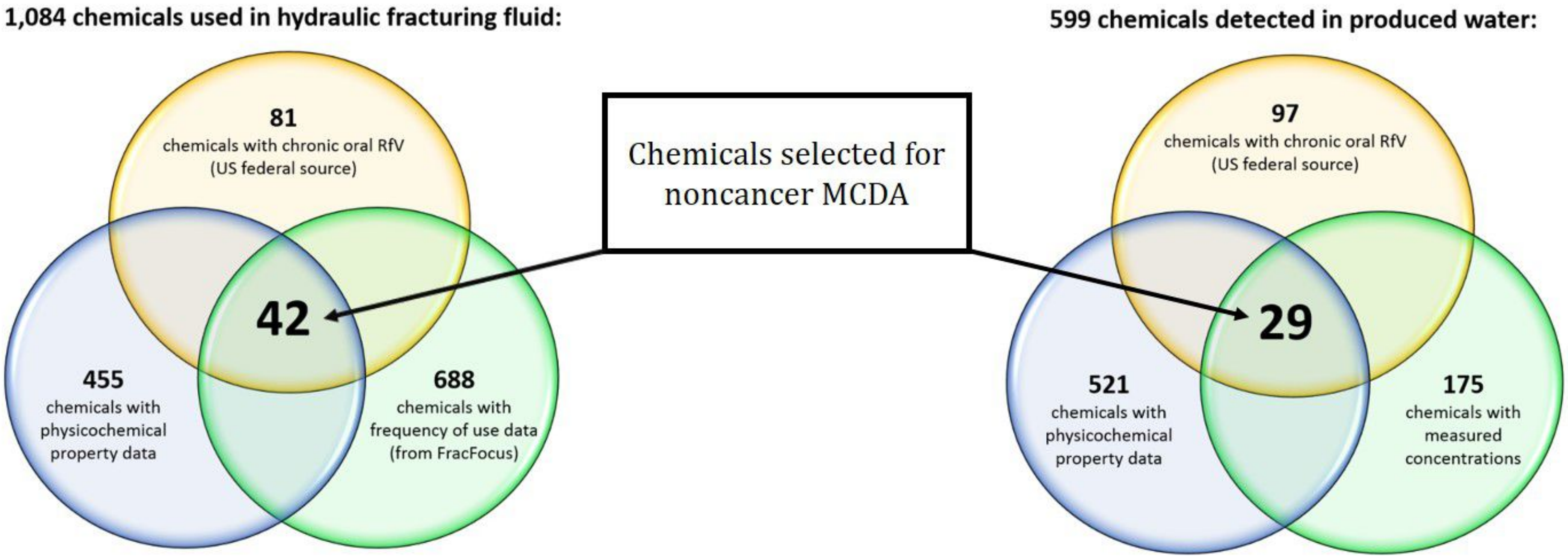

Figure 9-6. The subsets of chemicals selected for hazard evaluation using the noncancer MCDA framework included 42 chemicals used in hydraulic fracturing fluids and 29 chemicals detected in produced water.

For chemicals used in hydraulic fracturing fluids, subsets of these chemicals were also considered in state-specific analyses for Texas (36 chemicals), Pennsylvania (20 chemicals), and North Dakota (21 chemicals).

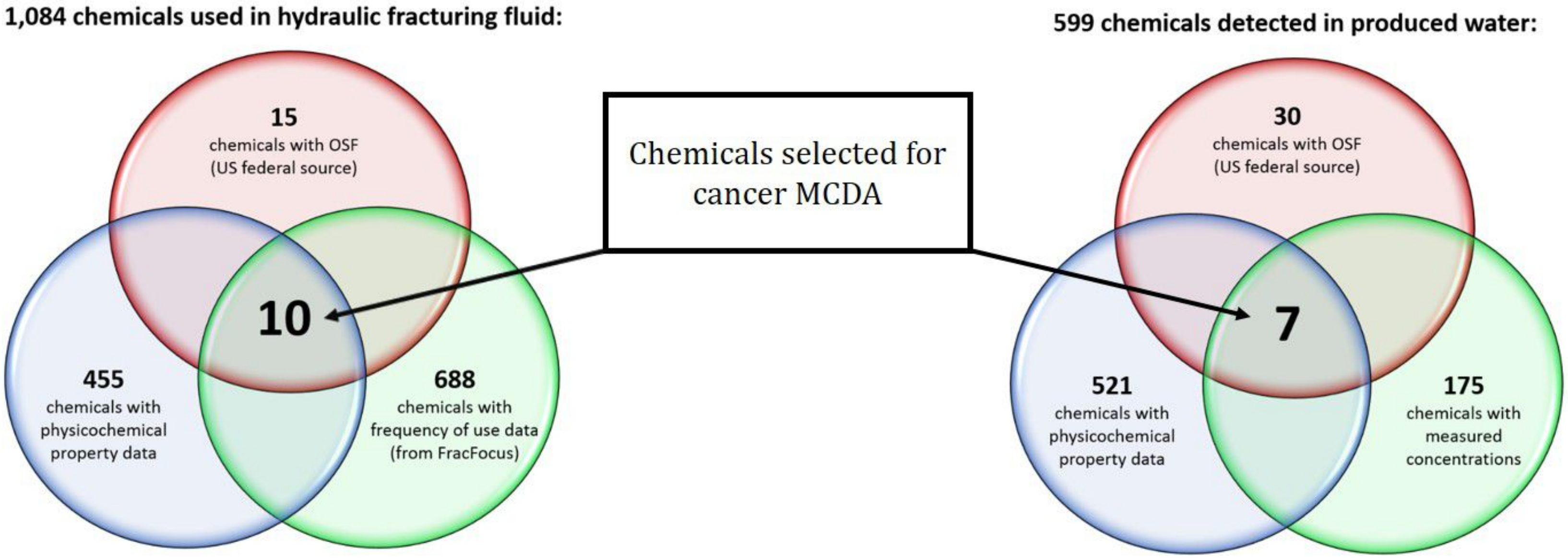

Figure 9-7. The subsets of chemicals selected for hazard evaluation using the cancer MCDA framework included 10 chemicals used in hydraulic fracturing fluids, and 7 chemicals detected in produced water.

9.6.3 Calculation of MCDA Scores

For each iteration of the MCDA, chemicals were assigned scores based on toxicity, occurrence, and physicochemical properties according to the protocol outlined by Yost et al. (In Press). These scores were then standardized to the highest and lowest score within the given subset of chemicals, and then summed to determine a total score and relative ranking for each chemical. The methods used to assign each score and calculate a total score are outlined below.

9.6.3.1 Toxicity Score (Noncancer MCDA)

For each noncancer MCDA, Toxicity Scores were calculated based on chronic oral RfVs from US federal sources (IRIS, PPRTV, ATSDR, and HHBP). If a chemical had a chronic oral RfV available from more than one of these sources, a single value was selected in this order, as described in Section 9.4: HHBP (pesticides), IRIS, PPRTV, ATSDR. Toxicity Scores for the noncancer MCDA were then assigned based on a relative ranking. Within each suite of chemicals considered in this analysis (chemicals used in hydraulic fracturing fluids, or chemicals detected in produced water), RfVs were ranked based on quartiles, and each chemical was assigned a Toxicity Score of 1 to 4 (Table 9-11). Chemicals in the lowest quartile received the highest Toxicity Score, as these chemicals have lower RfVs than other chemicals (i.e., may have lower thresholds for toxicity).

9.6.3.2 Toxicity Score (Cancer MCDA)

For each cancer MCDA, Toxicity Scores were calculated based on OSFs from US federal sources (IRIS, PPRTV, and HHBP). If a chemical had an OSF available from more than one of these sources, a single value was selected in this order, as described in Section 9.4: HHBP (pesticides), IRIS, PPRTV. Toxicity Scores for the cancer MCDA were assigned based on a relative ranking. Within each suite of chemicals considered in this analysis (chemicals used in hydraulic fracturing fluids, or chemicals detected in produced water), OSFs were ranked based on quartiles, and each chemical was assigned a Toxicity Score of 1 to 4 (Table 9-11). Chemicals in the highest quartile received the highest Toxicity Score, as these chemicals have higher OSFs than other chemicals (i.e., are associated with a higher increased risk of cancer per unit of exposure).

9.6.3.3 Occurrence Score

For each of the noncancer and cancer MCDAs, an Occurrence Score was calculated based on the frequency or concentration at which each chemical was reported within the hydraulic fracturing water cycle. For chemicals used in hydraulic fracturing fluids, the Occurrence Score was based on the number of well disclosures for each chemical in the EPA FracFocus 1.0 project database. For chemicals detected in produced water, the Occurrence Score was based on the average or median measured concentration reported in Appendix E. If an average or median concentration of a chemical was reported by multiple studies in Appendix E, the highest of these reported average or median concentrations was used for this calculation. Once a value was determined for each chemical, Occurrence Scores were then assigned based on a relative ranking. Within each suite of chemicals considered in this analysis (chemicals used in hydraulic fracturing fluids, or chemicals detected in produced water), chemical occurrence was ranked based on quartiles, with each chemical assigned an Occurrence Score of 1 to 4 (Table 9-11).

9.6.3.4 Physicochemical Properties Score

For each of the noncancer and cancer MCDAs, a Physicochemical Properties Score was calculated based upon inherent physicochemical properties that describe the likelihood that a chemical will be transported in water. The total Physicochemical Properties Score was calculated as the sum of three subcriteria scores: a Mobility Score, a Volatility Score, and a Persistence Score. The Mobility Score was assessed based upon three physicochemical properties that describe chemical solvency in water: the octanol-water partition coefficient (K_{ow}), the soil adsorption coefficient (K_{oc}), and aqueous solubility. The Volatility Score was assessed based on the Henry's law constant, which describes partitioning of a chemical between water and air. The Persistence Score was assessed based on estimated half-life in water, which describes how long a chemical will remain in water before it is degraded.

For input into the MCDA, experimentally measured physicochemical property values (provided in EPI Suite) were used whenever available. Otherwise, estimated values from EPI Suite were used. To classify these values and assign a score, these numerical values were compared against threshold values (Table 9-11). Each chemical was assigned a Mobility Score, Volatility Score, and Persistence Score (each on a scale of 1 to 4), which were then summed to calculate the Physicochemical Properties Score. The threshold values in Table 9-11 are based upon previously published values employed by existing exposure assessment models, including the EPA's Design for the Environment Alternatives Assessment Criteria for Hazard Evaluation (U.S. EPA, 2011b), the EPA's Pollution Prevention (P2) Framework (U.S. EPA, 2012i), and a peer-reviewed publication by Mitchell et al. (2013b). More details on the Physicochemical Properties Score calculation are provided in the Chapter 9 Annex, Section 9.8.1.

9.6.4 Total Hazard Potential Score

Within each iteration of the MCDA, the three criteria scores (Toxicity, Occurrence, Physicochemical Properties) were each standardized to the dataset by scaling to the highest and lowest respective score within the given subset of chemicals. The following equation was used:

$$S_{x\_final} = (S_x - S_{min}) / (S_{max} - S_{min})$$

in which S_x is the raw score for a particular chemical, S_{max} is the highest observed raw score within the set of chemicals, and S_{min} is the lowest observed raw score within the set of chemicals. S_{x_final} is the standardized score for the chemical. Each standardized score (Toxicity, Occurrence, or Physicochemical Properties) falls on a scale of 0 to 1, and represents a relative ranking within the given subset of chemicals.

The standardized Toxicity Score, Occurrence Score, and Physicochemical Properties Score were summed to calculate a Total Hazard Potential Score for each chemical. The Total Hazard Potential Scores fall on a scale of 0 to 3, with higher scores indicating chemicals that may be more likely to affect drinking water resources. Examples of the Total Hazard Potential Score calculation can be found in the Chapter 9 Annex, Section 9.8.2.

Table 9-11. Thresholds used for developing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score in this MCDA framework.
Adapted from Yost et al. (In Press).

Criteria	Sub-criteria	Value	Score			
			1	2	3	4
Toxicity (Noncancer MCDA)	NA	Chronic oral RfV (mg/kg-day)	>3rd quartile	>2nd quartile to ≤3rd quartile	>1st quartile to ≤2nd quartile	≤1st quartile
Toxicity (Cancer MCDA)	NA	OSF (per mg/kg-day)	<1st quartile	≥1st quartile to <2nd quartile	≥2nd quartile to <3rd quartile	≥3rd quartile
Occurrence	NA	Frequency of use (% of disclosures in EPA's FracFocus 1.0 project database) or Measured concentration in produced water (µg/L; Appendix E)	<1st quartile	≥1st quartile to <2nd quartile	≥2nd quartile to <3rd quartile	≥3rd quartile
Physico-chemical Properties	Mobility	Log K_{OW}	>5	>3 to ≤5	>2 to ≤3	≤2
		Log K_{OC}	>4.4	>3.4 to ≤4.4	>2.4 to ≤3.4	≤2.4
		Aqueous solubility (mg/L)	<0.1	≥0.1 to <100	≥100 to <1000	≥1000
	Volatility	Henry's law constant	>10^{-1}	>10^{-3} to ≤10^{-1}	>10^{-5} to ≤10^{-3}	≤10^{-5}
	Persistence	Half-life in water (days)	<16	≥16 to <60	≥60 to <180	≥180

9.6.5 MCDA Results

For each iteration of the MCDA, we first present the data used for input into the MCDA, including data on toxicity, occurrence, and physicochemical properties. We then present the results of each MCDA, which show a relative ranking of chemicals based on integration of these data. Lastly, we discuss the key limitations of this MCDA approach, which is intended as a preliminary analysis only.

9.6.5.1 Results: Noncancer MCDA for Chemicals Used in Hydraulic Fracturing Fluids

A total of 42 chemicals used in hydraulic fracturing fluids were evaluated in a noncancer MCDA (Table 9-12). Chronic oral RfVs within this suite of chemicals range from 0.001–20 mg/kg-day, with (E)-crotonaldehyde having the lowest chronic oral RfV and 1,2-propylene glycol having the highest. These RfVs were derived based on health effects including immune system effects, changes in body weight, changes in blood chemistry, cardiotoxicity, neurotoxicity, liver and kidney toxicity, and reproductive and developmental toxicity. The total UFs used in the derivation of these chronic oral RfVs (Table 9-12) reflect varying degrees of confidence surrounding the data sets for these chemicals. Three of the chemicals with the lowest chronic oral RfVs [(E)-crotonaldehyde, propargyl alcohol, benzyl chloride] have total UFs of 3000, indicating a relatively large amount of uncertainty in these values. Comparatively, chemicals such as benzene, acrylamide, and dichloromethane also have low chronic oral RfVs, but with much less uncertainty reflected in the values.

Figure 9-8 presents the results of a noncancer MCDA for these 42 chemicals in hydraulic fracturing fluids. Of these 42 chemicals, propargyl alcohol received the highest overall Total Hazard Potential Score. Propargyl alcohol was reported in 33% of disclosures nationally in the EPA FracFocus 1.0 project database, making it one of the most widely used chemicals that was considered in this analysis. It has physicochemical properties that are conducive to transport in water, and a low RfV. Given these properties, propargyl alcohol received the highest overall ranking based on hazard potential across all of the metrics that were considered in the MCDA.

Several of the other chemicals that received high Occurrence Scores also received among the highest Total Hazard Potential Scores, including 2-butoxyethanol, naphthalene, 1,2,4-trimethylbenzene, N,N-dimethylformamide, and formaldehyde (reported in 23%, 19%, 13%, 9%, and 7% of disclosures, respectively). Methanol, ethylene glycol, and formic acid (73%, 47%, and 11% of disclosures, respectively) received lower Total Hazard Potential Scores as a result of having higher RfVs. Likewise, didecyldimethylammonium chloride and dodecylbenzenesulfonic acid (8% and 7% of disclosures, respectively) received lower Total Hazard Potential Scores as a result of having higher RfVs and more hydrophobic properties.

The other chemicals that received high Toxicity Scores (i.e., had low chronic oral RfVs) received moderate to high Total Hazard Potential Scores overall. Acrylamide was reported in only 1% of disclosures, but has physicochemical properties that are very conducive to transport in water, and therefore received one of the highest overall Total Hazard Potential Scores. 1,2,4-Trimethylbenzene, benzyl chloride, and epichlorohydrin (13%, 6%, and 1% of disclosures in the EPA FracFocus 1.0 project database, respectively) scored slightly lower than acrylamide with regards to physicochemical properties. Other chemicals, including 1,2,3-trimethylbenzene, 1,3,5-trimethylbenzene, (E)-crotonaldehyde, benzene, dichloromethane, aniline, furfural, and 2-(Thiocyanomethylthio)benzothiazole, received lower overall scores because they are used more infrequently (the trimethylbenzenes were reported in <1% of disclosures, and the rest reported in <0.1% of disclosures).

9.6.5.2 Results: Noncancer MCDA for Chemicals Used in Hydraulic Fracturing Fluids (State-specific analysis for Texas, Pennsylvania, and North Dakota)

To investigate the extent of regional differences and examine the applicability of the MCDA model at the regional scale, we repeated the noncancer MCDA for hydraulic fracturing fluids for subsets of chemicals used in three representative states that have a significant amount of hydraulic fracturing activity: Texas, Pennsylvania, and North Dakota. The chemicals used in these state-specific analyses are subsets of the chemicals used nationally, and are indicated in Table 9-12. Some of the chemicals considered in the national analysis were not included in the state-specific analyses because they were not disclosed to FracFocus 1.0 as used in these states.

Results are presented in Figure 9-9 (Texas), Figure 9-10 (Pennsylvania), and Figure 9-11 (North Dakota). By comparing these results to each other and to the national noncancer MCDA (Figure 9-8), it is evident that there are some regional differences in the Total Hazard Potential Scores, although many chemicals were commonly used and received similar overall rankings.

Methanol, ethylene glycol, and 2-butoxyethanol were among the most frequently reported chemicals in all three state-specific analyses, while other chemicals differed distinctly between states. For instance, propargyl alcohol was frequently reported in Texas (39% of disclosures) and Pennsylvania (58% of disclosures), but not North Dakota (1% of disclosures). Likewise, naphthalene was reported frequently in Texas (14% of disclosures) and North Dakota (43% of disclosures), but not in Pennsylvania (1% of disclosures). The most toxic chemicals (occurring in the lowest quartile of chronic oral RfVs) common among all three states include propargyl alcohol, benzyl chloride, acrylamide, and 1,2,4-trimethylbenzene. Other chemicals receiving high Toxicity Scores in these states include epichlorohydrine (Texas and Pennsylvania), 1,3,5-Trimethylbenzene (Texas and Pennsylvania), 1,4-dioxane (North Dakota), naphthalene (North Dakota), benzene, aniline, and 1,2,3-Trimethylbenzene (Texas).

Overall, in Texas, propargyl alcohol received the highest possible Total Hazard Potential Score, with acrylamide receiving the second highest score. In Pennsylvania, propargyl alcohol also received the highest possible Total Hazard Potential Score, with 2-butoxyethanol receiving the second highest score. In North Dakota, 2-butoxyethanol received the highest Total Hazard Potential Score, with naphthalene receiving the second highest score.

The results of these state-specific MCDAs support the concept presented in Chapter 5 that there is no single hydraulic fracturing fluid formulation, and that the chemicals of most potential concern will vary between regions or even between wells.

Table 9-12. Data on the selected subset of chemicals in hydraulic fracturing fluids used for input into a noncancer MCDA.
Chemicals within the table are ordered from most toxic to least toxic based on chronic oral RfV.

Chemical Name	CASRN	Noncancer toxicity (chronic oral RfV)[a]			% disclosures in EPA FracFocus 1.0 project database[b]				Mobility			Volatility	Persistence
		RfV (mg/ kg-day)	Total UF	Source	National	TX	PA	ND	Log K_{OW}	Log K_{OC}	Solubility (mg/L)	Henry's Law Constant	Half-life in water (days)
(E)-Crotonaldehyde	123-73-9	0.001	3000	PPRTV	0.06%				0.6	0.254	41480	1.94E-05	15
Propargyl alcohol	107-19-7	0.002	3000	IRIS	33%	39%	58%	1%	-0.38	0.28	935500	1.15E-06	15
Benzyl chloride	100-44-7	0.002	3000	PPRTV	6%	7%	5%	0.80%	2.3	2.649	1030	4.12E-04	15
Acrylamide	79-06-1	0.002	30	IRIS	1%	2%	1%	1%	-0.67	0.755	504000	1.70E-09	15
Benzene	71-43-2	0.004	300	IRIS	0.006%	0.01%			2.13	1.75	2000	5.55E-03	37.5
Epichlorohydrin	106-89-8	0.006	1000	PPRTV	1%	0.20%	0.08%		0.45	1	50630	3.04E-05	15
Dichloromethane	75-09-2	0.006	30	IRIS	0.02%				1.25	1.44	10950	3.25E-03	37.5
Aniline	62-53-3	0.007	1000	PPRTV	0.02%	0.05%			0.9	1.6	20820	2.02E-06	15
1,2,4-Trimethylbenzene	95-63-6	0.01	300	IRIS	13%	11%	1%	25%	3.63	2.788	79.59	6.16E-03	37.5
1,3,5-Trimethylbenzene	108-67-8	0.01	300	IRIS	0.5%	0.80%	1%		3.42	2.82	120.3	8.77E-03	37.5
1,2,3-Trimethylbenzene	526-73-8	0.01	300	IRIS	0.4%	0.80%			3.66	2.8	75.03	4.36E-03	37.5
2-(Thiocyanomethylthio)benzothiazole	21564-17-0	0.01	300	HHBP	0.006%				3.3	3.528	41.67	6.49E-12	37.5
Furfural	98-01-1	0.01	3000	HHBP	0.003%				0.41	0.784	53580	3.77E-06	15
Naphthalene	91-20-3	0.02	3000	IRIS	19%	14%	1%	43%	3.3	2.96	142.1	4.40E-04	37.5

		Noncancer toxicity (chronic oral RfV)[a]			% disclosures in EPA FracFocus 1.0 project database[b]				Mobility			Volatility	Persistence
Chemical Name	**CASRN**	**RfV (mg/ kg-day)**	**Total UF**	**Source**	**National**	**TX**	**PA**	**ND**	**Log K_{OW}**	**Log K_{OC}**	**Solubility (mg/L)**	**Henry's Law Constant**	**Half-life in water (days)**
Chlorobenzene	108-90-7	0.02	1000	IRIS	0.003%	0.01%			2.84	2.15	400.5	3.11E-03	15
2-(2-Butoxyethoxy) ethanol	112-34-5	0.03	3000	PPRTV	0.6%	0.40%	4%		0.56	1	71920	7.20E-09	8.67
1,4-Dioxane	123-91-1	0.03	300	IRIS	0.3%	0.50%		0.80%	-0.27	0.421	213900	4.80E-06	15
1,3-Dichloropropene	542-75-6	0.03	100	IRIS	0.02%				2.04	1.82	1994	3.55E-03	37.5
Bisphenol A	80-05-7	0.05	1000	IRIS	0.006%	0.01%			3.32	4.576	172.7	9.16E-12	37.5
Toluene	108-88-3	0.08	3000	IRIS	0.7%	1%			2.73	2.07	573.1	6.64E-03	15
Ethylenediamine	107-15-3	0.09	100	PPRTV	0.01%	0.02%			-2.04	1.172	1000000	1.73E-09	15
2-Butoxyethanol	111-76-2	0.1	10	IRIS	23%	27%	21%	15%	0.83	0.451	64470	1.60E-06	8.67
N,N-Dimethylformamide	68-12-2	0.1	1000	PPRTV	9%	10%	11%	0.60%	-1.01	0	977900	7.39E-08	15
Didecyldimethylammonium chloride	7173-51-5	0.1	100	HHBP	8%	7%	12%	0.05%	4.66	5.546	0.9	6.85E-10	15
1-Butanol	71-36-3	0.1	1000	IRIS	1%	2%		0.70%	0.88	0.5	76700	8.81E-06	8.67
Cumene	98-82-8	0.1	1000	IRIS	0.5%	0.80%	1%		3.66	2.844	75.03	1.15E-02	15
Ethylbenzene	100-41-4	0.1	1000	IRIS	0.4%	0.50%		0.10%	3.15	2.23	228.6	7.88E-03	15
Acetophenone	98-86-2	0.1	3000	IRIS	0.04%	0.04%			1.58	1.8	4484	1.04E-05	15
Formaldehyde	50-00-0	0.2	100	IRIS	7%	8%	4%	8%	0.35	0	57020	3.37E-07	15
Xylenes	1330-20-7	0.2	1000	IRIS	2%	3%	1%	0.20%	3.2	2.25	207.2	7.18E-03	15

		Noncancer toxicity (chronic oral RfV)[a]			% disclosures in EPA FracFocus 1.0 project database[b]				Mobility			Volatility	Persistence
Chemical Name	**CASRN**	**RfV (mg/ kg-day)**	**Total UF**	**Source**	**National**	**TX**	**PA**	**ND**	**Log K_{OW}**	**Log K_{OC}**	**Solubility (mg/L)**	**Henry's Law Constant**	**Half-life in water (days)**
o-Xylene	95-47-6	0.2	30	ATSDR	0.05%	0.1%			3.12	2.25	224.1	5.18E-03	15
Phenol	108-95-2	0.3	300	IRIS	0.4%	0.80%		0.05%	1.46	1.9	26160	3.33E-07	15
2-Methyl-1-propanol	78-83-1	0.3	1000	IRIS	0.3%			4%	0.76	0.465	97120	9.78E-06	15
Dodecylbenzenesulfonic acid	27176-87-0	0.5	100	HHBP	7%	10%	2%	8%	4.71	4.066	0.8126	6.27E-08	15
Formic acid	64-18-6	0.9	300	PPRTV	11%	14%	8%	11%	-0.54	0	955200	1.67E-07	8.67
Ethyl acetate	141-78-6	0.9	1000	IRIS	0.4%	0.70%			0.73	0.747	29930	1.34E-04	15
Acetone	67-64-1	0.9	1000	IRIS	0.2%	0.02%		1%	-0.24	0.374	219900	3.50E-05	15
Methanol	67-56-1	2	100	IRIS	73%	80%	69%	54%	-0.77	0.44	1000000	4.55E-06	8.67
Ethylene glycol	107-21-1	2	100	IRIS	47%	60%	35%	37%	-1.36	0	1000000	6.00E-08	8.67
Hexanedioic acid	124-04-9	2	300	PPRTV	0.70%	1%			0.08	1.386	167300	4.71E-12	8.67
Benzoic acid	65-85-0	4	1	IRIS	0.06%	0.10%	0.04%		1.87	1.5	2493	3.81E-08	15
1,2-Propylene glycol	57-55-6	20	300	PPRTV	4%	4%	8%	8%	-0.92	0.36	811100	1.29E-08	8.67

CASRN = Chemical Abstract Service Registry Number; IRIS = Integrated Risk Information System; PPRTV = Provisional Peer Reviewed Toxicity Values; ATSDR = Agency for Toxic Substances and Disease Registry; HHBP = Human Health Benchmarks for Pesticides; K_{OW} = octanol-water partitioning coefficient; K_{OC} = soil adsorption coefficient

[a] Reference value (RfV): An estimate of an exposure for a given duration to the human population (including susceptible subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime. RfVs considered in the MCDA include chronic oral reference doses (RfD) from IRIS, PPRTV, and HHBP; and chronic oral minimal risk levels (MRLs) from ATSDR.

[b] The FracFocus frequency of use data presented in this chapter is based on 35,957 FracFocus disclosures that were deduplicated, within the study time period (January 1, 2011 to February 28, 2013), and with ingredients that have a valid CASRN.

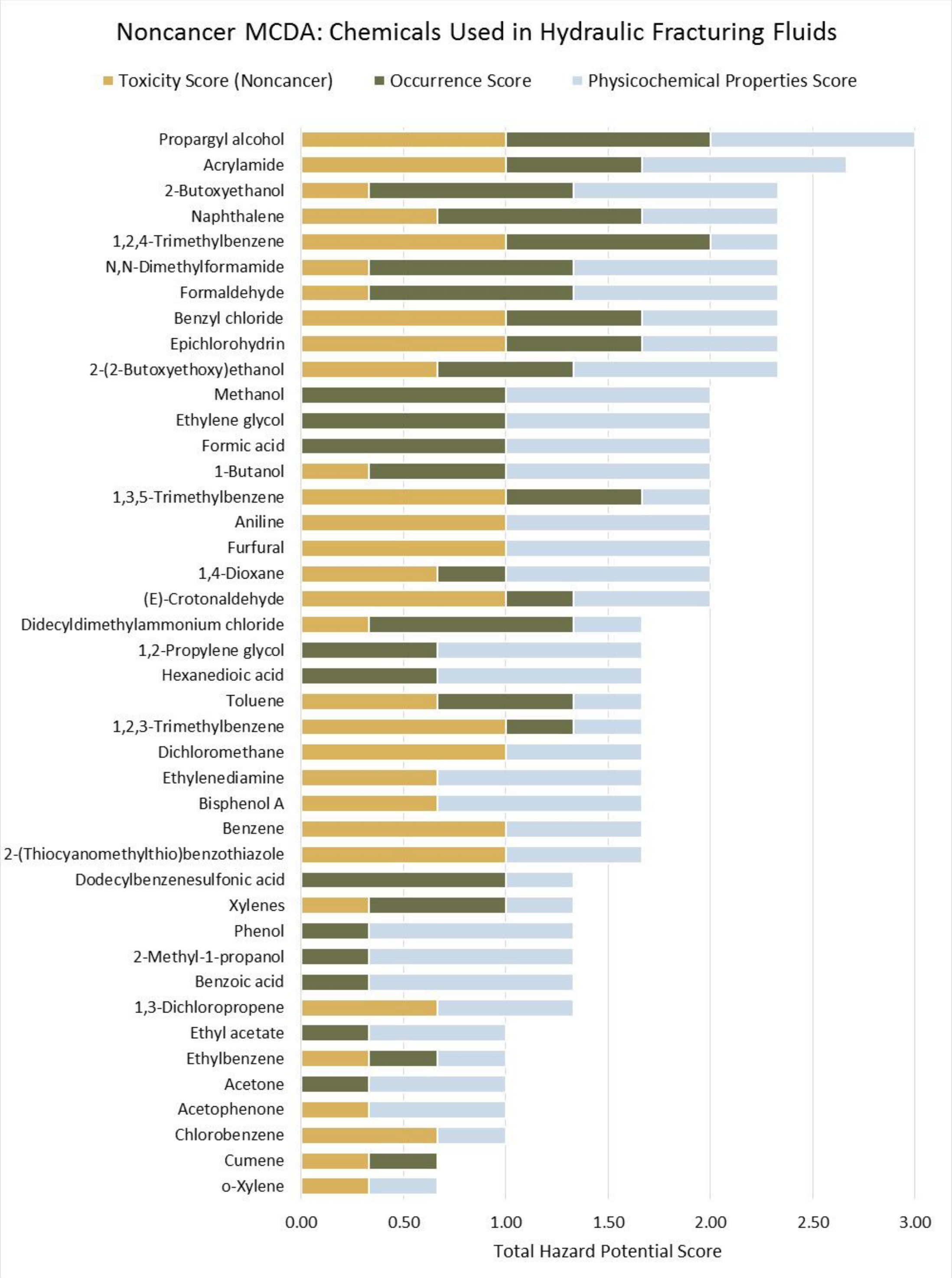

Figure 9-8. Noncancer MCDA results for 42 chemicals used in hydraulic fracturing fluids (national analysis), showing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score for each chemical.

Chemicals are ordered from high to low based on Total Hazard Potential Score. See Section 9.6.4 for details on the calculation.

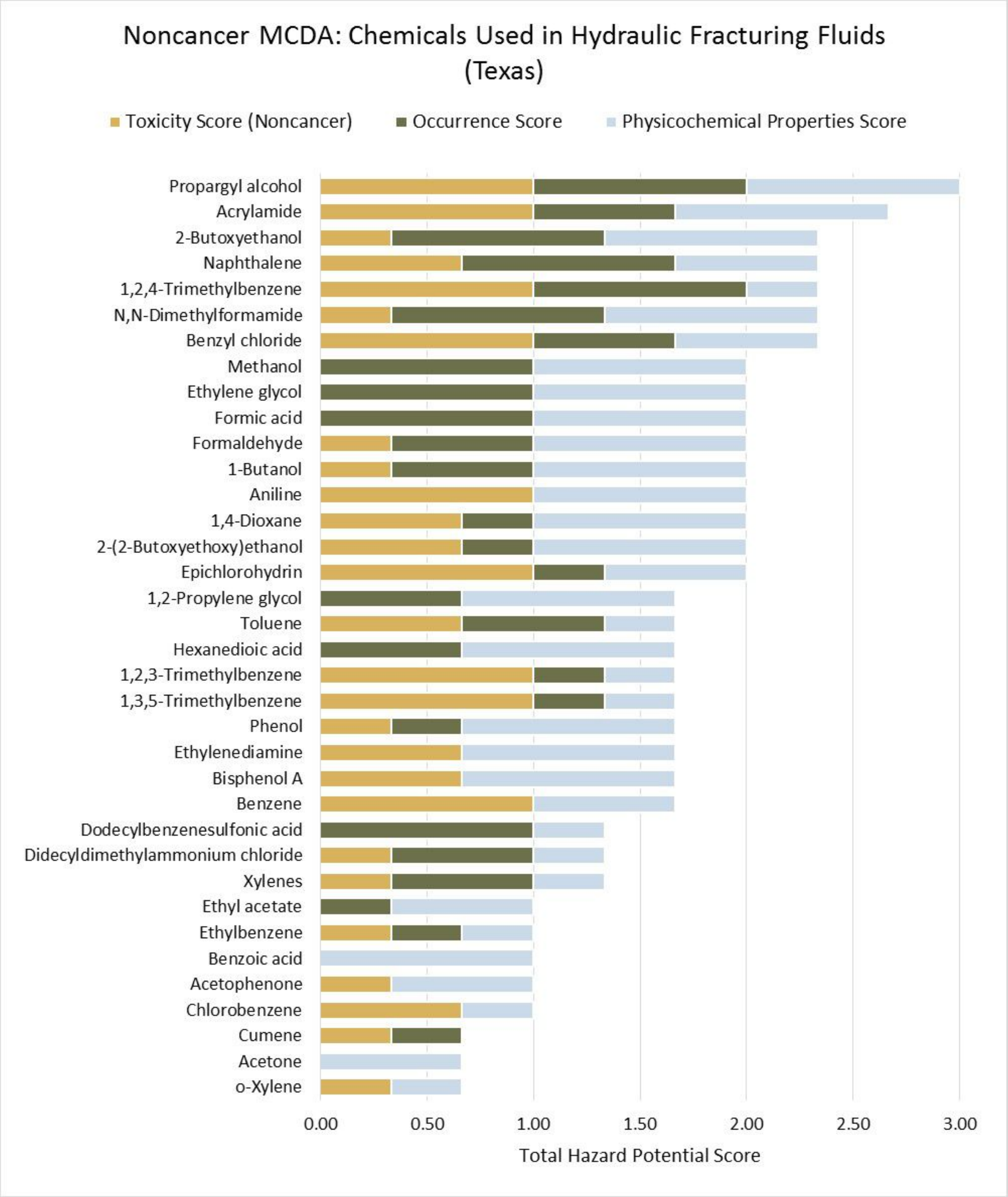

Figure 9-9. Noncancer MCDA results for 36 chemicals used in hydraulic fracturing fluids in Texas (state-specific analysis), showing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score for each chemical.

Chemicals are ordered from high to low based on Total Hazard Potential Score. See Section 9.6.4 for details on the calculation.

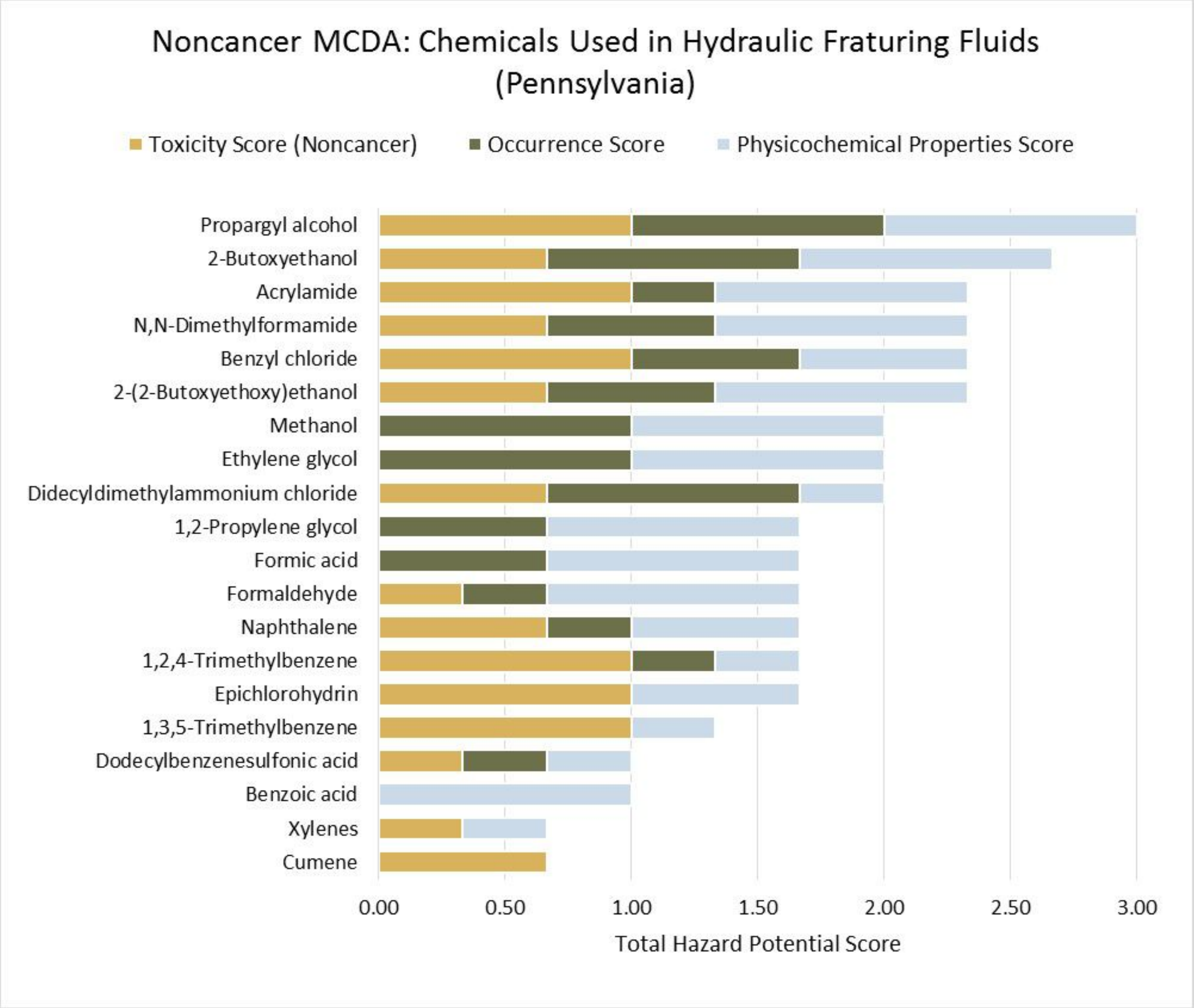

Figure 9-10. Noncancer MCDA results for 20 chemicals used in hydraulic fracturing fluids in Pennsylvania (state-specific analysis), showing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score for each chemical.

Chemicals are ordered from high to low based on Total Hazard Potential Score. See Section 9.6.4 for details on the calculation.

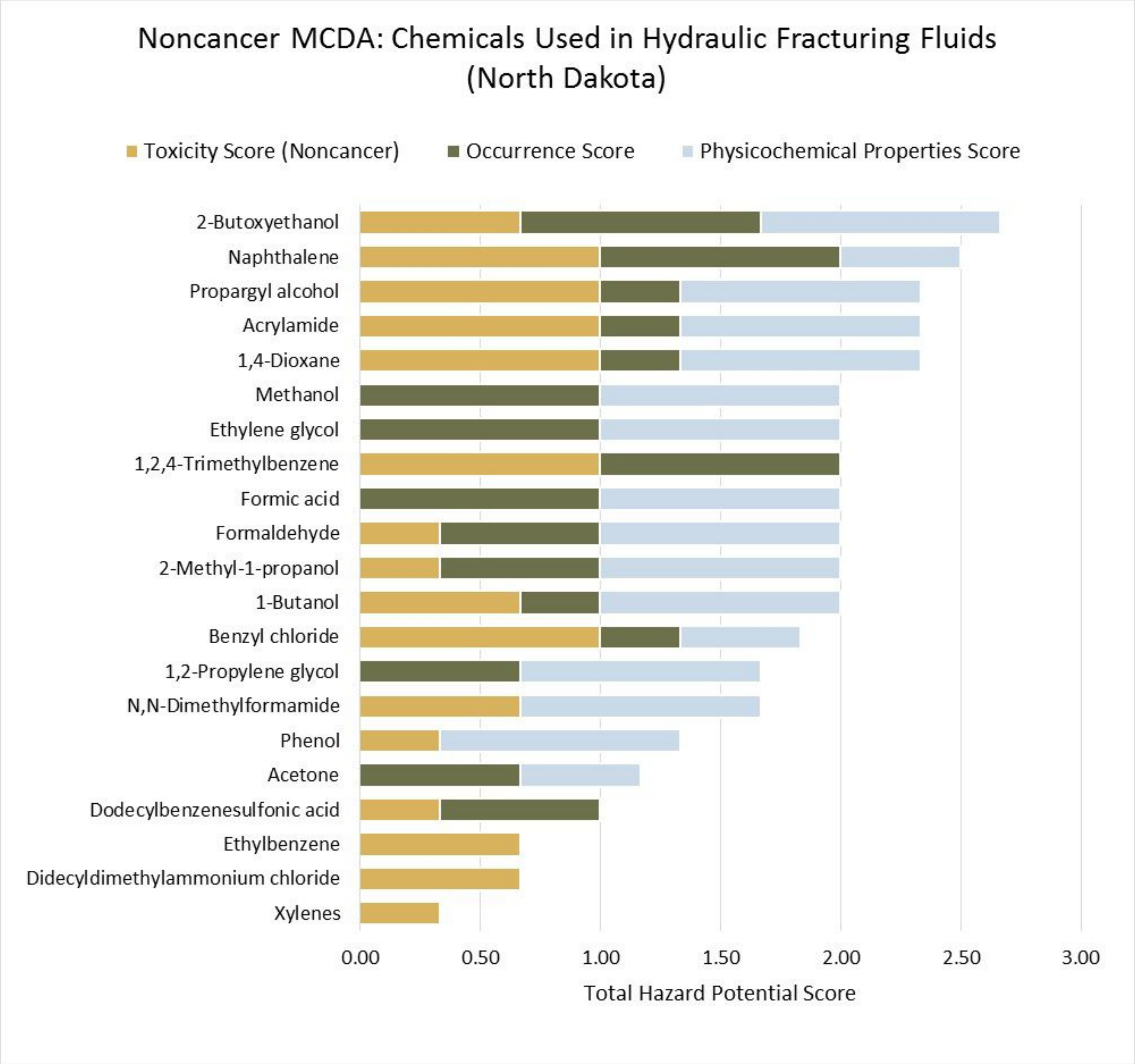

Figure 9-11. Noncancer MCDA results for 21 chemicals used in hydraulic fracturing fluids in North Dakota (state-specific analysis), showing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score for each chemical.

Chemicals are ordered from high to low based on Total Hazard Potential Score. See Section 9.6.4 for details on the calculation.

9.6.5.3 Results: Cancer MCDA for Chemicals Used in Hydraulic Fracturing Fluids

A total of 10 chemicals used in hydraulic fracturing fluids were evaluated in a cancer MCDA (Table 9-13). OSFs for these chemicals ranged from 0.002 to 3 per mg/kg-day, with quinoline having the highest OSF, and dichloromethane having the lowest. Benzene is the only one of these chemicals that is classified as a known human carcinogen by at least one of the sources in Table 9-1, while the other chemicals in this subset are classified as probable carcinogens in humans (Appendix Table G-1e).

Figure 9-12 presents the results from the cancer MCDA for chemicals used in hydraulic fracturing fluids. Of the 10 chemicals that were considered in this analysis, acrylamide received the highest Total Hazard Potential Score. Acrylamide has an OSF of 0.5 per mg/kg-day, which is one of the higher OSFs in this suite of chemicals, and has physicochemical properties that are highly conducive to transport in water. Acrylamide was reported in 1% of disclosures nationally in the EPA FracFocus 1.0 project database. This nevertheless places acrylamide in the top quartile in terms of frequency of use, as none of the chemicals within this subset were used with great frequency on a national basis.

Bis(2-chloroethyl)ether and quinoline, which are the two most potent carcinogens considered in the analysis and received high Toxicity Score, received the second and third highest Total Hazard Potential Scores within this suite of chemicals. Bis(2-chloroethyl)ether was reported in 0.7% of disclosures, while quinoline was reported in 0.02% of disclosures. Both are expected to be readily transported in water.

In addition to acrylamide, the other two chemicals receiving high Occurrence Scores were benzyl chloride and epichlorohydrin (6% and 1% of disclosures, respectively). These two chemicals both received moderate Total Hazard Potential Scores. Benzyl chloride has an OSF of 0.17 per mg/kg-day, while epichlorohydrine has an OSF of 0.0099 per mg/kg-day. Both received lower Physicochemical Properties Scores relative to other chemicals in this analysis, due in part to volatility.

Table 9-13. Data on the selected subset of chemicals in hydraulic fracturing fluids used for input into a cancer MCDA.
Chemicals within the table are ordered from most potent to least potent based on OSF.

		Cancer-specific toxicity (OSF)[a]		% disclosures in EPA FracFocus 1.0 project database[b]	Mobility			Volatility	Persistence
Chemical Name	**CASRN**	**OSF (per mg/kg-day)**	**Source**	**National**	**Log K_{OW}**	**Log K_{OC}**	**Solubility (mg/L)**	**Henry's Law Constant**	**Half-life in water (days)**
Quinoline	91-22-5	3	IRIS	0.02%	2.03	3.1	1711	1.67E-06	15
Bis(2-chloroethyl) ether	111-44-4	1.1	IRIS	0.7%	1.29	1.88	6435	1.70E-05	37.5
Acrylamide	79-06-1	0.5	IRIS	1%	-0.67	0.755	504000	1.70E-09	15
Benzyl chloride	100-44-7	0.17	IRIS	6%	2.3	2.649	1030	4.12E-04	15
1,4-Dioxane	123-91-1	0.1	IRIS	0.3%	-0.27	0.421	213900	4.80E-06	15
Benzene	71-43-2	0.015-0.055[c]	IRIS	0.006%	2.13	1.75	2000	5.55E-03	37.5
1,3-Dichloropropene	542-75-6	0.05	IRIS	0.02%	2.04	1.82	1994	3.55E-03	37.5
Epichlorohydrin	106-89-8	0.0099	IRIS	1%	0.45	1	50630	3.04E-05	15
Aniline	62-53-3	0.0057	IRIS	0.02%	0.9	1.6	20820	2.02E-06	15
Dichloromethane	75-09-2	0.002	IRIS	0.02%	1.25	1.44	10950	3.25E-03	37.5

CASRN = Chemical Abstract Service Registry Number; IRIS = Integrated Risk Information System; K_{OW} = octanol-water partitioning coefficient; K_{OC} = soil adsorption coefficient

[a] Oral slope factor (OSF): An upper-bound, approximating a 95% confidence limit, on the increased cancer risk from a lifetime oral exposure to an agent. This estimate, usually expressed in units of proportion (of a population) affected per mg/kg-day, is generally reserved for use in the low dose region of the dose response relationship, that is, for exposures corresponding to risks less than 1 in 100. OSFs considered in the MCDA include values from IRIS, PPRTV, and HHBP.

[b] The FracFocus frequency of use data presented in this chapter is based on 35,957 FracFocus disclosures that were deduplicated, within the study time period (January 1, 2011 to February 28, 2013), and with ingredients that have a valid CASRN.

[c] IRIS lists the OSF for benzene as a range from 0.015 to 0.055 per mg/kg-day. For input into the MCDA, we used the high end of this range (0.055 per mg/kg-day).

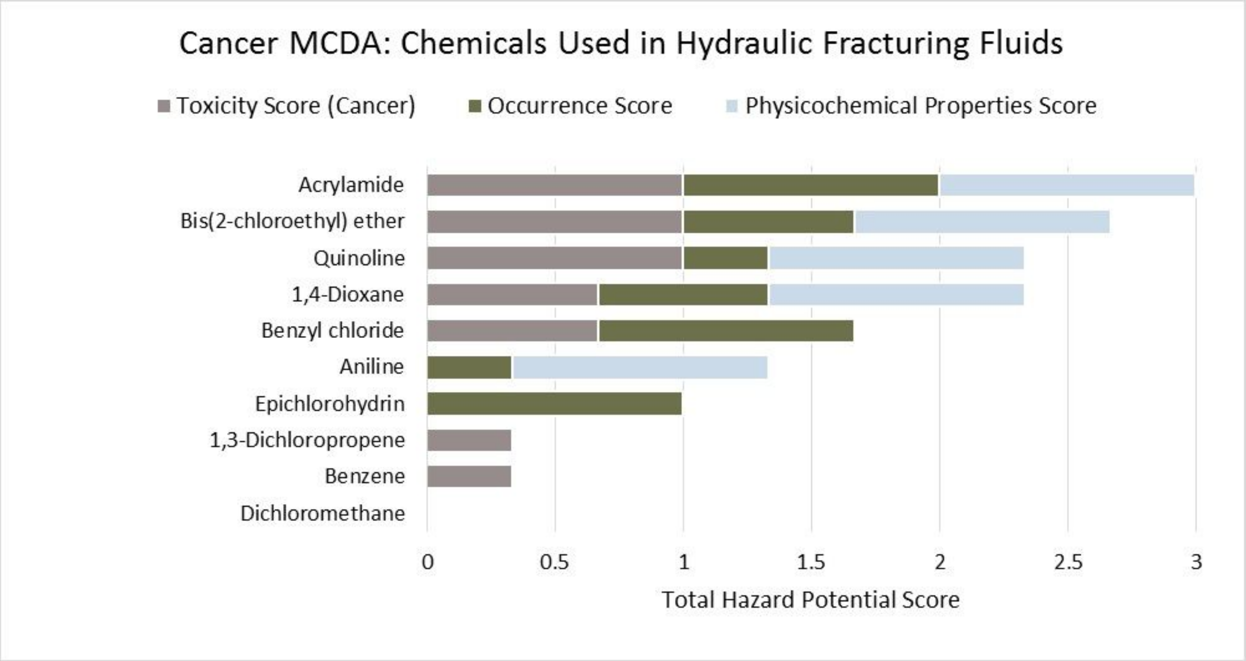

Figure 9-12. Cancer MCDA results for 10 chemicals used in hydraulic fracturing fluids, showing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score for each chemical.

Chemicals are ordered from high to low based on Total Hazard Potential Score. See Section 9.6.4 for details on the calculation.

9.6.5.4 Results: Noncancer MCDA for Chemicals in Produced Water

A total of 29 chemicals detected in produced water were evaluated in a noncancer MCDA (Table 9-14). Of these 29 chemicals, 13 were also included in the noncancer MCDA for hydraulic fracturing fluids. Chronic oral RfVs within this suite of chemicals range from 0.001 to 0.9 mg/kg-day, with pyridine having the lowest chronic oral RfV, and acetone having the highest. Chronic oral exposure to these chemicals may induce a variety of adverse outcomes, including immune system effects, changes in body weight, changes in blood chemistry, pulmonary toxicity, neurotoxicity, liver and kidney toxicity, and reproductive and developmental toxicity. The total UFs used in the derivation of these chronic oral RfVs (Table 9-14) reflect varying degrees of confidence surrounding the data sets for these chemicals.

Figure 9-13 presents the results of a noncancer MCDA for these 29 chemicals detected in produced water. Benzene, pyridine, and naphthalene received the highest Total Hazard Potential Scores, followed by 2-methylnaphthalene. These four chemicals all received high Toxicity Scores and high Occurrence Scores (with maximum average concentrations of 1500 μg/L, 413 μg/L, 238 μg/L, and 1362 μg/L in Barnett, Marcellus, or Powder River Basin produced water, respectively), but received moderate to low Physicochemical Property Scores.

Table 9-14. Data on the selected subset of chemicals detected in produced water used for input into a noncancer MCDA.

Chemicals within the table are ordered from most toxic to least toxic based on chronic oral RfV.

		Noncancer toxicity (chronic oral RfV)[a]			Occurrence (concentration in produced water)[b]		Mobility			Volatility	Persist-ence
Chemical Name	**CASRN**	**RfV (mg/kg-day)**	**Total UF**	**Source**	**Average or Median Conc. (µg/L)**	**Reference**	**Log K_{OW}**	**Log K_{OC}**	**Solubility (mg/L)**	**Henry's Law Constant**	**Half-life in water (days)**
Pyridine	110-86-1	0.001	1000	IRIS	413	Table E-11	0.65	1.6	729800	1.10E-05	15
Benzene	71-43-2	0.004	300	IRIS	1500	Table E-13	2.13	1.75	2000	5.55E-03	37.5
2-Methylnaphthalene	91-57-6	0.004	1000	IRIS	1362	Table E-11	3.86	3.6	41.42	5.18E-04	15
1,2,4-Trimethylbenzene	95-63-6	0.01	300	IRIS	173	Table E-11	3.63	2.788	79.59	6.16E-03	37.5
1,3,5-Trimethylbenzene	108-67-8	0.01	300	IRIS	59	Table E-11	3.42	2.82	120.3	8.77E-03	37.5
Chloroform	67-66-3	0.01	1000	IRIS	28	Table E-11	1.97	1.6	2096	3.67E-03	37.5
Tributyl phosphate	126-73-8	0.01	1000	PPRTV	0.26	Table E-12	4	3.371	7.355	1.41E-06	8.67
Naphthalene	91-20-3	0.02	3000	IRIS	238	Table E-11	3.3	2.96	142.1	4.40E-04	37.5
Di(2-ethylhexyl) phthalate[c]	117-81-7	0.02	1000	IRIS	210	Table E-11	7.6	4.94	0.001132	2.70E-07	15
Chlorobenzene[d]	108-90-7	0.02	1000	IRIS	100	Table E-13	2.84	2.15	400.5	3.11E-03	15
2,4-Dimethylphenol	105-67-9	0.02	3000	IRIS	14.5	Table E-11	2.3	2.692	4068	9.51E-07	15
Pyrene	129-00-0	0.03	3000	IRIS	13	Table E-11	4.88	4.9	0.2249	1.19E-05	60
1,4-Dioxane	123-91-1	0.03	300	IRIS	6.5	Table E-11	-0.27	0.421	213900	4.80E-06	15
Fluorene	86-73-7	0.04	3000	IRIS	8.4	Table E-11	4.1	3.614	20.13	1.59E-03	15
Fluoranthene	206-44-0	0.04	3000	IRIS	6.1	Table E-11	5.16	4.8	0.1297	8.86E-06	60
o-Cresol[e]	95-48-7	0.05	1000	IRIS	28.3	Table E-11	1.95	2.486	9066	1.20E-06	15
Toluene	108-88-3	0.08	3000	IRIS	760	Table E-9	2.73	2.07	573.1	6.64E-03	15

		Noncancer toxicity (chronic oral RfV)[a]			Occurrence (concentration in produced water)[b]		Mobility			Volatility	Persist-ence
Chemical Name	**CASRN**	**RfV (mg/kg-day)**	**Total UF**	**Source**	**Average or Median Conc. (µg/L)**	**Reference**	**Log K_{OW}**	**Log K_{OC}**	**Solubility (mg/L)**	**Henry's Law Constant**	**Half-life in water (days)**
Ethylbenzene	100-41-4	0.1	1000	IRIS	2010	Table E-13	3.15	2.23	228.6	7.88E-03	15
Carbon disulfide	75-15-0	0.1	100	IRIS	400	Table E-11	1.94	1.337	2928	1.44E-02	15
Cumene[f]	98-82-8	0.1	1000	IRIS	120	Table E-11	3.66	2.844	75.03	1.15E-02	15
Benzyl alcohol	100-51-6	0.1	1000	PPRTV	81.5	Table E-11	1.1	1.1	41050	3.37E-07	15
Dibutyl phthalate[g]	84-74-2	0.1	1000	IRIS	41	Table E-11	4.5	3.14	2.351	1.81E-06	8.67
Acetophenone	98-86-2	0.1	3000	IRIS	13	Table E-11	1.58	1.8	4484	1.04E-05	15
Diphenylamine	122-39-4	0.1	100	HHBP	5.3	Table E-11	3.5	2.78	63.61	2.69E-06	37.5
Xylenes	1330-20-7	0.2	1000	IRIS	360	Table E-9	3.2	2.25	207.2	7.18E-03	15
Benzyl butyl phthalate	85-68-7	0.2	1000	IRIS	34.3	Table E-11	4.73	3.72	0.9489	1.26E-06	0.04
Phenol	108-95-2	0.3	300	IRIS	63	Table E-11	1.46	1.9	26160	3.33E-07	15
Caprolactam	105-60-2	0.5	100	IRIS	0.75	Table E-12	0.66	1.3892	28720	2.53E-08	14508
Acetone	67-64-1	0.9	1000	IRIS	145	Table E-10	-0.24	0.374	219900	3.50E-05	15

CASRN = Chemical Abstract Service Registry Number; IRIS = Integrated Risk Information System; PPRTV = Provisional Peer Reviewed Toxicity Values; HHBP = Human Health Benchmarks for Pesticides; K_{OW} = octanol-water partitioning coefficient; K_{OC} = soil adsorption coefficient

[a] Reference value (RfV): An estimate of an exposure for a given duration to the human population (including susceptible subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime. RfVs considered in the MCDA include chronic oral reference doses (RfD) from IRIS, PPRTV, and HHBP; and chronic oral minimal risk levels (MRLs) from ATSDR.

[b] From Appendix E.

[c] Di(2-ethylhexyl) phthalate is listed under the name bis(2-ethylhexyl) phthalate in Appendix Table E-11.

[d] Chlorobenzene is listed under the name chloro-benzene in Appendix Table E-13.

[e] o-Cresol is listed under the name 2-methylphenol in Appendix Table E-11.

[f] Cumene is listed under the name isopropylbenzene in Appendix Table E-11.

[g] Dibutyl phthalate is listed under the name dibutyl-n-phthalate in Appendix Table E-11.

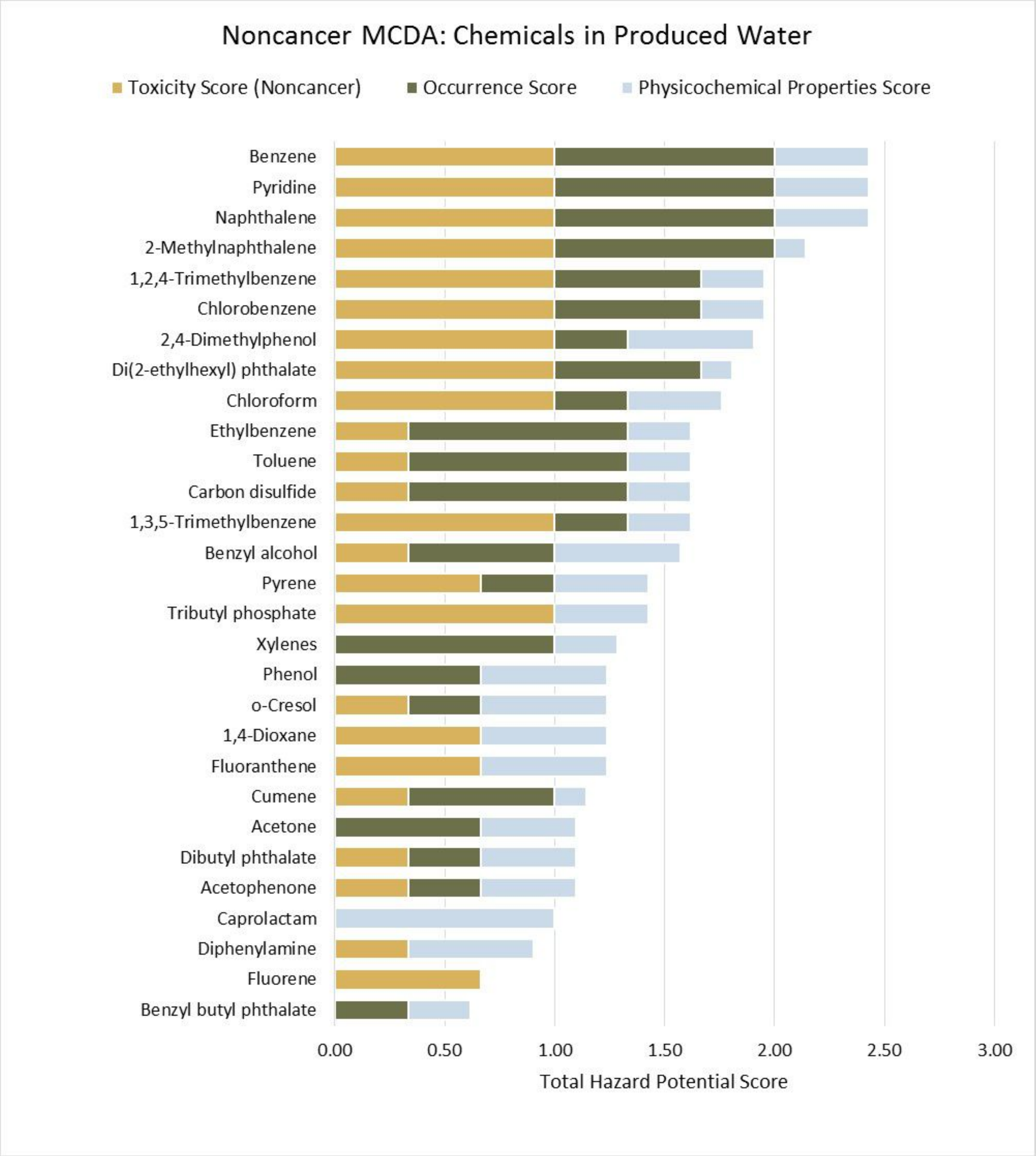

Figure 9-13. Noncancer MCDA results for a subset of 29 chemicals detected in produced water, showing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score for each chemical.

Chemicals are ordered from high to low based on Total Hazard Potential Score. See Section 9.6.4 for details on the calculation.

The other chemicals that received high Toxicity Scores were 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, chloroform, 2,4,-dimethylphenol, tributyl phosphate, di(2-ethylhexyl) phthalate, and chlorobenzene. These chemicals received moderate Total Hazard Potential Scores, as all were detected at lower concentrations compared to other chemicals considered in this analysis and are expected to have moderate transport in water.

The other chemicals that received high Occurrence Scores are ethylbenzene, toluene, xylenes, and carbon disulfide, which were detected at maximum average concentrations of 2010 µg/L, 760 µg/L, 360 µg/L, and 400 µg/L in Barnett, Marcellus, or Powder River Basin produced water. These chemicals received moderate Total Hazard Potential Scores, as all have as all have higher chronic oral RfVs relative to many of the other chemicals in the hazard evaluation, and are all expected to have moderate transport in water relative to the other chemicals.

9.6.5.5 Results: Cancer MCDA for Chemicals in Produced Water

A total of 7 chemicals reported in produced water were evaluated in a cancer MCDA (Table 9-15). OSFs within this suite of chemicals ranged from 7.3 to 0.0049 per mg/kg-day, with benzo(a)pyrene having the highest OSF and N-nitrosodiphenylamine having the lowest. Of these 7 chemicals, benzene and 1,4-dioxane were also included in the cancer MCDA for chemicals used in hydraulic fracturing fluids. Benzene and benzo(a)pyrene are both classified by at least one of the sources in Table 9-1 as a known human carcinogen, while the other chemicals as classified as likely or probable carcinogens in humans (Appendix G: Tables G-1e and G-2e).

Figure 9-14 presents the results of a cancer MCDA for these 7 chemicals in hydraulic fracturing fluids. Benzene and benzo(a)pyrene tied for highest Total Hazard Potential Scores. Of these, benzene was detected at the highest average concentrations in produced water (1500 µg/L in Power River Basin produced water), while benzo(a)pyrene were detected at lower average concentrations (6.7 µg/L in Barnett shale produced water). Benzo(a)pyrine and 1,2-diphenylhydrazine were the most potent carcinogens within this suite of chemicals and received high Toxicity Scores.

The other chemical that received a high Occurrence Score was di(2-ethylhexyl) phthalate, which was detected at an average concentration of 210 µg/L in Barnett Shale produced water. It received a moderate Total Hazard Potential Score because it is hydrophobic and not expected to be readily transported in water.

Table 9-15. Data on the selected subset of chemicals detected in produced water used for input into a cancer MCDA.
Chemicals within the table are ordered from most potent to least potent based on OSF.

		Cancer-specific toxicity (OSF)[a]		**Occurrence (concentration in produced water)[b]**		**Mobility**			**Volatility**	**Persistence**
Chemical Name	**CASRN**	**OSF (per mg/kg-day)**	**Source of OSF**	**Average or Median Conc. (µg/L)**	**Reference**	**Log K_{OW}**	**Log K_{OC}**	**Solubility (mg/L)**	**Henry's Law Constant**	**Half-life in water (days)**
Benzo(a)pyrene	50-32-8	7.3	IRIS	6.7	Table E-11	6.13	5.95	0.01038	4.57E-07	60
1,2-Diphenylhydrazine	122-66-7	0.8	IRIS	4.2	Table E-11	2.94	2.98	161.9	4.78E-07	28.17
1,4-Dioxane	123-91-1	0.1	IRIS	6.5	Table E-11	-0.27	0.421	213900	4.80E-06	15
Benzene	71-43-2	0.015-0.055[c]	IRIS	1500	Table E-13	2.13	1.75	2000	5.55E-03	37.5
Di(2-ethylhexyl) phthalate[d]	117-81-7	0.014	IRIS	210	Table E-11	7.6	4.94	0.001132	2.70E-07	15
Tributyl phosphate	126-73-8	0.009	PPRTV	0.26	Table E-12	4	3.371	7.355	1.41E-06	8.67
N-Nitrosodiphenylamine	86-30-6	0.0049	IRIS	8.9	Table E-11	3.13	3.42	94.85	1.21E-06	37.5

CASRN = Chemical Abstract Service Registry Number; IRIS = Integrated Risk Information System; PPRTV = Provisional Peer-Reviewed Toxicity Values; K_{OW} = octanol-water partitioning coefficient; K_{OC} = soil adsorption coefficient

[a] Oral slope factor (OSF): An upper-bound, approximating a 95% confidence limit, on the increased cancer risk from a lifetime oral exposure to an agent. This estimate, usually expressed in units of proportion (of a population) affected per mg/kg-day, is generally reserved for use in the low dose region of the dose response relationship, that is, for exposures corresponding to risks less than 1 in 100. OSFs considered in the MCDA include values from IRIS, PPRTV, and HHBP.

[b] From Appendix E.

[c] IRIS lists the OSF for benzene as a range from 0.015 to 0.055 per mg/kg-day. For input into the MCDA, we used the high end of this range (0.055 per mg/kg-day).

[d] Di(2-ethylhexyl) phthalate is listed under the name bis(2-ethylhexyl) phthalate in Appendix Table E-11.

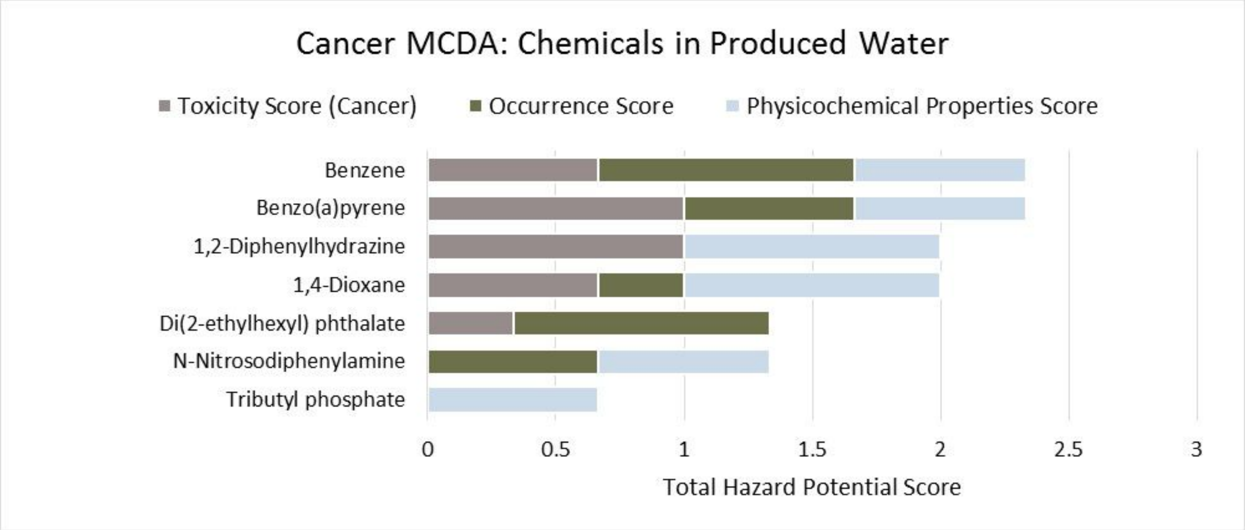

Figure 9-14. Cancer MCDA results for 7 chemicals detected in produced water, showing the Toxicity Score, Occurrence Score, and Physicochemical Properties Score for each chemical. Chemicals are ordered from high to low based on Total Hazard Potential Score. See Section 9.6.4 for details on the calculation.

9.6.6 Limitations and Uncertainty of the MCDA Framework

While this MCDA framework provides a simple and transparent tool for exploring the relative hazard potential of chemicals in the hydraulic fracturing water cycle, it is intended only as a preliminary analysis. It is important to acknowledge the limitations of this analysis, as well as the limitations of the parameters that were used for input in the MCDA.

Chronic oral RfVs and OSFs were selected for the MCDA because they are a primary focus of the toxicological evaluation presented in this chapter. We were interested in placing these values in the context of variables that may impact the likelihood of human exposure. These toxicity values were available for a relatively small fraction of chemicals on EPA's list, which limited the number of chemicals considered in the MCDA.

The FracFocus 1.0 data used in the MCDA does not represent a complete record of hydraulic fracturing chemical usage in the United States, as described in more detail in Chapter 5 and in Section 9.3.1. Frequency of use also does not reflect the volume or concentration of chemical usage, and therefore is an incomplete metric for potential exposure. The EPA FracFocus 1.0 project database provides data on the maximum concentration of chemicals in additives and in hydraulic fracturing fluid, as discussed in Section 5.4, but we elected not to use this data in the MCDA because reported concentrations for each chemical varied widely between disclosures (see Table 5-5 and volume estimates in Figure 5-5), making it difficult to determine a chemical concentration to use in an MCDA. Additionally, many chemicals in the EPA FracFocus 1.0 project database did not have valid concentration data; for instance, the maximum concentrations of a chemical in additive often added up to greater than 100%. We therefore elected to focus on frequency of use as a general metric of chemical occurrence in the hydraulic fracturing water cycle.

The produced water concentrations used in the MCDA are based on the compilation of data presented in Appendix E. While this data reflects the findings of recent studies, it does not represent a complete record of chemicals present in produced water, as described in more detail in Chapter 7 and in Section 9.3.2. Concentrations in produced water also do not necessarily reflect the concentrations in treated wastewater, drinking water wells, or residuals in soil or sediment. Concentrations of these chemicals in treated wastewater or well water would likely be more dilute compared to concentrations in produced water. Concentrations in soils or sediments may be higher, particularly for hydrophobic chemicals.

The physicochemical properties from EPI Suite used in the MCDA are useful for making comparison across chemicals, but these values are also subject to uncertainty. Many of the values used in the MCDA were estimated by EPI Suite, and therefore are subject to the inherent limitations of the EPI Suite model (Section 5.8). Chemical fate and transport will be also influenced by environmental and site-specific conditions, which are outside the scope of this analysis. For instance, the half-lives used to develop the Physicochemical Properties Score are estimated values that assume aerobic conditions, and thus may underestimate the expected half-life under anaerobic conditions (e.g., in a groundwater contaminant plume). If chemicals are present in a mixture, as inevitably occurs in hydraulic fracturing fluids and in the subsurface environment, fate and transport will be influenced by changes in solubility or degradation resulting from interactions with other chemicals.

There are also fundamental limitations with regards to the scope of the MCDA. The chemicals used in these analyses may not be representative of chemicals at a specific field site. The analysis only examined organic chemicals, as EPI Suite is not able to estimate physicochemical properties of inorganic chemicals. Additionally, the physicochemical properties used in the MCDA were chosen specifically to reflect chemical transport in water, and therefore do not highlight the potential hazards of hydrophobic or volatile chemicals. Hydrophobic chemicals may serve as long-term sources of pollution by sorbing to soils or sediments at contaminated sites, and volatile chemicals may be hazardous when inhaled. This analysis also does not attempt to address bioavailability or toxicokinetics, which may be influenced by physicochemical properties such as log K_{ow}. For instance, chemicals with log K_{ow} of 2-4 tend to absorb well through biological membranes, while chemicals with log K_{ow} > 4 tend not to absorb well, and those with log K_{ow} of 5-7 tend to bioconcentrate (U.S. EPA, 2012i).

9.6.7 Application of the MCDA Framework for Preliminary Hazard Evaluation

The MCDA framework presented here is intended as a preliminary analysis, and illustrates one possible method for integrating data to explore potential hazards. By combining multiple lines of data, we can stratify chemicals according to estimated hazard potential, and gain preliminary insight into those chemicals that may be of more concern than others to drinking water resources.

Researchers may find this approach useful in their efforts to explore the potential hazards of chemicals present at specific field sites, particularly in instances when exposure assessment data is not available. The MCDA framework is flexible, and could be adapted to incorporate site-specific data on chemical usage, different types of toxicity data, as well as other variables that may be of interest for risk assessment. For instance, rather than focusing on RfVs and OSFs from US federal sources, one could choose to derive the Toxicity Score using other sources of relevant toxicity information. Additionally, one could choose to perform this analysis using different physicochemical property inputs, to highlight chemical interactions with different environmental media (e.g., hydrophobic or volatile chemicals). Researchers could also choose to apply different weights to each of the three criteria considered in this analysis (toxicity, occurrence, physicochemical properties), to reflect expert judgement of each variable's relative importance.

9.7 Synthesis

The overall objective of this chapter was to identify and provide information on the toxicological properties of chemicals used in hydraulic fracturing and of hydraulic fracturing wastewater constituents, and to evaluate the potential hazards of these chemicals for drinking water resources. Toward this end, the EPA developed a list of 1,606 chemicals that are reported to be associated with hydraulic fracturing, separating them into subsets based on whether they were reported to have been used in hydraulic fracturing fluids (1,084 chemicals total) or detected in produced water (599 chemicals total). To evaluate the potential hazards of these chemicals, the EPA compiled chronic oral RfVs, OSFs, and qualitative cancer classifications from selected federal, state, and international sources that met the EPA's criteria for consideration in this assessment. This toxicological information was used to conduct an initial identification of the potential human health hazards associated with several subsets of chemicals identified as being of particular interest in previous chapters of this report. Finally, in order to illustrate how data integration could be used to explore potential hazards, an MCDA framework was used to evaluate selected subsets of chemicals based on toxicity, environmental occurrence, and physicochemical properties affecting chemical transport in water.

9.7.1 Summary of Findings

A major finding of this chapter was that chronic oral RfVs and OSFs were not available for the majority of chemicals that the EPA has identified as being associated with hydraulic fracturing activity, indicating that the majority of these chemicals have not undergone significant toxicological evaluation. Similarly, there have been several recent peer-reviewed studies that have attempted to gather toxicological information for subsets of chemicals that are used in hydraulic fracturing fluids, and they have found that many of these chemicals do not have toxicity values available (Elliott et al., 2016; Wattenberg et al., 2015; Stringfellow et al., 2014; Colborn et al., 2011). Taken together, this suggests a potentially significant knowledge gap exists with respect to the scientific community's understanding of the potential human health impacts of these chemicals. With the limited availability of toxicity values, risk assessment is difficult, and potential impacts on drinking water resources may not be assessed adequately. This lack of toxicity values is not unique to the hydraulic fracturing industry; in fact, it has been estimated that there are tens of thousands of chemicals in commercial use that have not undergone significant toxicological evaluation (Judson et al., 2009).

There are a variety of chemicals associated with hydraulic fracturing known to be hazardous to human health. Chronic oral RfVs or OSFs from the sources considered by the EPA in this assessment were available for 98 (9%) of the 1,084 chemicals used in hydraulic fracturing fluids, and 120 (20%) of the 599 chemicals detected in hydraulic fracturing produced water. Potential hazards associated with chronic oral exposure to these chemicals include carcinogenesis, immune system effects, changes in body weight, changes in blood chemistry, cardiotoxicity, neurotoxicity, liver and kidney toxicity, and reproductive and developmental toxicity. Methane is not considered to be toxic when ingested, but may accumulate to explosive levels or act as an asphyxiant. DBPs formed during wastewater treatment can contribute to an increased risk of cancer, anemia, liver and kidney effects, and central nervous system effects, with brominated forms of DBPs considered to be more cytotoxic, genotoxic, and carcinogenic than chlorinated species.

To assess the toxicity of chemicals that lack chronic oral RfVs and OSF, risk assessors will need to turn towards alternative data sources. This chapter explored two alternative data sources that may provide useful information. QSAR-based toxicity estimates—specifically, rat chronic oral LOAEL estimates generated using TOPKAT—were available for many of the chemicals that lacked chronic oral RfVs and OSFs from the sources considered in this assessment, and may be used to rank chemicals based on toxicity when other data are not available. Additionally, many of these chemicals have information available on the EPA's ACToR database, which is an online data warehouse designed to consolidate large and disparate amounts of chemical data. The information available in the ACToR data warehouse ranges from the selected RfVs and OSFs discussed in this assessment, which have undergone extensive peer review, to toxicological data that have undergone little-to-no peer review.

When considering the potential impact of chemicals on drinking water resources and human health, it is important to consider exposure as well as toxicological properties. As discussed in previous chapters of this report and highlighted in this chapter, events such as spills, leaks from storage pits, and discharge of inadequately treated wastewater have led to the entry of hydraulic fracturing-related chemicals into drinking water resources. In some instances, chemical concentrations in surface water or groundwater were in exceedance of MCLs, indicating their presence at levels that could impact human health. While these studies demonstrate the potential entry of these chemicals into drinking water resources, there is a lack of systematic studies examining actual human exposures to these chemicals in drinking water as a result of hydraulic fracturing activity.

In the absence of exposure assessment data, the MCDA framework presented in this chapter provides a preliminary analysis of the relative hazard potential of these chemicals. In this context, occurrence and physicochemical property data were used as metrics to estimate the likelihood that a chemical could reach and impact drinking water, and toxicity data was used as a metric for the potential severity of an impact. This analysis highlighted several chemicals that may be more likely than others to reach drinking water and create a toxicological hazard. Of the chemicals used in hydraulic fracturing fluids that were considered in this analysis, chemicals such as propargyl alcohol stood out as having high potential toxicity, high frequency of use, and physicochemical properties that are conducive to transport in water. Of the chemicals in produced water, chemicals such as benzene, pyridine, 2-methylnaphthalene, and naphthalene stood out as having high potential toxicity, high concentrations in produced water, and physicochemical properties that are conducive to transport in water.

9.7.2 Factors Affecting the Frequency or Severity of Impacts

There are multiple pieces of information that could be taken into account when evaluating the frequency and severity of impacts that these chemicals may have on drinking water resources. This includes knowledge of the chemicals used at a given site, the toxicological and physicochemical properties of these chemicals, the amount of fluid being used and recovered, the likelihood of mechanical integrity failures, the likelihood of spills and other unintentional releases, and the efficiency of chemical removal during wastewater treatment. The MCDA presented in this chapter incorporated parameters that may impact the likelihood of chemical exposure, including frequency of use, measured concentration, and transport in water, and was used to stratify and rank chemicals based on relative hazard potential. However, it should be considered only as a preliminary analysis, and should not be used in place of local data on the concentrations and volumes of chemicals in areas of hydraulic fracturing activity.

Analysis of the chemicals used in hydraulic fracturing fluids indicated that the majority of chemicals on the EPA's list are used in <1% of wells nationally (Figure 9-4). Therefore, potential exposure to the majority of these chemicals is more likely to be a local issue, rather than a national one. Given that the analysis of the EPA FracFocus 1.0 project database presented in this chapter was based on 35,957 disclosures, a chemical used in <1% of wells nationally could still be used in several hundred wells. Chemicals used infrequently on a national basis could still be used more frequently within certain areas or counties, increasing the potential for local exposure to that chemical.

As an example of how an infrequently used chemical could have local impacts, consider (E)-crotonaldehyde, which had one of the lowest chronic oral RfVs among the chemicals considered in the noncancer MCDA for hydraulic fracturing chemicals, and was reported in approximately 0.06% of disclosures in the EPA FracFocus 1.0 project database. If the EPA FracFocus 1.0 project database is a representative sample of all of the wells across the country, then the likelihood of (E)-crotonaldehyde contamination on a national scale is limited. However, this in no way diminishes the likelihood or potential severity of (E)-crotonaldehyde contamination at sites where this chemical is used.

This is in contrast with frequently used chemicals such as methanol. Methanol was reported in 73% of wells in the EPA FracFocus 1.0 project database, and was the most frequently used chemical considered in the noncancer MCDA for chemicals used in hydraulic fracturing fluids. Methanol is soluble and relatively mobile in water, but has a higher chronic oral RfV compared other chemicals considered in this analysis. Therefore, methanol may be expected to have a higher exposure potential on a national basis compared to other chemicals, with a moderate hazard potential due to its relatively high RfV.

Even if no chemicals were added to hydraulic fracturing fluids, there is still a potential for impacts from constituents naturally present in the subsurface which could be brought to the surface in produced water. As described in Section 9.5, many of the naturally occurring chemicals in produced water—e.g., organic chemicals (e.g., BTEX and related hydrocarbons), metals, anions, and TENORM—are hazardous to human health and have been reported in drinking water resources as a result of hydraulic fracturing activity, sometimes at concentrations exceeding MCLs. The constituents of produced water that contribute to the formation of DBPs, specifically bromide, chloride, iodine, and ammonium, are naturally occurring and are characteristic of wastewater from hydraulically fractured wells.

Overall, contamination of drinking water resources depends on site-, chemical-, and fluid-specific factors (Goldstein et al., 2014), and the exact mixture and concentrations of chemicals at a site will depend upon the geology and the chemicals used in the oil and gas extraction processes. Therefore, potential hazard and risk considerations are best made on a site-specific, well-specific basis.

9.7.3 Uncertainties

There are notable uncertainties in the chemical and toxicological data limiting a comprehensive assessment of the potential health impacts of hydraulic fracturing on drinking water resources.

For human health risk assessment, a significant data gap is the lack of chronic oral RfVs and OSFs from sources meeting the EPA's criteria for inclusion in this report. For instance, of the 34 chemicals (excluding water, quartz, and sodium chloride) that were reported in ≥10% of disclosures in the EPA FracFocus 1.0 project database, 9 chemicals have chronic oral RfVs available, and none have OSFs (Table 9-2). Without reliable and peer reviewed toxicity values, comprehensive hazard evaluation and hazard identification of chemicals is difficult, and the ability to consider the potential cumulative effects of exposure to chemical mixtures in hydraulic fracturing fluid or produced water may be limited. Although there are other potential sources of toxicity information for many of these chemicals, some of it may be limited or of lesser quality. Consequently, potential impacts on drinking water resources and human health may not be assessed adequately.

An equally significant data gap is the lack of exposure assessment data for drinking water resources in areas of hydraulic fracturing activity. As discussed in Text Box 9-1, data on exposure potential is a critical component of the risk assessment process, and is necessary for risk characterization. In the absence of exposure assessment information, the MCDA framework presented in this chapter may be useful for exploring the potential hazards of hydraulic fracturing-related chemicals, but should be considered as a preliminary analysis only. The MCDA presented in this chapter considered only a small subset of chemicals that had data available, was limited in scope, and may not be representative of the chemicals that are present at a specific field site. It should be emphasized that this MCDA framework represents just one method that can be used to integrate chemical data for hazard evaluation, and is readily adaptable to include different variables, different weights for the variables, and site-specific considerations.

There is also uncertainty surrounding the EPA's list of chemicals associated with hydraulic fracturing activity. As discussed in Section 5.4 and Section 9.3.1, there is incomplete information available on chemicals used in hydraulic fracturing fluids due to industry use of CBI as well as incomplete reporting of chemical use. For instance, the EPA's analysis of the FracFocus 1.0 project database found that approximately 11% of ingredients were reported as CBI, and that more than 70% of FracFocus 1.0 disclosures contained at least one CBI ingredient. There may also be regional limitations in the disclosures submitted to FracFocus 1.0, as 78% of chemical disclosures in came from five states, and 47% were from Texas (U.S. EPA, 2015a). Despite these limitations, FracFocus remains the most complete source for tracking hydraulic fracturing chemical usage in the United States, and therefore was the best available source for the hazard evaluation in this chapter. Although the sources used to compile the chemical list represented the best available data at the time of this study, it is possible that some of these chemicals are no longer used at all, and many of these chemicals may only be used infrequently. Therefore, it may be possible that significantly fewer than 1,084 chemicals are currently used in abundance. As practices evolve, it is likely that chemicals are used or will be used that are not included on this chemical list. Having a better understanding of the chemicals and formulations, including those that are CBI, along with their frequency of use and volumes, would greatly benefit risk assessment and risk management decisions.

Additionally, the list of produced water chemicals identified in this chapter is almost certainly incomplete. As discussed in Chapter 7, chemicals and their metabolites may go undetected because they were not included in the analytical methodology, or because an analytical methodology was not available. Chemical analysis of produced water can also be challenging because high levels of dissolved solids in produced water and wastewater can interfere with chemical detection. As a result, there are likely chemicals of concern in produced water that have not been detected or reported, and are not included on the chemical list presented in this report.

9.7.4 Conclusions

The EPA identified 1,606 chemicals associated with the hydraulic fracturing water cycle, including 1,084 chemicals used in hydraulic fracturing fluids, and 599 chemicals detected in produced water. Toxicity-based chronic oral RfVs and/or OSFs from sources meeting selection criteria were not available for the majority (89%) of the chemicals on this total list. Thirty-seven percent of chemicals on the EPA's list that are used in hydraulic fracturing fluids lack data on their frequency of use. Current understanding of the chemical composition of produced water is constrained by analytical chemistry limitations and by the likelihood that chemical composition will vary between wells. A limited number of studies have detected these chemicals in surface water, groundwater, or well water near areas of hydraulic fracturing activity, suggesting the potential for human exposure; however, actual human exposures to these chemicals in drinking water resources has not been well characterized. Given the large number of chemicals used or detected in various stages of the hydraulic fracturing water cycle, as well as the large number of hydraulically fractured wells nationwide, this missing chemical information represents a significant data gap.

While it remains challenging to fully understand the toxicity and potential public health impacts of these chemicals for drinking water resources, the toxicological data, occurrence data, and physicochemical data compiled in this report provide a resource for assessing the potential hazards of chemicals in the hydraulic fracturing water cycle. The MCDA framework presented here illustrates one method for integrating these data for a preliminary hazard evaluation, which may be useful when exposure assessment data are not available. While the analysis in this chapter is constrained to the assessment of chemicals on a national scale, this approach is readily adaptable for use on a regional or site-specific basis.

This collection of data provides a tool to inform decisions about protection of drinking water resources. Stakeholders may use these results to prioritize chemicals for hazard assessment or for determining future research priorities. Industry may use this information to prioritize chemicals for replacement with less toxic, persistent, and mobile alternatives.

9.8 Annex

9.8.1 Calculation of Physicochemical Property Scores (MCDA Hazard Evaluation)

Section 9.6.3 describes how Physicochemical Properties Scores for the noncancer and cancer MCDAs were calculated based on three subcriteria which affect the likelihood that a chemical will be transported in water: mobility, volatility, and persistence. Calculation of these subcriteria scores was performed as described by Yost et al. (In Press), as follows:

9.8.1.1 Mobility Score

Chemical mobility in water was assessed based upon three physicochemical properties that describe chemical solvency in water: the octanol-water partition coefficient (K_{OW}), the soil adsorption coefficient (K_{OC}), and aqueous solubility. K_{OW} describes the partitioning of a chemical between water and a carbon-based media (octanol), while K_{OC} described the partitioning of a chemical between water and organic carbon in soil. K_{OW} and K_{OC} are generally represented on a logarithmic scale. Aqueous solubility is the maximum amount of a chemical that will dissolve in water in the presence of pure chemical. Chemicals with low K_{OW}, low K_{OC}, or high aqueous solubility are more likely to solubilize and move with water, and therefore were ranked as having greater potential to affect drinking water resources.

For input into the MCDA, we used experimentally measured values (provided in EPI Suite) whenever available. Otherwise, we used the following estimated values from EPI Suite: log K_{OW} estimated using the KOWWIN™ model, log K_{OC} estimated using the KOCWIN™ Sabljic molecular connectivity method, and aqueous solubility estimated using the WSKOWWIN™ model. Using the thresholds designated in Table 9-11, each of these properties was assigned a score of 1-4. The highest of these three scores (K_{OW}, K_{OC}, or solubility) was designated as the Mobility Score for each chemical.

9.8.1.2 Volatility Score

Chemical volatility was assessed based on the Henry's law constant, which is the ratio of the concentration of a chemical in air to the concentration of that chemical in water. Chemicals with low Henry's law constants are less likely to leave water via volatilization, and were therefore ranked as having greater potential to affect drinking water resources.

For input into the MCDA, we used experimentally measured values (provided in EPI Suite) whenever available. Otherwise, we used Henry's Law constants that were estimated using the EPI Suite HENRYWIN™ model, which generates values using two different methods (group contribution and bond contribution); the lower of these two estimated values was used as input into the MCDA.

Using the thresholds designated in Table 9-11, the Henry's law constant for each chemical was assigned a score of 1-4. This value was designated as the Volatility Score for each chemical.

9.8.1.3 Persistence Score

Chemical persistence was assessed based on estimated half-life in water, which describes how long a chemical will persist in water before it is transformed or degraded. Chemicals with longer half-lives are more persistent, and were therefore ranked as having greater potential to impact drinking water resources.

EPI Suite estimates biodegradation time using the BIOWIN™ 3 model, which provides an indication of a chemical's environmental biodegradation rate in relative terms (e.g., hours, days, weeks, etc.), assuming aerobic conditions. These BIOWIN3 estimates are converted to numerical half-life values for use in EPI Suite's Level III Fugacity model. For input into the MCDA, we used the same estimated half-life in water that is used in the Level III Fugacity model. Using the thresholds designated in Table 9-11, the half-life in water of each chemical was assigned a score of 1-4. This value was designated as the Persistence Score for each chemical.

9.8.1.4 Total Physicochemical Properties Score

For each chemical, the Mobility Score, Volatility Score, and Persistence Score (each on a scale of 1 to 4) were summed to calculate a total Physicochemical Properties Score. Higher Physicochemical Properties Scores indicate chemicals that are more likely to be transported in water, with a maximum possible score of 12.

9.8.2 Example of MCDA Score Calculation

The methods used for MCDA score calculation are described in Section 9.6.3. For an example of how the MCDA scores were calculated, consider benzene, which was included in both the noncancer MCDA (national analysis) and cancer MCDA for chemicals used in hydraulic fracturing fluids. This demonstrates how MCDA scores were calculated for benzene for these two different analyses.

9.8.2.1 Score Calculation for Benzene in Noncancer MCDA for Hydraulic Fracturing Fluids

- **Toxicity Score (Noncancer):** Benzene has a chronic oral RfV of 0.004 mg/kg-day (source: IRIS). Across the 42 chemicals that were considered in the noncancer MCDA (national analysis), chronic oral RfVs ranged from 0.001 mg/kg-day [(E)-crotonaldehyde] to 20 mg/kg-day (1,2-propylene glycol). The chronic oral RfV of benzene falls in the lowest (most toxic) quartile of these chemicals, and therefore benzene was assigned a Toxicity Score of 4. When the results were standardized to the highest Toxicity Score (4) and lowest Toxicity Score (1) within the set of chemicals, benzene was calculated to have a final Toxicity Score of 1, as follows:

$$1 = (4 - 1) / (4 - 1)$$

- **Occurrence Score:** Benzene was used in 0.006% of wells nationally. For the 42 chemicals considered in the national noncancer MCDA, frequency of use ranged from 73%

(methanol) to 0.003% (furfural) of wells nationally. Benzene falls in the lowest quartile with regards to frequency of use, and therefore benzene was assigned an Occurrence Score of 1. When the results were standardized to the highest Occurrence Score (4) and lowest Occurrence Score (1) within the set of chemicals, benzene was calculated to have a final Occurrence Score of 0, as follows:

$$0 = (1 - 1) / (4 - 1)$$

- **Physiochemical Properties Score:** Benzene received a Mobility Score of 4 (log K_{OW} = 2.13; log K_{OC} = 1.75; solubility = 2000 mg/l), a Volatility Score of 2 (Henry's law constant = 0.00555), and a Persistence Score of 2 (half-life in water = 37.5 days). This sums to a Total Physicochemical Properties Score of 8. Within the 42 chemicals considered in the national noncancer MCDA, several chemicals received Total Physicochemical Properties Scores of 9, which was the highest observed score. Cumene received a Total Physicochemical Properties Scores of 6, which was the lowest score. When the results were standardized to the highest (9) and lowest (6) of these scores, benzene was calculated to have a final Total Physicochemical Properties Scores of 0.67, as follows:

$$0.67 = (8 - 6) / (9 - 6)$$

- **Total Hazard Potential Score (Noncancer MCDA):** For benzene, the Toxicity Score (1), Occurrence Score (0), and Physicochemical Properties Score (0.67) were summed to calculate a Total Hazard Potential Score of 1.67. The relative contribution of the three criteria scores to this total score is depicted as a graphic in Figure 9-8.

9.8.2.2 Score Calculation for Benzene in Cancer MCDA for Hydraulic Fracturing Fluids

- **Toxicity Score (Cancer):** Benzene has an OSF of 0.055 per mg/kg-day (source: IRIS). Within the entire set of 10 chemicals that was considered in the cancer MCDA, OSFs ranged from 3 (quinoline) to 0.002 (dichloromethane) per mg/kg-day. The OSF of benzene falls in the second quartile of these scores, and therefore was assigned a Toxicity Score of 2. When the results were standardized to the highest Toxicity Score (4) and lowest Toxicity Score (1) within the set of chemicals, benzene was calculated to have a final Toxicity Score of 0.33, as follows:

$$0.33 = (2 - 1) / (4 - 1)$$

- **Occurrence Score:** As described in the noncancer MCDA above, benzene was used in 0.006% of wells nationally. This was the lowest frequency of use among the 10 chemicals that were considered in the cancer MCDA, with benzyl chloride (used in 6% of wells) having the highest. Benzene therefore falls in the lowest quartile with regards to frequency of use, and was assigned an Occurrence Score of 1. When the results were standardized to the highest Occurrence Score (4) and lowest Occurrence Score (1) within the set of chemicals, benzene was calculated to have a final Occurrence Score of 0, as follows:

$$0 = (1 - 1) / (4 - 1)$$

- **Physiochemical Properties Score:** As described in the noncancer MCDA above, benzene received a Total Physicochemical Properties Score of 8. Within the 10 chemicals that were considered in the cancer MCDA, all chemicals either received a Total Physicochemical Properties Score of 8 or 9. When the results were standardized to these high and low scores, benzene was calculated to have a final Total Physicochemical Properties Scores of 0 as follows:

$$0 = (8 - 8) / (9 - 8)$$

- **Total Hazard Potential Score (Cancer MCDA):** The Toxicity Score (0.33), Occurrence Score (0), and Physicochemical Properties Score (0) were summed to calculate a Total Hazard Potential Score of 0.33. The relative contribution of the three criteria scores to this total score is depicted as a graphic in Figure 9-12.

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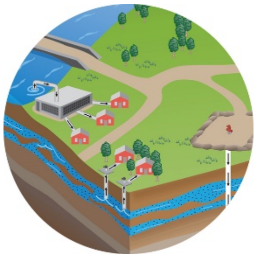
Chapter 10. Synthesis



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10. Synthesis

Introduction

The goals of this report were to assess the potential for activities in the hydraulic fracturing water cycle to impact the quality or quantity of drinking water resources, and to identify factors affecting the frequency or severity of those impacts. Overall, we conclude activities in the hydraulic fracturing water cycle can impact drinking water resources under some circumstances. Impacts can range in frequency and severity, depending on the combination of hydraulic fracturing water cycle activities and local- or regional-scale factors. The following combinations of activities and factors are more likely than others to result in more frequent or more severe impacts:

- Water withdrawals for hydraulic fracturing in times or areas of low water availability, particularly in areas with limited or declining groundwater resources;
- Spills during the management of hydraulic fracturing fluids and chemicals or produced water that result in large volumes or high concentrations of chemicals reaching groundwater resources;
- Injection of hydraulic fracturing fluids into wells with inadequate mechanical integrity, allowing gases or liquids to move to groundwater resources;
- Injection of hydraulic fracturing fluids directly into groundwater resources;
- Discharge of inadequately treated hydraulic fracturing wastewater to surface water resources; and
- Disposal or storage of hydraulic fracturing wastewater in unlined pits, resulting in contamination of groundwater resources.

These conclusions are based on cases of identified impacts and other data, information, and analyses presented in this report. Cases of impacts were identified for all stages of the hydraulic fracturing water cycle. Identified impacts generally occurred near hydraulically fractured oil and gas production wells and ranged in severity, from temporary changes in water quality to contamination making private drinking water wells unusable. The inherent characteristics of groundwater resources make them more vulnerable to impacts from activities in the hydraulic fracturing water cycle compared to surface water.

We see the identification of factors affecting the frequency or severity of impacts, and uncertainties and data gaps in this report as particularly useful for decision makers. Factors often can be managed, changed, or used to identify areas for specific monitoring or modification of practices. Thus, in the short-term, information on factors can help decision makers reduce current vulnerabilities of drinking water resources to activities in the hydraulic fracturing water cycle. In the longer term, reducing the uncertainties and filling the data gaps could enhance science-based decisions to protect drinking water resources in the future.

The purpose of this chapter is to synthesize for decision makers the information on factors, uncertainties, and data gaps presented in this assessment. In Section 10.2, we focus on factors increasing or decreasing the frequency or severity of impacts at each stage of the hydraulic fracturing water cycle. In Section 10. 3, we discuss major uncertainties and data gaps identified in this assessment. Finally, in Section 10.4, we discuss potential uses for this assessment.

10.1 Factors Affecting the Frequency or Severity of Impacts

10.1.1 Water Acquisition

Groundwater and surface water resources serve as both sources of water for hydraulic fracturing and public and private drinking water supplies. Thus, water withdrawals for hydraulic fracturing can impact the quantity or quality of drinking water resources under certain circumstances. Since, by definition, every water withdrawal affects water quantity, we focused in this assessment not on all water withdrawals per se, but rather on those with the potential to limit the availability of drinking water or alter its quality. Whether a withdrawal has this potential depends upon a combination of factors at the local scale. Factors can either increase or decrease the frequency or severity of impacts. In this section on water acquisition, we combine our discussion of frequency and severity because all of the factors we discuss in this section affect both frequency and severity in a similar fashion (i.e., either increase both frequency and severity, or decrease both frequency and severity).

10.1.1.1 Frequency and Severity

The local balance between water withdrawals and water availability is the most important factor determining whether water acquisition impacts are likely to occur or be severe. Impacts are more likely to be frequent or severe where or when hydraulic fracturing water withdrawals are relatively high and water availability is low. In contrast, the same amount of water withdrawn can have a negligible effect if withdrawn in an area of—or at a time of—higher water availability. For this reason, it is important not to focus solely on the amount withdrawn, but the balance between water withdrawals and availability in place and time.

For this assessment, we developed county-level estimates of water use (i.e., water withdrawals) for hydraulic fracturing, which were then compared to an index of readily available fresh water. This readily available fresh water index included unappropriated surface water and groundwater, and appropriated water potentially available for purchase (Tidwell et al., 2013) (Text Box 4-2).[1] In the majority of counties where hydraulic fracturing takes place, hydraulic fracturing water use was less than 1% of this index of readily available fresh water. We did find, however, a small number of counties with higher percentages. There were 45 counties out of the almost 400 surveyed where hydraulic fracturing water use was above 10% of the index. Of these counties, 35 exceeded 30%, and 17 of these counties had hydraulic fracturing water use exceeding the index. All of the counties in this latter category are located in Texas.

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[1] In the western United States, water is generally allocated by the principle of prior appropriation—that is, first in time of use is first in right. New development must use unappropriated water or purchase appropriated water from vested users. In the index of readily available fresh water, it was assumed 5% of appropriated irrigated water could be purchased. See Text Box 4-2 for more details about this analysis.

This does not mean impacts to drinking water quantities occurred or will occur in these counties, nor does it mean that impacts did not or will not occur in counties with relatively low percentages. To truly determine whether impacts occurred, water withdrawals and availability need to be compared at the scale of the drinking water resource. For instance, groundwater withdrawals for hydraulic fracturing could affect water levels in nearby private water wells. As a national assessment, we could not often examine impacts at this local scale, although we did cite studies of local impacts where available. Nevertheless, our county level assessment does point to places where the potential for impacts is higher. This information may be useful to focus efforts on reducing the fresh water demand of hydraulic fracturing.

Beyond our county level assessment, we conclude that declining groundwater resources are particularly vulnerable to water quantity and quality impacts from withdrawals. Groundwater recharge rates can be low, and groundwater withdrawals are exceeding recharge in areas of the country (Konikow, 2013). When withdrawals exceed recharge, the result is declining water levels. For this reason, water levels in some aquifers in the United States have declined substantially over the last century (Konikow, 2013). Although irrigated agriculture is often the dominant user of groundwater, hydraulic fracturing withdrawals now also contribute to declining groundwater levels in some areas (e.g., southern Texas; Steadman et al., 2015; Scanlon et al., 2014b) Cumulative groundwater withdrawals can also impact water quality by mobilizing chemicals, such as uranium, from naturally occurring sources in the surrounding rock into the groundwater (DeSimone et al., 2014).

In certain instances, state and local governments have encouraged or mandated the use of surface water in place of groundwater, as evidenced in both Louisiana and North Dakota. In 2008, the state of Louisiana asked oil and gas companies to switch from groundwater to surface water to mitigate stress on the Carrizo-Wilcox aquifer, a critical source of drinking water in the region. Likewise, the state of North Dakota requested the oil industry obtain water from the Missouri river system, and not from stressed groundwater sources. By contrast, surface water availability is limited in other regions and cannot provide an alternative source of water (e.g., western Texas).

Among surface water sources, small streams are particularly vulnerable to impacts. This is the case across the country, even in the eastern United States where surface water is generally more plentiful. An EPA study of the Susquehanna River Basin in northeastern Pennsylvania found that the smallest streams (with less than 10 mi^2 of contributing area–i.e., the watershed area drained by the stream) would be the most likely to be impacted from water withdrawals in the absence of protective passby flows; see discussion below and U.S. EPA (2015e).[1] While the amount of contributing area varies by geographic location due to differences in runoff, the finding that the smallest streams are the most vulnerable to withdrawals holds across all landscapes.

Not only does water availability vary from one location to another, but it can also vary temporally at a given location, often due to variations in precipitation. Because of this dynamic, long-term or seasonal drought can increase the frequency or severity of impacts from withdrawals by decreasing water availability. The EPA study of the Susquehanna River Basin found even larger streams (up to

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[1] Passby flows are low stream flow thresholds below which withdrawals are not allowed.

600 mi^2 of contributing area) would be vulnerable to impacts at times of drought, again absent passby flows (U.S. EPA, 2015e). Dry conditions can also stress groundwater supplies by simultaneously increasing water demand (e.g., irrigation water demand increases in dry conditions) while also decreasing groundwater recharge. Much of the western United States has experienced extended periods of drought over the last decade. Climate change is likely to exacerbate these conditions in certain locations (Meixner et al., 2016).

Conversely, there are factors that can reduce the frequency or severity of impacts. Reuse of hydraulic fracturing wastewater (i.e., produced water managed for reuse, treatment and discharge, or disposal), for example, can reduce demands on fresh water resources.[1] Reuse does not appear to be driven by water scarcity, but rather by the cost of disposal. Operators are likely to dispose of wastewater when it is less expensive than reuse. For instance, greater reuse of wastewater occurs in the Marcellus Shale in Pennsylvania than in the Barnett Shale in Texas, even though water availability is generally higher in the Marcellus region (Figure 10-1). The general lack of disposal wells in Pennsylvania means disposing of wastewater requires trucking to Ohio or other locations with disposal wells. Because of this expense, operators reuse substantial proportions of their wastewater, in contrast to the Barnett Shale where disposal wells are readily available.

The reuse of wastewater to offset fresh water use in hydraulic fracturing is often limited by the amount of wastewater available. The volume of produced water from a single well can be relatively small compared to the volume needed to fracture a well (Figure 10-1a). This means produced water would need to be aggregated from multiple wells to equal the volume needed to hydraulically fracture an additional well. For instance, it would take 10 wells to make enough water to fracture an 11th well if, as has been shown in the Marcellus Shale in Pennsylvania, produced water volumes are 10% of injected volumes (Figure 10-1a). Thus, reuse is a factor that can reduce fresh water demand, but not eliminate it in most cases. Nevertheless, even a marginal decline in fresh water demand can make a difference in the frequency or severity of impacts.

The use of brackish groundwater is also a factor reducing fresh water demand, in some cases to a much greater degree than reuse. In the Permian Basin in western Texas, for instance, brackish water makes up 30 to 80% of water used for hydraulic fracturing, and 20% in the Eagle Ford Shale in southern Texas (Nicot et al., 2012). Our county level estimates suggest brackish water availability could entirely meet current hydraulic fracturing water demand in Texas and many other locations.[2] In 35 counties nationally, hydraulic fracturing water use equaled or exceeded 30% of an index of fresh water availability; when brackish water and wastewater were considered in addition to fresh water availability, only two counties equaled or exceeded 30% (Text Box 4-2).

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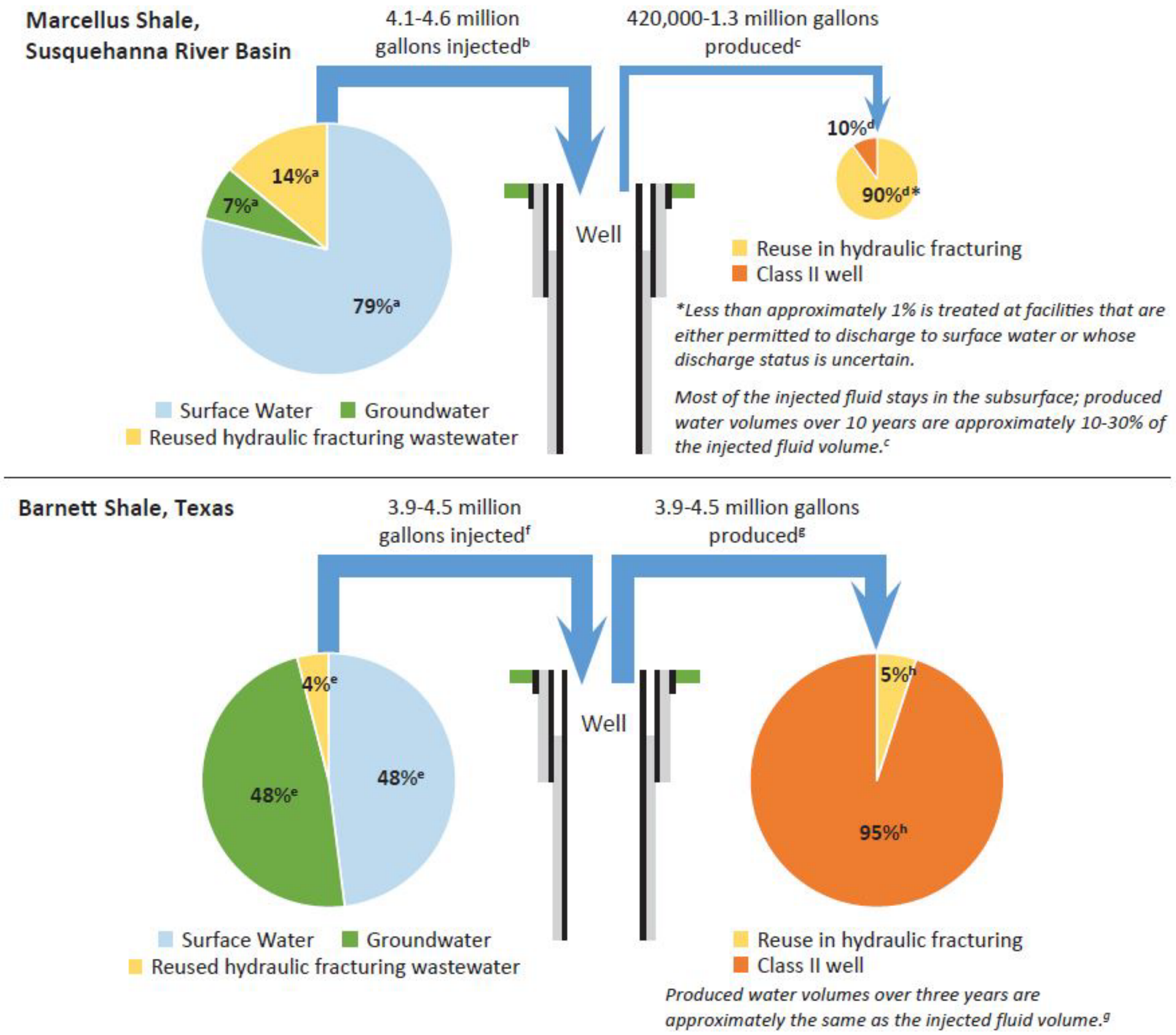
[1] Hydraulic fracturing wastewater is produced water that is managed using practices that include, but are not limited to, reuse in subsequent hydraulic fracturing operations, treatment and discharge, and injection into disposal wells. The term is being used in this study as a general description of certain waters and is not intended to constitute a term of art for legal or regulatory purposes (see Chapter 8 and Appendix J, the Glossary, for more detail).

[2] Brackish water for the purposes of this analysis ranged from 3,000 to 10,000 ppm of total dissolved solids (TDS), and from 50 to 2,500 ft (15-760 m) below the surface (Tidwell et al., 2013). (See Text Box 4-2 for more details.)



**Less than approximately 1% is treated at facilities that are either permitted to discharge to surface water or whose discharge status is uncertain.*

Most of the injected fluid stays in the subsurface; produced water volumes over 10 years are approximately 10-30% of the injected fluid volume.[c]

Produced water volumes over three years are approximately the same as the injected fluid volume.[g]

Figure 10-1. Water budgets representative of practices in (top) the Marcellus Shale in the Susquehanna River Basin in Pennsylvania and (bottom) the Barnett Shale in Texas.

Pie size and arrow thickness represent the relative volume of water as it flows through the hydraulic fracturing water cycle. Water budgets illustrative of typical water management practices in the Marcellus Shale in the Susquehanna River Basin between approximately 2008 and 2013 and the Barnett Shale in Texas between approximately 2011 and 2013. They do not represent any specific well. Sources for the top figure (a) Tables 4-1 and 4-2 (SRBC, 2016)—note, surface water, groundwater, and reuse values of 92%, 8%, and 16% in table normalized to 79%, 7%, 14%, respectively, for this chart (this was done to represent reuse on the same chart as surface water and groundwater—in the original tabular values, reuse is expressed as a percentage of total water used, and surface water and groundwater are expressed in percentages relative to each other); (b) Appendix Table B-5 (U.S. EPA, 2015a); (c) Table 7-2 (Ziemkiewicz et al., 2014)—note: produced water volumes estimated from percentages applied to volumes injected, and value from the West Virginia portion of the Marcellus Shale used in this chart since it was the longest term measurement of produced water volumes; (d) Figure 8-4 (PA DEP, 2015a) and Table 8-6 (Ma et al., 2014; Shaffer et al., 2013). Sources for the bottom figure: (e) Tables 4-1 and 4-2 (Nicot et al., 2014; Nicot et al., 2012)—note, surface water, groundwater, and reuse values of 50%, 50%, and 5% in the tables normalized to 48%, 48%, and 4%, respectively, for this chart (see reason for this above); (f) Appendix Table B-5 (U.S. EPA, 2015a; Nicot et al., 2012; Nicot et al., 2011)—note: see median value for Fort Worth Basin; (g) Table 7-2 (Nicot et al., 2014); (h) Table 8-6 (Nicot et al., 2012)—note, percentage going to disposal wells estimated by subtracting reuse values from 100%.

Finally, passby flows can be a factor reducing the frequency or severity of surface water impacts. Passby flows are low stream flow thresholds below which withdrawals are not allowed. This management practice has been shown to be protective of streams from over-withdrawals in the Susquehanna River Basin in northern Pennsylvania (U.S. EPA, 2015e). This is likely most important for protecting aquatic life in smaller streams, but may also aid in protecting drinking water supplies.

10.1.2 Chemical Mixing and Produced Water Handling

Like water acquisition, activities in the chemical mixing and produced water handling stages of the hydraulic fracturing water cycle can impact drinking water in some instances. We combine our discussion of the two stages here because activities in these stages both affect drinking water resources primarily through spills. The chemical mixing stage encompasses management of fluids on the well pad to create hydraulic fracturing fluid. Chemicals are mixed with a base fluid, typically water, and then injected into the production well. After the pressure is released post-fracturing, produced water flows from the well and needs to be collected and managed in the produced water handling stage.

Chemical mixing and produced water handling activities can impact drinking water resources through spills of chemicals used to make hydraulic fracturing fluid, hydraulic fracturing fluid itself, or produced water reaching surface water or groundwater.[1] There is some information on spill frequencies—although limited—and spill severities are most often uncharacterized. Nevertheless, we could identify factors affecting the frequency or severity of impacts from chemical mixing or produced water spills. In the section below, we discuss these factors, with those affecting frequency first, followed by those affecting severity. We discuss each of the factors individually, but spill events in reality exhibit combinations of these factors. These factors can interact to increase or decrease the frequency or severity of a spill beyond the effect of an individual factor.

10.1.2.1 Frequency

An impact on the quality of a drinking water resource from a spill first depends on a spill occurring. Most spill frequency estimates are of spills in total, and not the subset reaching drinking water resources. Spill estimates from three states (Colorado, North Dakota, and Pennsylvania) ranged from 0.4 to 12.2 reported spills per 100 hydraulically fractured wells (Appendix C.4).[2] The estimates from Pennsylvania and Colorado included hydraulic fracturing chemicals, fluids, and produced water; while the North Dakota estimate was based on spills of hydraulic fracturing chemicals and fluids only.[3] Spill rates can also be expressed on a per-active-well basis. This may be

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[1] In Chapter 5 and elsewhere in this assessment, the chemicals added to the base fluid (most often water) and proppant (most often sand) are referred to as "additives" since this is the term used in FracFocus. Here, this chapter simply refers to them as "chemicals." It does this to discuss chemicals in a unified manner in this combined section on chemical mixing and produced water.

[2] Since most wells are not reported hydraulically fractured in databases, these estimates used spudded, completed, or installed wells as proxies for hydraulically fractured wells. (See Appendix Section C.4 for more detail.)

[3] These estimates from Pennsylvania and Colorado also included spills of diesel fuel and drilling muds, which could not be separated out from the total frequency estimate even though they were generally out-of-scope of this assessment (diesel fuel was in scope if used in hydraulic fracturing fluid).

more appropriate for produced water spills since they can occur years or even decades after hydraulic fracturing. An analysis of North Dakota produced water spills found there were approximately 5 to 7 spills of produced water per 100 active wells between 2010 and 2015 (Appendix E.5). We conclude from these data that spills do occur in both the chemical mixing and produced water stages of the hydraulic fracturing water cycle, generally in the range of 1 to 10% of hydraulically fractured or active wells.

Not all spills, however, reach and therefore impact a drinking water resource. In U.S. EPA (2015m), 32 of the 457 (7%) spills characterized were reported to have reached surface water or groundwater. The California Office of Emergency Services estimated 18% of produced water spills reached waterways between January 2009 and December 2014 (CCST, 2015b). It is unclear if this estimate included groundwater, or was limited to surface water. If, however, roughly 5 to 20% of spills reach surface water or groundwater (encompassing the U.S. EPA and California estimates above), we would expect a spill to occur and reach a drinking water resource at approximately 0.05 to 2% of active or hydraulically fractured wells.[1] This estimate of spills reaching drinking water resources would be broadly consistent with estimates from the limited number of published studies addressing this topic (e.g., Brantley et al., 2014; Gross et al., 2013).[2] If a 0.05 to 2% frequency rate is applied to the estimates of approximately 275,000 to 370,000 new wells hydraulically fractured nationally between 2000 and part of 2013 and 2000 and part of 2014, respectively (Chapter 3), we would expect roughly 140 to 7,400 spills to reach a drinking water resource during this almost 14-to-15 year time-period. This would be approximately 10 to 500 spills per year reaching a drinking water resource, dividing by the respective time periods. This large range reflects the high uncertainty of these estimates and the lack of data on this topic.

Despite the data limitations and uncertainties surrounding estimates of spills, we can with more certainty identify factors likely affecting the frequency of spills reaching drinking water resources. These factors include spill characteristics, encompassing the volume of the chemical spilled; factors related to the environmental fate and transport of the spill, such as properties of the chemical spilled and characteristics of the site where the spill occurred; and finally, factors related to spill prevention and response.

Everything else being equal, a larger volume spill will be more likely to reach a drinking water resource than a smaller spill (U.S. EPA, 2015m). On-site spills in the chemical mixing and produced water handling stages are typically in the hundreds of gallons (U.S. EPA, 2015m). Larger spills, though less common, do occur. Well blowouts, pipeline leaks, and impoundment failures are sources of some of the largest individual spill volumes. Well blowouts were responsible for the

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[1] Estimated by multiplying the 1 to 10% spill rate for active or hydraulically fractured wells by 5% to 20% for spills reaching drinking water, and then reconverting to a percentage by multiplying by 100.

[2] Brantley et al. (2014) estimated approximately 0.4 to 0.8 spills per 100 hydraulically fractured wells reached surface water in Pennsylvania between 2008 to September 2013. These were spills of 400 gal (1,514 L) or more, containing hydraulic fracturing chemicals, fluids, or produced water. This might be an underestimate of spills reaching surface water since spill volumes were limited to only 400 gal (1,514 L) or more. In estimate of the frequency of spills reaching groundwater, Gross et al. (2013) examined oil and produced water spills between July 2010 and July 2011 in Weld County, Colorado. They counted 77 such spills reaching groundwater, approximately 0.4% of the nearly 18,000 active wells in the county.

highest volume spills on average in 2015 in North Dakota. In Bradford County, Pennsylvania, a well blowout resulted in a spill of approximately 10,000 gal (38,000 L) of produced water into a tributary of Towanda Creek, a state designated trout fishery. The largest volume spill identified in this assessment occurred in North Dakota, where approximately 2.9 million gal (11 million L) of produced water spilled from a broken pipeline and impacted surface water and groundwater. Though relatively rare compared to smaller volume spills, these types of spills are more likely to reach—and therefore impact—a drinking water resource because they are of larger volumes.

By this same principle, produced water spills are more likely to impact drinking water resources than chemical mixing spills. In an analysis of on-site spills, the median volume of produced water spills was approximately twice as large as that in the chemical mixing stage (990 versus 420 gal, or 3,750 versus 1,590 L; U.S. EPA (2015m)). Additionally, offsite, large pipeline spills of produced water can occur. It is possible that spills of produced water are larger, in part, because they are less likely to be stopped as quickly as spills in the chemical mixing stage. Spills in the chemical mixing stage are likely to occur when people are on-site, and so the spills can be quickly addressed. In contrast, spills of produced water may occur when no one is on-site or, in the case of pipelines, near the off-site location of the spill. This may delay a response, allowing larger volumes to spill, increasing the likelihood of the spill reaching a drinking water resource.

Properties of the chemicals spilled also affect the frequency of impacts. We identified or estimated chemical and physical properties for almost half of the chemicals used in hydraulic fracturing fluids between 2006 and 2013 (455 of the 1,084 chemicals). These were individual organic chemicals, not inorganic chemicals, polymers, or mixtures. Volatility, solubility, and hydrophobicity/hydrophilicity are three properties, among others, affecting whether a spill reaches a drinking water resource (hydrophobic chemicals tend to repel or fail to mix with water, while hydrophilic chemicals tend to mix with water). The vast majority of organic chemicals in hydraulic fracturing fluid do not readily volatilize or evaporate, meaning these chemicals tend to remain in water if spilled. These chemicals also vary widely in their solubility and hydrophobicity/hydrophilicity, defying a general characterization. Nevertheless, of the 20 chemicals most frequently used according to our analysis of FracFocus, most are highly soluble and hydrophilic, meaning they will be mobile if spilled (Chapter 5). For example, methanol, isopropanol, and ethylene glycol are all likely to travel quickly through the environment. Thus, these chemicals may more frequently reach drinking water because of two unrelated, yet compounding factors: relatively high frequency of use in hydraulic fracturing operations and relatively high mobility in the environment.

Site characteristics are also an important factor determining whether a spill reaches a drinking water resource (Figure 10-2). Site characteristics facilitating infiltration to groundwater are of particular concern, since spills into groundwater are more likely to have severe impacts than those into surface water (discussed in the severity section below). More permeable, sandier soils allow greater infiltration of spilled fluids, whereas less permeable soils with more clay content can greatly slow infiltration. More permeable rock also facilitates infiltration and movement of spills through preferential flow paths—for example, in fractured or karst bedrock. Thus, sandier soils and more permeable rock can increase the potential for spills to reach groundwater.

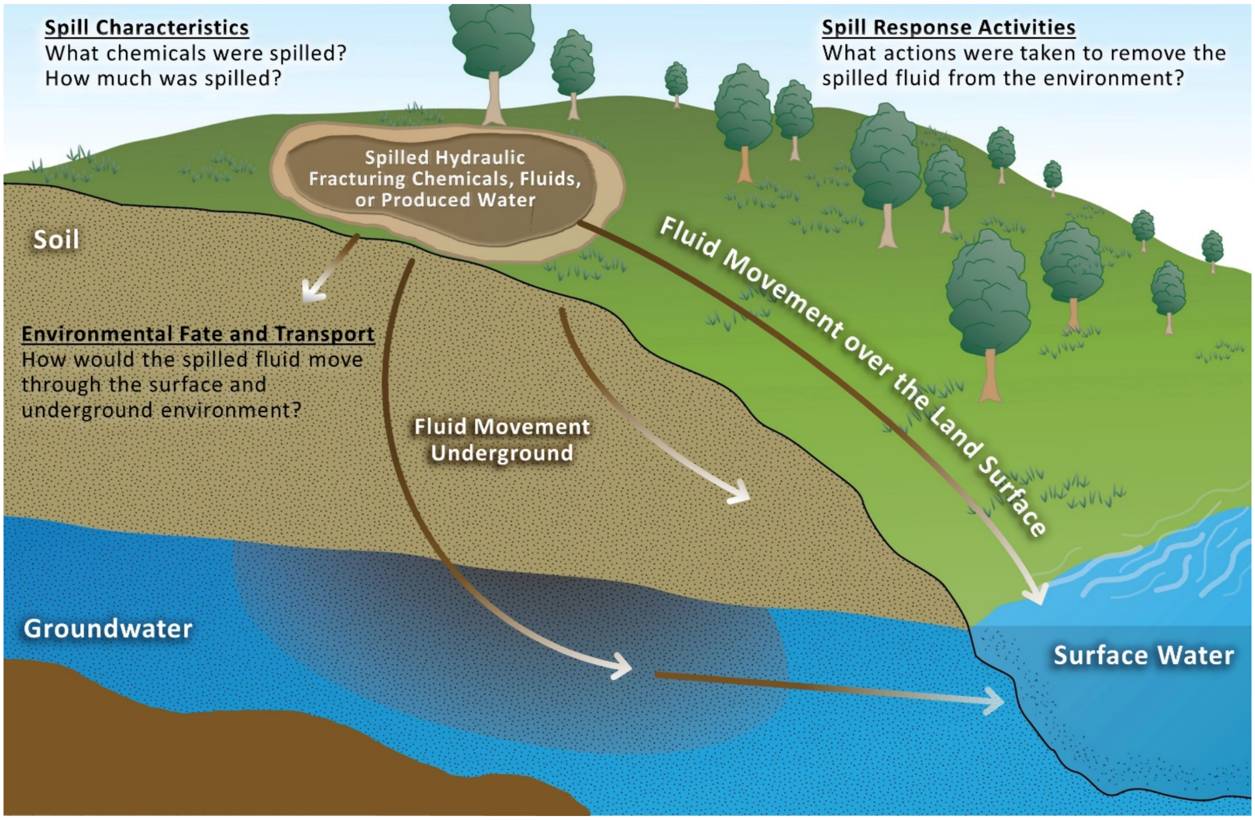

Figure 10-2. Fate and transport schematic for a spill of chemicals, hydraulic fracturing fluid, or produced water.
Schematic shows the potential paths, transport processes, and factors governing potential impacts of spills to drinking water resources.

There are spill prevention and response factors that reduce the frequency of impacts to drinking water resources from spills. Spill containment systems include primary, secondary, and emergency containment systems. Primary containment systems are the storage units, such as tanks or totes. Secondary containment systems, such as liners and berms installed during site set-up, are intended to contain spilled fluids until they can be cleaned up. Emergency containment systems, such as berms, dikes, and booms, can be implemented temporarily in response to a spill. Remediation is the action taken to clean up a spill and its affected environmental media. One of the most commonly reported remediation activities is the removal of spilled fluid and/or affected media, typically soil (U.S. EPA, 2015m). Other remediation methods include the use of absorbent material, vacuum trucks, flushing the affected area with water, and neutralizing the spilled material (U.S. EPA, 2015m). It was beyond the scope of this assessment to evaluate the implementation and efficacy of spill prevention practices and spill response activities.

10.1.2.2 Severity

In addition to frequency, there are also factors affecting the severity of an impact on a drinking water resource from a spill. For a given concentration, a larger volume spill will be more severe than a smaller spill (see frequency section above for discussion of spill volumes). In addition to volume, the concentration and toxicity of the chemicals reaching a drinking water resource affect severity, as well as site characteristics.

A spill with higher chemical concentrations will be more severe than a more dilute spill of equal volume. In the chemical mixing stage, chemicals are stored in concentrated form on-site, prior to diluting with a base fluid. Approximately 3,000 to 30,000 gal (11,000 to 114,000 L) of chemicals are used per well on average, with up to twice that amount stored on site. If multiple wells are fractured per site, tens to hundreds of thousands of gallons of chemicals are likely stored in containers at a single site during the hydraulic fracturing of these wells. These storage containers are a relatively frequent source of spills during the chemical mixing stage. Spills from these storage containers, even if low in volume, may be severe if they reach a drinking water resource because they often contain concentrated chemicals.

In the produced water handling stage, the severity of impacts from a spill also increases with higher concentrations, especially if the spill reaches groundwater (see site characteristics below). Produced water can vary substantially in chemical concentrations, including total dissolved solids (TDS), metals, radioactive isotopes, and organic chemicals. Within the Marcellus Shale, for example, produced water can range in TDS from less than 1,500 mg/L to over 300,000 mg/L (Rowan et al., 2011). By comparison, the average salinity concentration for seawater is 35,000 mg/L. The more concentrated the produced water, the more likely impacts will be severe if a spill reaches a drinking water resource. When a spilled fluid has greater concentrations of TDS than groundwater, the higher-density fluid can move downward through the groundwater resource. Depending on the flow rate and other properties of the groundwater, impacts from produced water spills can last for years.

In addition to concentration, the toxicity of chemicals affects the severity of the impact if they enter a drinking water resource. There were 37 chemicals listed in 10% or more of all FracFocus disclosures between January 1, 2011 and February 28, 2013. Of these 37 chemicals, nine had chronic oral reference values meeting the criteria used in this assessment. [1] These nine chemicals are associated with health effects including liver toxicity, kidney toxicity, developmental toxicity, reproductive toxicity, and/or carcinogenesis. Chemicals used in hydraulic fracturing fluids and detected in produced water will vary from site to site, so human health hazards are best evaluated on a site-specific basis. Nevertheless, the multi-criteria decision analysis (MCDA) presented in Chapter 9 highlighted certain chemicals that may have greater hazard potential. Propargyl alcohol, 2-butoxyethanol, and N,N-dimethylformamide are three such chemicals having relatively greater hazard potential in the MCDA based on toxicity, frequency of use in hydraulic fracturing fluids, and mobility in water.

Many of the chemicals in produced water are also known or suspected to cause cancer and/or non-cancer health effects in humans. Associated health effects include liver toxicity, kidney toxicity, neurotoxicity, reproductive and developmental toxicity, and carcinogenesis, based on the produced

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[1] The analysis of toxicity presented in Chapter 9 included chemicals regardless of accompanying concentration data in FracFocus, and therefore listed 37 chemicals that were reported in 10% or more disclosures. Comparatively, Chapter 5 listed 35 chemicals that had valid concentration data from FracFocus and were reported in 10% of more disclosures.

water chemicals having chronic oral reference values meeting the criteria used in this assessment. Benzene, pyridine, and naphthalene are three of the chemicals highlighted in the MCDA as having relatively greater hazard potential based on toxicity, measured concentrations in produced water, and mobility in water.

We did not evaluate trends in chemical use by toxicity (e.g., the trends in the use of less toxic chemicals). However, a more recent study of FracFocus data evaluated disclosures dating from March 9, 2011, to April 13, 2015 (Dayalu and Konschnik, 2016; Konschnik and Dayalu, 2016). When compared to the list of 1,084 chemicals used in hydraulic fracturing operations between 2005 and 2013 compiled for this assessment (Appendix H), an additional 263 chemicals were identified (Chapter 5). Only one of these 263 chemicals was reported in more than 1% of disclosures. This comparison of chemical lists does not address potential shifts in volumes of chemicals used, but it does suggest that a shift to new types of chemicals–less toxic or otherwise–did not occur between 2013 and early 2015.

Finally, site characteristics also affect the severity of the impact. Spills into groundwater are likely to be more severe than spills into surface water, everything else being equal. This is not to say that spills into surface water cannot be severe, especially in the immediate vicinity of the spill. For instance, a tank overflowed on a well site in Kentucky spilling fluid into a nearby stream at concentrations sufficient to kill fish in the area (Papoulias and Velasco, 2013). Chemicals can also associate with stream sediments, forming a source of long-term contamination (e.g., radium). In general, however, surface water dilutes a spilled chemical much more rapidly than groundwater. Groundwater often moves slowly between areas of recharge and discharge. Groundwater movement can be as slow as one foot per year or even one foot per decade (Alley et al., 1999). Because of this dynamic, chemicals from multiple spills can accumulate over time in groundwater. Multiple chemical mixing and produced water spills, even if individually small, may impact a groundwater resource in aggregate. Additionally, groundwater contamination may not be as readily apparent as that in surface water because of the need to install monitoring wells to detect contamination in groundwater. Lastly, groundwater can be difficult and expensive to remediate, adding to the severity of impacts if spills reach groundwater (Alley et al., 1999).

10.1.3 Well Injection

Like the water acquisition, chemical mixing, and produced water handling stages, activities in the well injection stage of the hydraulic fracturing water cycle can affect drinking water resources in some instances. The well injection stage involves the injection of hydraulic fracturing fluids through the production well and into the targeted rock formation at sufficient pressure to fracture the rock. There are two fundamental pathways outlined in this assessment by which activities in the well injection stage have the potential to affect drinking water resource quality. They are: (1) fluid (meaning, liquid or gas) movement into a drinking water resource through defects or deficiencies in the production well casing and/or cement; and (2) fluid movement into a drinking water resource through the fracture network. The fluids potentially affecting drinking water resources include hydraulic fracturing fluids, hydrocarbons (including methane gas), and naturally occurring brines. The drinking water resources impacted directly in this stage are almost always groundwater resources, rather than surface water.

Though we could not in this assessment quantify an overall frequency of groundwater quality impacts from the well injection stage, we can describe factors which make impacts more or less frequent or more or less severe, as we did for other stages. We describe these factors below, first with frequency and then severity. Within the frequency discussion, we address factors by each pathway type.

10.1.3.1 Frequency

Pathway #1: Fluid movement into a drinking water resource through defects or deficiencies in the production well casing and/or cement.

To reach and then fracture the production zone, an oil or gas well must first be drilled and constructed down through the subsurface rock formations, often containing an overlying drinking water resource. Since the well passes through the drinking water resource, this means defects or deficiencies in the production well can lead to unintended movement of fluid into the drinking water resource. This can occur regardless of the vertical separation between the drinking water and the production zone.

The relatively brief hydraulic fracturing phase will likely impose the highest stresses to which the well will be exposed during its entire life. If the well cannot withstand the stresses experienced during hydraulic fracturing, the casing or cement can fail, resulting in the loss of mechanical integrity and the unintended movement of fluids into the surrounding environment.

A few studies have estimated rates of mechanical integrity failure of production wells resulting in the loss of *all* barriers protecting the groundwater or in contamination of groundwater in areas with hydraulic fracturing activity (Table 10-1). The estimates are all approximately equal to or less than 1% of wells drilled or hydraulically fractured over varying time frames. For most of these estimates, it is not possible to tell whether failures occurred during hydraulic fracturing or at some other point in the well's life, with the exception of the EPA's Well File Review (U.S. EPA, 2015n). If the failure rate from the Well File Review (0.5%) is applied to the estimates of 275,000 to 370,000 new wells hydraulically fractured nationally between 2000 and part of 2013 and 2000 and part of 2014, respectively (Chapter 3), we would expect roughly 1,370 to 1,850 mechanical integrity failures during this time-period (almost 14 to 15 years). Dividing by each time period yields approximately 100 to 125 mechanical integrity failures per year on average, resulting in the loss of all barriers protecting the groundwater during hydraulic fracturing. These estimates also have a high degree of uncertainty like the spills estimates. This not only stems from the lack of certainty about failure rates, but also uncertainties surrounding the estimates of the number of wells hydraulically fractured (Chapter 3). These are likely low estimates because they do not include mechanical integrity failures occurring outside of the hydraulic fracturing process (e.g., during the production phase), nor do they consider failures in re-fractured wells.

Table 10-1. Literature estimates of mechanical integrity failure rates resulting in contamination of groundwater or failure of all well barriers, potentially exposing the groundwater.

Citation	Mechanical Integrity Failure Rate (%)	Geographic Scope	Key Findings & Description of Mechanical Integrity Failure[a,b]
Fleckenstein et al. (2015)	0.06	Colorado-Wattenberg Field	An overall catastrophic failure rate of 0.06% was found for 16,828 wells studied (out of 17,948 total wells) drilled in the Wattenberg Field between 1970 and 2013. The timing of the failures was unknown, but most of the failures occurred in the older wells. The Wattenberg Formation is 4,400 ft (1,300m) below surface and typically is hydraulically fractured. A catastrophic failure was considered to have occurred when there was contamination of drinking water aquifers (i.e., the presence of thermogenic gas in a drinking water well) and evidence of a well defect such as exposed intermediate gas formations or casing leaks.
Considine et al. (2012)	0.06	Pennsylvania	Two wells were cited between 2008 and 2011 by PA DEP for causing methane migration into an aquifer. In this same time period, 3,533 wells were drilled.
Brantley et al. (2014)	0.12–1.1	Pennsylvania	Based on positive determination letters (PDLs) for violations that occurred between 2008 and 2012, Brantley et al. estimated between 7 and 64 problematic unconventional wells contaminated 85 properties. Since PDLs are tied to drinking water wells and not gas wells, Brantley et al. made assumptions about how many unconventional gas wells were represented by each PDL. This equates to problematic unconventional gas wells compromising approximately 0.1 to 1% of the 6,061 wells spudded between 2008 and 2012.[c] Not all of these PDLs may be due to mechanical integrity failures–they could also be due to other causes, such as spills, or methane migration from natural or other anthropogenic sources.
Vidic et al. (2013)	0.25	Pennsylvania	Of the 6,466 wells studied, 16 received notices regarding contamination of groundwater with gas or other fluids from the PA DEP associated with incidents that occurred between 2008 and 2013.

Citation	Mechanical Integrity Failure Rate (%)	Geographic Scope	Key Findings & Description of Mechanical Integrity Failure[a,b]
U.S. EPA (2016c)	0.5	National	In an estimated 0.5% of the approximately 28,500 hydraulic fracturing jobs surveyed, a failure occurred during hydraulic fracturing, such that there was no additional barrier between the annular space with fluid and the protected drinking water resource. While it could not definitively be determined whether fluid movement into the protected drinking water resource occurred, in these cases, all of the protective barriers intended to prevent such fluid migration had failed, leaving the groundwater source vulnerable to contamination.

[a] Note: While some information is available on the age of the wells studied, it is unclear whether the failure occurred during the hydraulic fracturing event, with the exception of the U.S. EPA (2016c) study. In that study, the failures occurred during hydraulic fracturing.

[b] While the Pennsylvania studies did not specifically identify whether the wells were involved in hydraulic fracturing operations, a significant portion of Pennsylvania's recent oil and gas activity is in the Marcellus Shale; therefore, many of the wells in these studies were most likely used for hydraulic fracturing.

[c] Spudding refers to starting the well drilling process by removing rock, dirt, and other sedimentary material with the drill bit (U.S. EPA, 2013f).

Not all wells are equally likely to lose mechanical integrity; instead, there are factors that make some wells more likely to experience a mechanical integrity failure than others. Well design and construction are two such factors. First, a primary element of well design is the placement of at least one additional layer of casing (besides the production casing) from the surface through the lowest depth of the drinking water resource. This additional casing provides redundancy if the production casing fails. In a study of 731 saltwater injection wells in the Williston Basin in North Dakota, Michie and Koch (1991) found the risk of aquifer contamination from leaks into the drinking water resource was 7 in 1,000,000 injection wells if a surface casing, in addition to the production casing, was set deep enough to cover the drinking water resource. The risk increased to 6,000 per 1,000,000 wells (or 6 in 1,000) if this additional casing was not set deeper than the bottom of the drinking water resource.

Second, fully cementing casing(s) through the entire drinking water resource affects the frequency of impacts. Uncemented sections of surface casing increase the frequency of fluid leaks from the well that can reach groundwater (Fleckenstein et al., 2015; Watson and Bachu, 2009). The EPA's Well File Review estimated that a portion of the protected groundwater resource identified by well operators was uncemented in 3% of the wells surveyed (U.S. EPA, 2015n). With approximately 25,000 to 30,000 new wells hydraulically fractured a year (Chapter 3), this percentage means 750 to 900 of the wells used in hydraulic fracturing operations annually might lack this protection. Adding re-fractured wells would increase the estimate of wells lacking this protection. Knowing the depth of the groundwater resource at the point of drilling and then setting and cementing casings below the lowest part of the drinking water resource can reduce the frequency or likelihood of an impact.

Third, the well's casing, cement, and components need to be designed and constructed to withstand the stresses applied to the well during hydraulic fracturing. In an example of inadequate well construction, hydraulic fracturing of a gas well with insufficient and improperly placed cement in Bainbridge Township, Ohio led to gas contamination of 26 domestic water supply wells and an explosion in the basement of one of the nearby homes. This was due in part to a failure to cement through the over-pressured gas formations and proceeding with the fracturing operation without adequate cement (ODNR, 2008). In another case, casings at an oil well near Killdeer, North Dakota, ruptured in 2010 following a pressure spike during hydraulic fracturing, allowing fluids to escape to the surface. Brine and tert-butyl alcohol were detected in two nearby water wells. Following an analysis of potential sources, the only potential source consistent with the conditions observed in the two impacted water wells was the ruptured well (U.S. EPA, 2015i).

In addition to well design and construction, the degradation or corrosion of well components can also increase the frequency of impacts to drinking water quality. Older wells exhibit more integrity problems as cement and casings age. The EPA's Well File Review estimated at least 10% of the wells represented in the national survey were greater than five years old at the time of hydraulic fracturing. Hydraulic fracturing or re-fracturing older wells has the potential to increase the frequency of casing or cement failures allowing unintended fluid migration into drinking water resources.

Confirming well mechanical integrity can reduce the frequency of water quality impacts. Pressure testing the casing used for hydraulic fracturing prior to the job can help detect problematic casing—and provide an opportunity to make needed repairs if necessary. Monitoring the annular space behind the casing used for hydraulic fracturing during the hydraulic fracturing job can detect well component failure in real time and signal for an immediate shut down. Based on the EPA's Well File Review study, casing pressure testing occurred at slightly less than 60% of the approximately 28,500 hydraulic fracturing jobs represented in that time frame (primarily 2009-2010) and annulus monitoring took place during slightly more than 50% of these same jobs, implying these activities did not always occur (U.S. EPA, 2016c). It is unclear whether the frequency of these practices have changed since this time period.

Pathway #2: Fluid movement into a drinking water resource through the fracture network.

The other potential pathway for fluid movement into a drinking water resource is through the fracture network. This could occur indirectly if the fracture network extends to a nearby well or its fracture network, or to another permeable subsurface feature, such as natural fractures or faults, which then allow the fluid to reach an underground drinking water resource. It could also occur directly by the fracture network extending out of the production zone into a drinking water resource, or hydraulic fracturing into a drinking water resource itself.[1] Key factors affecting the frequency of this pathway are the presence, distance, and condition of nearby wells; and the vertical

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[1] Hereafter, fractures extending out of the production zone are referred to as "out-of-zone" fractures, consistent with Chapter 6.

separation distance and the characteristics of the intervening rock between the production zone and the drinking water resource.

Nearby wells (often called offset wells) can be a pathway for fluid movement, with hydraulic fracturing fluid from one production well moving through the subsurface and entering another nearby oil or gas well or its fracture network. These events are commonly referred to as "well communication events" or "frac hits." The communication event might simply be registered as an increase in pressure in the nearby well; yet there is also the possibility of damage to the nearby well or its components, causing a surface spill or a subsurface release of fluids. The EPA's Well File Review found 1% of the wells represented in the study experienced a frac hit, and the EPA spills report identified 10 spills attributed to well communication events (U.S. EPA, 2015m, n). It is unknown whether any fluid reached a drinking water resource from these spills. Where active nearby wells exist, operators of those wells can shut them in temporarily during the nearby hydraulic fracturing to reduce the possibility of spills or damage to their wells, and therefore, the potential for drinking water resource contamination.

The distance to the nearby well can affect the frequency of these communication events. In one study, the likelihood of a frac hit was less than 10% in hydraulically fractured wells more than 4,000 ft (1,219 m) apart, while nearly 50% in wells less than 1,000 ft (300 m) apart (Ajani and Kelkar, 2012). Distance was measured from the mid-point of each horizontal lateral. Thus, the closer the nearby wells, the more likely a communication event.

If nearby wells are in good condition and can withstand an increase in pressure, then an impact is unlikely to occur. However, if the nearby well is not able to withstand the pressure of the fluid, well components may fail and allow fluid to move into a drinking water resource. Because of this, nearby older or abandoned wells are of particular concern. In older wells near a hydraulic fracturing operation, plugs and cement may have degraded over time; in some cases, abandoned wells may never have been plugged properly. This can be a significant issue in areas with legacy (i.e., historic) oil and gas exploration. A Pennsylvania Department of Environmental Protection (PA DEP) report cited three cases where migration of natural gas had been caused by well communication events via old, abandoned wells (PA DEP, 2009c). In Tioga County, Pennsylvania, following hydraulic fracturing of a shale gas well, an abandoned well nearby produced a 30 ft (9 m) geyser of brine and gas for more than a week (Dilmore et al., 2015). Various studies estimate the number of abandoned wells in the United States to be significant. For example, the Interstate Oil and Gas Compact Commission (IOGCC, 2008) estimates that approximately 1 million wells were drilled in the United States prior to a formal regulatory system, and the status and location of many of these wells are unknown. Hydraulic fracturing operators can reduce the possibility of impacts by identifying nearby wells, and if necessary, plugging or otherwise addressing deficiencies in these wells.

If nearby wells serve as a pathway, fluid movement can bypass layers of intervening rock. In the absence of this pathway, however, vertical distance and the intervening rock between the production zone and the drinking water resource are factors affecting the possible movement of fluid into a drinking water resource. The extension of fractures out of the oil and/or gas production zone can—and does—occur. Examples have been reported in Greene County, Pennsylvania (Hammack et al., 2014); at the Killdeer site in Dunn County, North Dakota (U.S. EPA, 2015i); and in other wells within the Bakken Shale (Arkadakskiy and Rostron, 2013; Arkadakskiy and Rostron, 2012; Peterman et al., 2012). In a study across several major shale formations, Davies et al. (2012) found upward vertical fracture growth was often on the order of tens-to-hundreds of feet. One percent of the fractures had a fracture height greater than 1,148 ft (350 m), and the maximum fracture height among all of the data reported was 1,929 ft (588 m). This would suggest that substantial vertical separation could preclude out-of-zone-fractures from directly reaching the drinking water resource, although these measurements were only conducted in shale formations and the extension of fractures is not the only way the drinking water resource could be contaminated from out-of-zone fractures (see below). A modeling study also suggests fractures are unlikely to extend from the production zone directly to a shallow drinking water resource in a deep Marcellus-like environment (Kim and Moridis, 2015).

Not all fracturing occurs, however, with substantial vertical separation between the production zone and the drinking water resource (Figure 10-3). The EPA's Well File Review found that 20% of wells used for hydraulic fracturing had less than 2,000 ft (600 m) between the shallowest point of fracturing and the base of the protected groundwater resource (U.S. EPA, 2015n). In coalbed methane (CBM) plays, typically shallower than shale gas plays, these separation distances can be smaller. For example, in the Raton Basin of southern Colorado and northern New Mexico, approximately 10% of CBM wells have less than 675 ft (206 m) of separation between the production zone and the depth of local water wells. In certain areas of the basin, this distance is less than 100 ft (31 m) (Watts, 2006). Many of these areas are shallower in depth, and fracture growth has been shown to be primarily horizontal, rather than vertical, at less than 2,000 ft (600 m) from the surface (Fisher and Warpinski, 2012). Nevertheless, the possibility of an out-of-zone fracture reaching a drinking water resource is more likely in a setting with less vertical separation than with more.

Even if an out-of-zone fracture does not extend into a drinking water resource, it could connect to other permeable subsurface features, such as natural fractures or faults, which could then connect to a drinking water resource. Thus, properties of the intervening rock can also make this pathway more or less frequent or likely. For instance, in the Pavillion gas field in Wyoming, there are no laterally-continuous confining layers to prevent upward movement of fluids into the groundwater (Digiulio and Jackson, 2016). While flow of subsurface fluids generally tends to be downward, local areas of upward flow have been observed (Digiulio and Jackson, 2016).

There are cases of hydraulic fracturing without vertical separation between the drinking water resource and the production zone (Figure 10-3). The co-location of the oil or gas formation with the drinking water resource is the factor affecting the frequency of an impact in these cases. Directly fracturing into a drinking water resource causes an impact because it changes the quality of the resource by introducing hydraulic fracturing fluids. The EPA's Well File Review found an estimated 0.4% of the wells represented in the study had perforations used for hydraulic fracturing shallower than the base of the protected groundwater resource, as reported by well operators (U.S. EPA, 2015n). The EPA's Well File Review did not examine these instances by formation type. This practice may be concentrated in locations in western states, especially in CBM plays. Examples include the Raton Basin in Colorado (U.S. EPA, 2015k), the San Juan Basin of Colorado and New

Mexico (U.S. EPA, 2004a), and the Powder River Basin of Montana and Wyoming (Dahm et al., 2011; ALL Consulting, 2004; U.S. EPA, 2004a). This is a concern in the short term (should there be people using these drinking water resources currently) and the long term (if drought or other conditions necessitate the future use of these drinking water resources). For the most part in this chapter, we focused on factors which can be managed, changed, or used to identify areas to target monitoring efforts. In this situation, hydraulic fracturing directly into a drinking water resource would need to cease if it was decided the resulting impacts to drinking water resource quality were unacceptable.

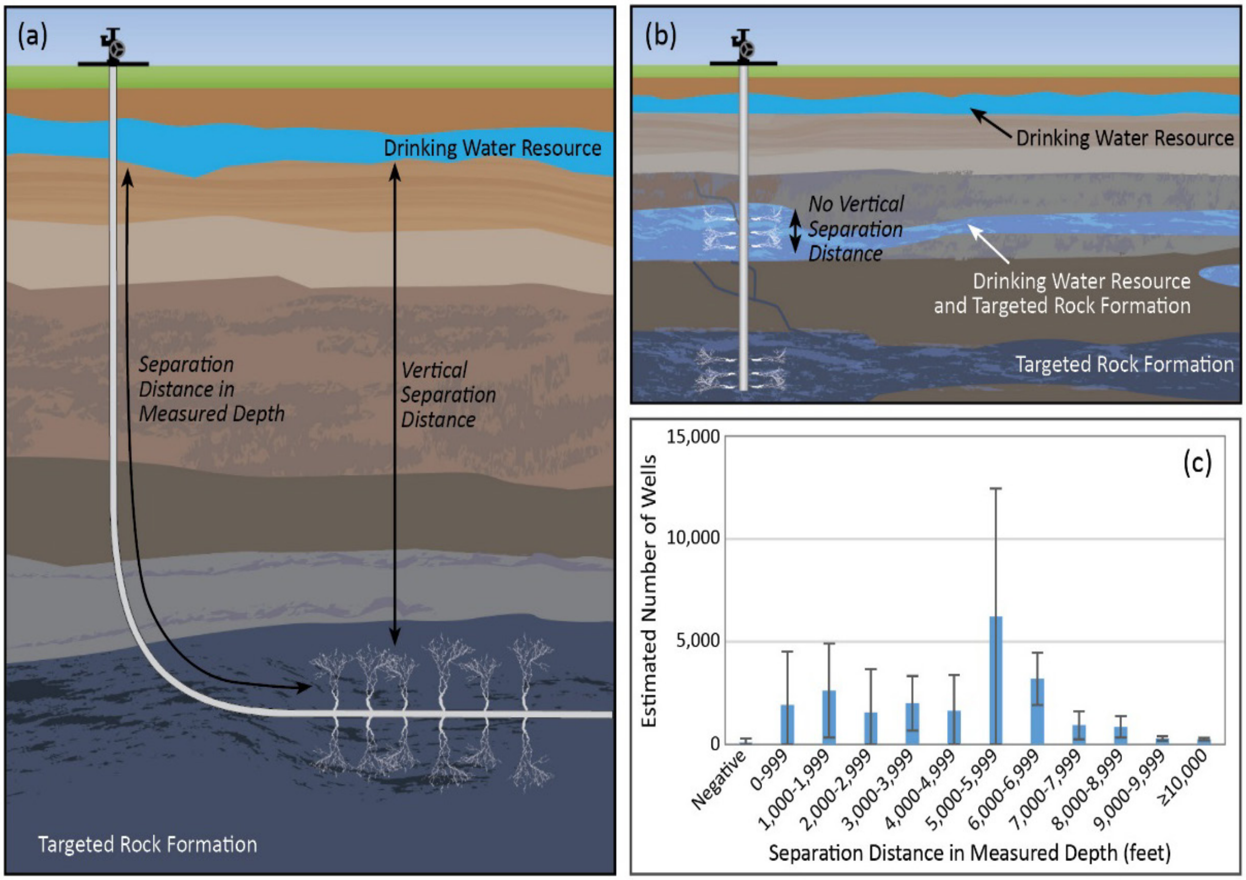

Figure 10-3. Separation in measured depth between drinking water resources and hydraulically fractured intervals in wells.

In panel (a), the oil- and gas-bearing formation (dark gray) being hydraulically fractured is much deeper than the depth where drinking water resources (light blue) exist, and hence a comparatively large separation distance exists. In panel (b), there are two oil- and gas-bearing formations (dark gray and grayish blue) being hydraulically fractured. The shallower formation has no separation distance, because the water also contained in this formation is a drinking water resource. Panel (b) also shows another subsurface drinking water zone at a shallower depth (light blue). Multiple groundwater zones of varying qualities can exist between the production zone and the surface. These two panels depict end-member cases of separation distance: from large separation distances to no separation distance. The graph in panel (c) illustrates the distribution of separation distances among the approximately 23,000 oil and gas production wells hydraulically fractured by nine service companies between 2009 and 2010 (U.S. EPA, 2015n). Error bars in the panel (c) display 95% confidence intervals.

Lastly, the presence of gas, as opposed to liquids, in the subsurface may be a factor affecting the frequency of impacts from fluid movement via defects or deficiencies in the well (pathway #1), or through the fracture network (pathway #2). The low density of gas compared to liquids makes it buoyant, which creates an upward drive toward the surface. Thus, gas found in the subsurface, such as methane, can exploit pathways in a well (such as along a well lacking mechanical integrity), or in the surrounding rock (such as induced or naturally occurring fractures). If a pathway exists and gas is present, it can reach groundwater used for drinking. Consequently, gases could be more likely to contaminate drinking water resources than liquids (Li et al., 2016a).

10.1.3.2 Severity

The well injection chapter (Chapter 6) focused primarily on the potential for impacts to occur and factors affecting frequency. By contrast, we have little-to-no information on factors affecting the severity of impacts for this stage of the hydraulic fracturing water cycle. Severity would likely be affected by the chemical composition of the fluid entering the drinking water resource; the volume of the fluid; the duration in which that volume is delivered; and the concentration of the fluid and its specific components, among other factors. Logically, the relatively simple pathway of a mechanical integrity failure might result in the highest fluid volume delivered to a drinking water resource over a short period of time—e.g., contamination of water wells in Bainbridge Township, Ohio. By contrast, fluid movement through a fracture network, then through the intervening rock, and finally into a drinking water resource may take a longer time and deliver a comparatively lower volume. Even in this case, however, the impacts could still be severe if the fluid movement was to go undetected and unaddressed.

10.1.4 Wastewater Disposal and Reuse

The last stage of the hydraulic fracturing water cycle is wastewater disposal and reuse. Produced water from hydraulically fractured oil or gas production wells is managed predominantly through disposal in underground Class II wells. Secondarily, it is disposed of via other practices, such as discharge to surface waters or disposal in pits or evaporation ponds, or reused in other hydraulic fracturing operations. Activities in the wastewater disposal and reuse stage of the hydraulic fracturing water cycle can impact drinking water resources in some instances. Two such activities are: the discharge of inadequately treated wastewater to surface water, and the storage or disposal of wastewater in unlined pits or impoundments leading to contamination of surface water or groundwater. In this section, we address factors increasing or decreasing the frequency or severity of impacts from these activities. As in the water acquisition section, we combine our discussion of frequency and severity here.

10.1.4.1 Frequency and Severity

Discharge of inadequately treated wastewater has impacted surface water. The quality of the wastewater discharged is a factor affecting the frequency and severity of impacts. This factor is a function of the chemical characteristics of the wastewater prior to treatment (i.e., the composition and concentration of chemicals in the wastewater) and the efficacy of the treatment process. The pre-2011 treatment of Marcellus wastewater in Pennsylvania illustrates this combination. In

Pennsylvania before 2011, wastewater from shale gas operations was treated at centralized waste treatment facilities (CWTs) and publicly owned treatment works (POTWs). The POTWs and some CWTs at the time were not equipped to adequately treat high TDS wastewater. This resulted in wastewater discharges containing elevated levels of TDS, including bromide and iodide, to surface waters.

The elevated levels of TDS raised concerns about the formation of disinfection byproducts (DBPs) after treatment at downstream drinking water facilities. Disinfection byproducts are formed when organic material comes in contact with disinfectants (e.g., chlorine, chloramine, chlorine dioxide or ozone). Many DBPs have long-term health effects including an increased risk of cancer, anemia, liver and kidney effects, and central nervous system effects. Of particular concern are DBPs formed in the presence of bromide or iodide, which are considered particularly toxic. Management of DBPs places a burden on downstream drinking water utilities. Concerns regarding elevated TDS (in particular high bromide) and the potential for formation of DBPs led the PA DEP to take steps in 2010 and 2011 to route Marcellus Shale wastewater away from POTWs and CWTs (that could not treat for TDS) to alternate options such as disposal via injection wells, on-site reuse, or reuse after limited treatment at CWTs. By 2014, only a small percentage (approximately less than 1%) of Marcellus wastewater went to CWTs permitted to discharge to surface waters (Figure 10-1). Additionally, the new EPA pretreatment standards prohibit oil and gas operators from sending unconventional oil and gas wastewater directly to POTWs (U.S. EPA, 2016d).

The combination of wastewater composition and inadequate treatment have also resulted in the discharge of other constituents such as barium, strontium, and radium into surface waters in Pennsylvania. Marcellus Shale wastewater contains radium, naturally occurring in the subsurface formation. Radium has been found in stream sediments at discharge points for POTWs and CWT facilities that have accepted Marcellus Shale wastewater. The ratio of radium isotopes (radium-228 to radium-226) in these sediments is consistent with ratios in Marcellus Shale wastewater (Warner et al., 2013a). Radium-226, with a half-life of approximately 1,600 years, causes long-term contamination. The practice of management of wastewaters via POTWs and CWTs without TDS removal has declined, yet it remains uncertain whether the discharge of radionuclides to surface waters from the oil and gas industry in Pennsylvania has ceased entirely (PA DEP, 2015b).

The storage or disposal of wastewater in pits or impoundments can also lead to contamination of surface water or groundwater resources. This can occur via surface spills or overflows. It can also occur via infiltration into the soil and percolation to groundwater through the pit itself. Whether the pit or impoundment is lined is an important factor affecting the frequency and severity of impacts on groundwater due to subsurface leaching. Historically, unlined pits have been used to dispose of wastewater via percolation (or evaporation). While this practice has been banned in most states, it is allowed in certain locations or instances (e.g., storage of wastewater, but not disposal) as of July 2016. Even where prohibited, unpermitted unlined disposal or storage pits exist. For example, approximately 1,000 unlined storage or disposal pits of oil and gas wastewater are located in the Central Valley Region of California (California State Water Resources Control Board, 2016; Esser et al., 2015). Of these, approximately 60% were still active as of July 2016, and roughly 20% of those pits lacked permits (CA Water Board, 2016).

Unlined pits have been shown to cause contamination of drinking water resources. The presence of BTEX (benzene, toluene, ethylbenzene, and xylenes) and other organics in groundwater are linked to pits in California and New Mexico (California Regional Water Quality Control Board Central Valley Region, 2015; Sumi, 2004; Eiceman, 1986). Groundwater impacts downgradient of an unlined pit in Oklahoma included high salinity (3500-25,600 mg/L) and the presence of volatile organic compounds (Kharaka et al., 2002). Impacts can also occur in the case of disposal of relatively low TDS wastewater (Healy et al., 2011; Healy et al., 2008). For example, a CBM wastewater impoundment in the Powder River Basin of Wyoming resulted in high concentrations of TDS, chloride, nitrate, and selenium in the groundwater (Healy et al., 2011; Healy et al., 2008). Total dissolved solids exceeded 100,000 mg/L in one groundwater sample, despite the much lower concentrations (2,300 mg/L) in the wastewater being discharged (Healy et al., 2008). Most of the solutes found in the groundwater did not originate with the CBM wastewater, but rather resulted from dissolution of previously existing salts and minerals in the subsurface. Lining pits or using closed-loop systems (i.e., tanks) can decrease the frequency of such impacts.

10.1.5 Summary

In the above section, we synthesized the information in this assessment by discussing factors increasing or decreasing the frequency or severity of impacts from activities in the hydraulic fracturing water cycle. We focused particularly on factors that could be managed, changed, or used to identify locations for additional monitoring or alteration of practices. Based on the information reviewed, we conclude the following combinations of activities and factors are more likely than others to result in more frequent or more severe impacts:

- Water withdrawals for hydraulic fracturing in times or areas of low water availability, particularly in areas with limited or declining groundwater resources;
- Spills during the management of hydraulic fracturing fluids and chemicals or produced water that result in large volumes or high concentrations of chemicals reaching groundwater resources;
- Injection of hydraulic fracturing fluids into wells with inadequate mechanical integrity, allowing gases or liquids to move to groundwater resources;
- Injection of hydraulic fracturing fluids directly into groundwater resources;
- Discharge of inadequately treated hydraulic fracturing wastewater to surface water resources; and
- Disposal or storage of hydraulic fracturing wastewater in unlined pits, resulting in contamination of groundwater resources.

Conversely, the scientific literature and data provide evidence that certain factors can reduce the frequency or severity of impacts. Based on the information reviewed in this assessment, we conclude the following factors are likely to reduce the frequency or severity of impacts:

- Passby flows, or low-flow criteria, for surface water withdrawals, and the use of brackish groundwater or reused wastewater as substitutes for fresh water withdrawals;

- Implementation of spill prevention and response measures;
- Design and placement of well casing and cement able to withstand the stresses imposed by hydraulic fracturing (including identifying the depth of the drinking water resource at the point of drilling, and setting and cementing casings through the entire drinking water resource);
- Confirming mechanical integrity of oil and gas wells prior to, during, and after hydraulic fracturing, and correcting deficiencies if necessary;
- Identification of active or abandoned wells near hydraulic fracturing operations and, if necessary, adjustment of the operations to minimize well-to-well communication and/or plugging improperly abandoned wells;
- The use of treatment technologies to remove TDS, and other constituents, such as radium, when present prior to discharge; and
- Storage of wastewater in lined pits or the use of closed-loop systems instead of pits.

The above factors are not the only factors that can reduce the frequency or severity of impacts, yet are the ones most emphasized by the information reviewed for this assessment. It should be noted that the above factors reduce, but do not completely eliminate, the possibility of an impact occurring. In the case of hydraulic fracturing directly into a drinking water resource or disposal of wastewater via unlined pits, we did not identify factors which could reduce the frequency or severity of impacts, besides restricting the activity itself.

10.2 Uncertainties and Data Gaps

In this assessment, we identified impacts on drinking water resources in all stages of the hydraulic fracturing water cycle and described the factors affecting the frequency or severity of impacts. The major conclusions presented above (in Section 10.2.5) are the strongest conclusions based on data and information synthesized for the assessment.

There were also many areas within the assessment for which strong conclusions could not be reached. This was because of the lack of publicly available data and large uncertainties in available sources of information. Below, we provide perspective on what data gaps and uncertainties prevented us from drawing additional strong conclusions about the potential for impacts and/or the factors affecting the frequency or severity of impacts.

We encountered uncertainties associated with, and gaps in, aggregated, publicly accessible information about both activities in the hydraulic fracturing water cycle and groundwater data. In general, comprehensive information on the location of activities in the hydraulic fracturing water cycle is lacking, either because it is not collected, not publicly-available, or prohibitively difficult to aggregate. Thus, we lacked complete information on the geographic locations of well sites (both new and existing) where the chemical mixing, well injection, and produced water handling stages take place; the depth(s) of zones that have been hydraulically fractured in these wells; where water is being acquired (i.e., the source water) for hydraulic fracturing; and where hydraulic fracturing wastewater is treated and/or disposed. FracFocus provided data on well locations, and water and other chemicals used at those locations. However, reporting to FracFocus at the time period studied was not always required, making it difficult to determine the completeness or representativeness of the information.

In addition, there are uncertainties about where groundwater resources are located. This includes the thickness of the resource, from its top to its lowest depth, and its relation to the shallowest depth where hydraulic fracturing occurred. If comprehensive data about the locations of both drinking water resources and activities in the hydraulic fracturing water cycle were available, it would have been possible to more completely identify areas in the United States where hydraulic fracturing-related activities and drinking water resources overlap.

There are also uncertainties and data gaps related to chemicals used in hydraulic fracturing fluid and those detected in produced water. Some chemicals and chemical mixtures remain undisclosed because of confidential business information (CBI) claims. Well operators claimed at least one chemical as CBI at more than 70% of disclosures reported to FracFocus between 2011 and early 2013. Data suggests this practice is increasing. Konschnik and Dayalu (2016) reported that 92% of FracFocus disclosures submitted between approximately March 2011 and April 2015 included at least one chemical claimed as confidential. When chemicals are claimed as CBI, there is no public means of accessing information on these chemicals. Furthermore, many of the chemicals and chemical mixtures disclosed, or those detected in produced water, lack information on properties affecting their movement, persistence, and toxicity in the environment should they be spilled. Better information on these chemicals would allow for a more robust evaluation of potential human health hazards posed, and thus a better understanding about the severity of impacts should the chemicals reach drinking water resources.

In places where we know hydraulic fracturing water cycle activities have occurred, data to assess impacts are often either not collected or are not publicly available in accessible forms. Specifically, local water quality monitoring and well mechanical integrity integrity data are not consistently collected or readily available. In particular, sufficient baseline data on local water quality are needed to quantify any changes post-hydraulic fracturing. There are exceptions to this, for example, the state of California recently implemented a plan to make water quality monitoring information public (Text Box 10-1). In general, however, the limited amount of data collected before, during, and after hydraulic fracturing activities and made public, reduces the ability to determine whether hydraulic fracturing affected drinking water resources.

Text Box 10-1. Hydraulic Fracturing and Groundwater Quality Monitoring in California.

In July 2015, the California Water Resources Control Board adopted Senate Bill 4 (SB4), *Model Criteria for Groundwater Monitoring in Areas of Oil and Gas Well Stimulation*. This resolution directed the establishment of a "comprehensive regulatory groundwater monitoring and oversight program...in order to assess the potential effects of well stimulation treatment activities on the state's groundwater resources" (California State Water Resources Control Board, 2015). The adoption of SB4 concluded a multi-year process, which incorporated stakeholder engagement, review by the public, and consultation with an expert scientific panel.

(Text Box 10-1 is continued on the following page.)

Text Box 10-1 (continued). Hydraulic Fracturing and Groundwater Quality Monitoring in California.

The recommendations of the expert panel informed the creation and implementation of SB4 with respect to criteria "to be used for assessment, sampling, analytical testing, and reporting of water quality associated with oil and gas well stimulation activities" (Esser et al., 2015).

The resolution requires two different scales of groundwater monitoring for different purposes. First, it requires well-by-well (also called "area-specific") groundwater monitoring by well operators. This includes groundwater monitoring conducted for all hydraulic fracturing projects initiated after July 2015. Each oil or gas production well operator must submit a design and timeline for monitoring groundwater resources in proximity to its proposed well. The State Water Resources Control Board approves the monitoring plan before hydraulic fracturing can proceed. The groundwater monitoring plan must include:

- The installation of monitoring wells within 0.5 miles of the wellhead. At least one monitoring well must be upgradient of the production well and two monitoring wells must be downgradient. Should the production well penetrate more than one protected groundwater resource (as defined by the resolution), monitoring wells must facilitate sampling of at least one that is shallow and one that is deep.
- A monitoring timeline that includes sampling prior to production well construction and hydraulic fracturing, as well as semi-annual sampling after completion.
- A list of water quality parameters and constituents to be monitored, including TDS, specific metals, and specific organic compounds.

The area-specific monitoring requirements also include submission of information by well operators about geologic and human-made features in the subsurface that could serve as pathways for impacts to groundwater, aspects of production well construction, and hydraulic fracturing fluid composition.

Second, a regional groundwater monitoring program will document trends in baseline water quality and locate protected groundwater state-wide. In addition to monitoring for trends in groundwater quality related to activities at well sites, it will also be designed to detect trends related to impacts from wastewater disposal practices.

All data from the monitoring programs will be publicly accessible in a state-maintained database. The database is intended to support public health, scientific, and academic needs, as well as future "investigation, assessment, and research relevant to oil and gas development impacts on groundwater quality" (Esser et al., 2015).

Together, the data and information collected and made publicly available as part of the area-specific and regional groundwater monitoring in California will help fill data gaps identified in this section of the assessment by locating groundwater resources, monitoring drinking water resources at spatial and temporal scales relevant for detecting impacts from activities in the hydraulic fracturing water cycle, and distinguishing impacts from hydraulic fracturing activities from the impacts of other potential sources.

In the cases where effects are suspected, it is often difficult to separate the potential effects of hydraulic fracturing activities from effects of broader oil and gas industry activities and other industries or causes. The use of long-lasting, mobile tracer chemicals added to hydraulic fracturing fluids to monitor for impacts has been proposed (Kurose, 2014), but has received relatively little attention in the scientific literature as of mid-2016. Instead, measured changes in water quality parameters can be associated with, but not necessarily diagnostic of, impacts from hydraulic fracturing activities. For instance, measurable changes in methane levels, TDS, ratios of geochemical constituents, and isotopic ratios might suggest impacts from hydraulic fracturing but could also be from other sources, either natural or anthropogenic. To try to assign a cause, these measurements often have to be followed with further collection of evidence supporting or refuting hydraulic fracturing activities as the cause of the changes. (See Text Box 10-2 for discussion of causal assessments.)

Text Box 10-2. Causal Assessment and Hydraulic Fracturing Water Cycle Activities.

A number of recent studies have conducted regional-scale assessments of trends in water quality in areas with hydraulic fracturing activity, showing either no trend or trends linked temporally or spatially with hydraulic fracturing (Burton et al., 2016; Hildenbrand et al., 2016; Hildenbrand et al., 2015; Siegel et al., 2015; Darrah et al., 2014; Fontenot et al., 2013; Warner et al., 2013b) Regional assessments can be important for integrating information over broader scales, and for posing hypotheses about how hydraulic fracturing water cycle activities may impact drinking water resources. Oftentimes, however, activities in the hydraulic fracturing water cycle are merely one of several possible causes of an observed change in water quality or quantity at a specific site. In this case, more thorough, site-specific investigations are often necessary. Causal assessment (also called causal analysis) involves collecting multiple kinds of evidence to determine which of several possible causes of contamination is most likely.

Causal assessment requires several steps. First, the spatial and temporal scope of the issue is defined, including a description of all the possible causes of an observed impact, in this case the change in quality or quantity of a drinking water resource. Once this is done, evidence is collected and assembled to support or refute the potential causes. Evidence indicating how a potential cause and an observed effect are related in time can help support or refute potential causes. Other kinds of evidence can also be useful in identifying a cause, including: determining whether the composition and volume of a leaked, spilled, or treated and discharged fluid are capable of causing observed impacts on water quality; and determining whether a physical pathway between a well or well site exists by measuring the mechanical integrity of hydraulically fractured wells and/or establishing the presence/absence of a contaminant plume.

Ideally, the evidence helps exclude possible causes of the reported contamination, narrowing down the list of potential causes to a single cause. Causal assessments can take a long time to complete and can require a lot of resources and expertise. In some situations, available data and resources are simply not sufficient to definitively identify the cause. Nevertheless, causal assessments conducted in a consistent and transparent way can help enable the identification of the likely cause(s) of contamination of drinking water resources.

The retrospective case studies conducted by the EPA under the Study Plan are examples of scientific investigations using a multiple lines of evidence approach consistent with the principles of causal assessment (U.S. EPA, 2015i, j, l, 2014f, g). These case studies were cited throughout this report. For instance, as noted previously, the Killdeer, North Dakota case study found that an inner string of casing burst during hydraulic fracturing of an oil well, resulting in a release of hydraulic fracturing fluids and formation fluids that impacted a groundwater resource (U.S. EPA, 2015i). Following an analysis of potential sources, the only potential source consistent with the conditions observed was the ruptured well (U.S. EPA, 2015i).

Regardless of whether a single cause can be determined, actions can still be taken to mitigate one or more potential causes of contamination. Information gained once the suspected activity has been halted or at least reduced could elucidate whether hydraulic fracturing operations are more or less likely to have been the source of the contamination.

Many members of the public are interested in understanding the national frequency of impacts to drinking water resources from activities across the entire hydraulic fracturing water cycle. Because of the significant data gaps and uncertainties in the available data, it was not possible to estimate the national frequency of impacts to drinking water resources from activities in the hydraulic fracturing water cycle collectively. We were, however, able to estimate impact frequencies in some, limited cases within the larger hydraulic fracturing water cycle (i.e., spills of hydraulic fracturing fluids or produced water, and mechanical integrity failures). These more specific estimates had a high degree of uncertainty, but were the best estimates that could be provided with the data and literature currently available.

Finally, it should be recognized that this assessment is a snapshot in time. Our understanding of the factors affecting the frequency or severity of impacts may change in the future as industry practices evolve and new information becomes available.

10.3 Use of this Assessment

This assessment contributes to the understanding of the potential impacts to drinking water resources by activities in the hydraulic fracturing water cycle and the factors influencing those impacts. The scientific information presented can be used by federal, tribal, state, and local officials; industry; and the public to better understand and address vulnerabilities of drinking water resources to activities in the hydraulic fracturing water cycle.

The uncertainties and data gaps identified throughout this assessment could be used to identify future data collection efforts. Data collection efforts could include, for example, surface water and groundwater monitoring programs in areas with hydraulically fractured oil and gas production wells; collection and the public dissemination of data on the condition of hydraulically fractured wells; or targeted research programs to better characterize the environmental fate and transport and human health hazards associated with chemicals in the hydraulic fracturing water cycle. Data collected and analyzed through new data collection efforts may identify new factors increasing or decreasing the frequency or severity of impacts.

In the near term, decision-makers could focus their attention on the combinations of activities and factors that we conclude are more likely than others to result in more frequent or more severe impacts (Section 10.2.5). By focusing attention on the above combinations, impacts to drinking water resources from activities in the hydraulic fracturing water cycle can be prevented or reduced.

Overall, the practice of hydraulic fracturing is expanding and continues to change. Oil and gas production associated with hydraulic fracturing was insignificant in 2000, but by 2015 it accounted for an estimated 51% of U.S. oil production and 67% of U.S. gas production (EIA, 2016c, d). The number of wells drilled and hydraulically fractured is likely to continue to increase in the coming decades (EIA, 2014a). The work of evaluating potential impacts from combinations of activities and factors in the hydraulic fracturing water cycle will need to keep pace with this industry and as new scientific studies are produced. This assessment provides a foundation for those efforts, while offering information to support the reduction of current vulnerabilities of drinking water resources.

Chapter 11. References

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Chapter 11. References

Hyperlinks to the reference citations throughout this document will take you to the ORD National Center for Environmental Assessment HERO database (Health and Environmental Research Online) at https://hero.epa.gov/hero. HERO is a database of scientific literature used by the U.S. EPA in the process of developing selected science assessments.

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Front cover (top): Illustrations of activities in the hydraulic fracturing water cycle.
From left to right: Water Acquisition, Chemical Mixing, Well Injection, Produced Water Handling, and Wastewater Disposal and Reuse.

Front cover (bottom): Aerial photographs of hydraulic fracturing activities.
Left: Near Williston, North Dakota. Image ©J Henry Fair / Flights provided by LightHawk.
Right: Springville Township, Pennsylvania. Image ©J Henry Fair / Flights provided by LightHawk.

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