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United States
Environmental Protection
Agency

Assessment of the Potential Impacts of Hydraulic Fracturing for Oil and Gas on Drinking Water Resources

Office of Research and Development
Washington, D.C.

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U.S. Environmental Protection Agency
Washington, DC 20460

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List of Acronyms/Abbreviations

Acronym	Definition
2BE	2-butoxyethanol
ACToR	Aggregated Computational Toxicology Resource database
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
CDWR	Colorado Division of Water Resources
CFR	Code of Federal Regulations
CICAD	Concise International Chemical Assessment Document
CM	chemical mixing
COGCC	Colorado Oil and Gas Conservation Commission
CWCB	Colorado Water Conservation Board
CWT	centralized waste treatment
CWTF	centralized water treatment facility
DBNM	dibromochloronitromethane
DBP	disinfection by-products
DecaBDE	decabromodipheyl ether
DfE	Design for the Environment
DI	Drilling Info, Inc.
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
DOJ	U.S. Department of Justice
DOT	U.S. Department of Transportation
DRO	diesel range organics
EERC	Energy and Environmental Research Center, University of North Dakota
EIA	U.S. Energy Information Administration
EPA	U.S. Environmental Protection Agency

Acronym	Definition
EPA OW	U.S. Environmental Protection Agency's Office of Water
EPI	estimation programs interface
ERCB	Energy Resource Conservation Board
ERG	Eastern Research Group
ESN	Environmental Services Network
FRS	fluids recovery services
GES	Groundwater & Environmental Services, Inc.
GNB	Government of New Brunswick
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
HUC	hydrological unit code
IAEA	International Atomic Energy Agency
IARC	International Agency for Research on Cancer
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
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
MIT	mechanical integrity test
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
NDSWC	North Dakota State Water Commission
NETL	National Energy Technology Laboratory
NGO	non-governmental organization
NM OCD	New Mexico Oil Conservation Division

Acronym	Definition
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
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
ODNR, DMRM	Ohio Department of Natural Resources, Division of Mineral Resources Management
OEPA	Ohio Environmental Protection Agency
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

Acronym	Definition
PAH	polycyclic aromatic hydrocarbon
PFBC	Pennsylvania Fish and Boat Commission
PDL	positive determination letter
PMF	Positive Matrix Factorization
POD	point-of-departure
POTW	publicly owned treatment work
PPRTV	provisional peer-reviewed toxicity value
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
QSAR	Quantitative Structure Activity Relationship
RfD	reference dose
RfV	reference value
RO	reverse osmosis
SAB	Science Advisory Board
SAIC	Science Applications International Corporation
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

Acronym	Definition
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
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
TPH	total petroleum hydrocarbons
TSS	total suspended solids
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
VOC	volatile organic compounds
WAWSA	Western Area Water Supply Authority
WFR	Well File Review
WHO	World Health Organization
WRF	Water Research Foundation
WVDEP	West Virginia Department of Environmental Protection
WWTP	wastewater treatment plant
WYOGCC	Wyoming Oil and Gas Conservation Commission

Preface

The U.S. Environmental Protection Agency (EPA) is conducting a study of the potential impacts of hydraulic fracturing for oil and gas on drinking water resources. This study was initiated in Fiscal Year 2010 when Congress urged the EPA to examine the relationship between hydraulic fracturing and drinking water resources in the United States. In response, EPA developed a research plan (*Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*) that was reviewed by the Agency's Science Advisory Board (SAB) and issued in 2011. A progress report on the study (*Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources: Progress Report)*, detailing the EPA's research approaches and next steps, was released in late 2012 and was followed by a consultation with individual experts convened under the auspices of the SAB.

The EPA's study includes the development of several research projects, extensive review of the literature and technical input from state, industry, and non-governmental organizations as well as the public and other stakeholders. A series of technical roundtables and in-depth technical workshops were held to help address specific research questions and to inform the work of the study. The study is designed to address research questions posed for each stage of the hydraulic fracturing water cycle:

- Water Acquisition: What are the possible impacts of large volume water withdrawals from ground and surface waters on drinking water resources?
- Chemical Mixing: What are the possible impacts of surface spills of hydraulic fracturing fluid on or near well pads on drinking water resources?
- Well Injection: What are the possible impacts of the injection and fracturing process on drinking water resources?
- Flowback and Produced Water: What are the possible impacts of surface spills of flowback and produced water on or near well pads on drinking water resources?
- Wastewater Treatment and Waste Disposal: What are the possible impacts of inadequate treatment of hydraulic fracturing wastewaters on drinking water resources?

This report, *Assessment of the Potential Impacts of Hydraulic Fracturing for Oil and Gas on Drinking Water Resources*, includes both the literature review and results from the research projects conducted as part of the EPA's study. It will undergo independent, external peer review in accordance with Agency policy and all of the peer review comments received will be considered in the development of the final report.

The EPA's study will contribute to the understanding of the potential impacts of hydraulic fracturing activities for oil and gas on drinking water resources and the factors that may influence those impacts. The study will help facilitate and inform dialogue among interested stakeholders, including Congress, other Federal agencies, states, tribal government, the international community, industry, non-governmental organizations, academia, and the general public.

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Executive Summary

Executive Summary

Since the early 2000s, oil and natural gas production in the United States has been transformed through technological innovation. Hydraulic fracturing, combined with advanced directional drilling techniques, made it possible to economically extract oil and gas resources previously inaccessible. The resulting surge in production increased domestic energy supplies and brought economic benefits to many areas of the United States.

The growth in domestic oil and gas production also raised concerns about potential impacts to human health and the environment, including potential effects on the quality and quantity of drinking water resources. Some residents living close to oil and gas production wells have reported changes in the quality of drinking water and assert that hydraulic fracturing is responsible for these changes. Other concerns include competition for water between hydraulic fracturing activities and other water users, especially in areas of the country experiencing drought, and the disposal of wastewater generated from hydraulic fracturing.

The U.S. Congress urged the U.S. Environmental Protection Agency (EPA) to study the relationship between hydraulic fracturing and drinking water. This report synthesizes available scientific literature and data to assess the potential for hydraulic fracturing for oil and gas to change the quality or quantity of drinking water resources, and identifies factors affecting the frequency or severity of any potential changes. This report can be used by federal, tribal, state, and local officials; industry; and the public to better understand and address any vulnerabilities of drinking water resources to hydraulic fracturing activities.

What is Hydraulic Fracturing?

Hydraulic fracturing is a stimulation technique used to increase oil and gas production from underground rock formations. Hydraulic fracturing involves the injection of fluids under pressures great enough to fracture the oil- and gas-producing formations. The fluid generally consists of water, chemicals, and proppant (commonly sand). The proppant holds open the newly created fractures after the injection pressure is released. Oil and gas flow through the fractures and up the production well to the surface.

Hydraulic fracturing has been used since the late 1940s and, for the first 50 years, was mostly used in vertical wells in conventional formations.[1] Hydraulic fracturing is still used in these settings, but the process has evolved; technological developments (including horizontal and directional drilling) have led to the use of hydraulic fracturing in unconventional hydrocarbon formations that could not otherwise be profitably produced (see Figure ES-1). These formations include:

[1] Conventional formations often allow oil and natural gas to flow to the wellbore without hydraulic fracturing and typically contain trapped oil and natural gas that migrated from other subsurface locations. Hydraulic fracturing can be used to enhance oil and gas production from these formations. In unconventional formations, hydraulic fracturing is needed to extract economical quantities of oil and gas.

- **Shales.** Organic-rich, black shales are the source rocks in which oil and gas form on geological timescales. Oil and gas are contained in the pore space of the shale. Some shales contain predominantly gas or oil; many shale formations contain both.
- **Tight formations**. "Tight" formations are relatively low permeability, non-shale, sedimentary formations that can contain oil and gas. Like in shales, oil and gas are contained in the pore space of the formation. Tight formations can include sandstones, siltstone, and carbonates, among others.
- **Coalbeds**. In coalbeds, methane (the primary component of natural gas) is generally adsorbed to the coal rather than contained in the pore space or structurally trapped in the formation. Pumping the injected and native water out of the coalbeds after fracturing serves to depressurize the coal, thereby allowing the methane to desorb and flow into the well and to the surface.

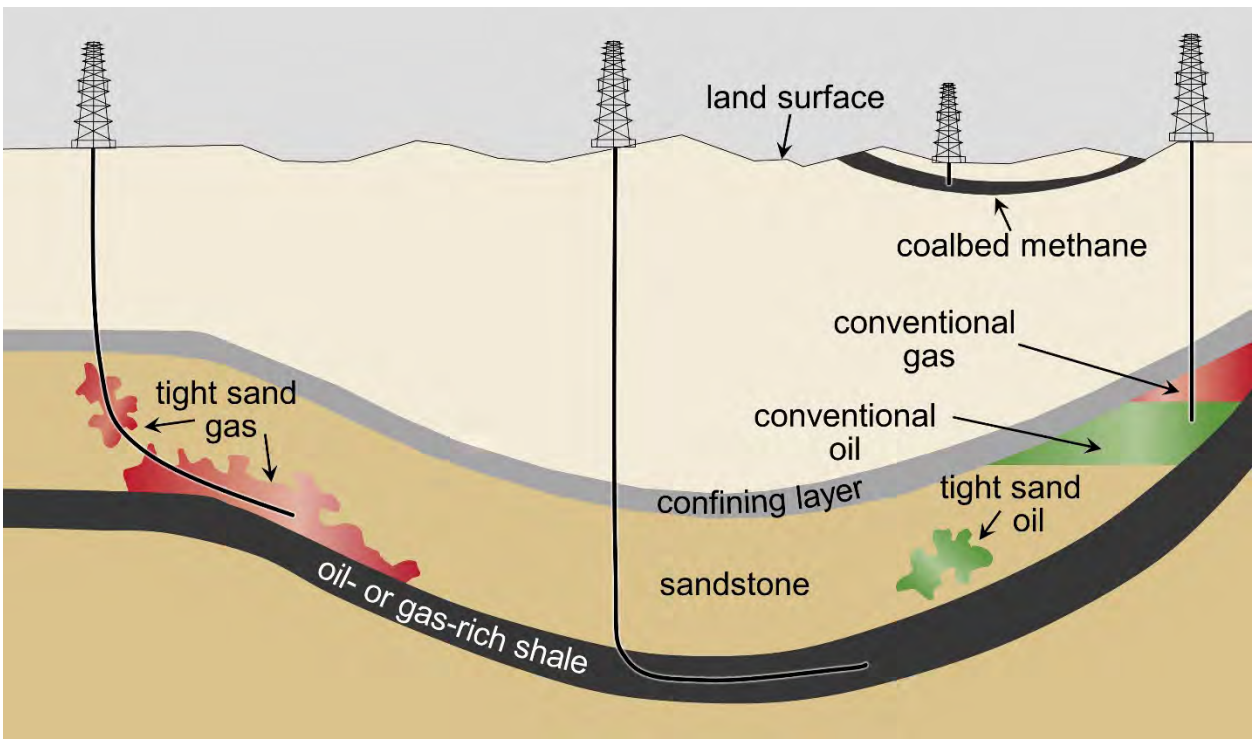

Figure ES-1. Schematic cross-section of general types of oil and gas resources and the orientations of production wells used in hydraulic fracturing.

Shown are conceptual illustrations of types of oil and gas wells. A vertical well is producing from a conventional oil and gas deposit (right). In this case, a gray confining layer serves to "trap" oil (green) or gas (red). Also shown are wells producing from unconventional formations: a vertical coalbed methane well (second from right); a horizontal well producing from a shale formation (center); and a well producing from a tight sand formation (left). Note: Figure not to scale. Modified from USGS (2002) and Newell (2011).

The combined use of hydraulic fracturing with horizontal (or more generically, directional) drilling has led to an increase in oil and gas activities in areas of the country with historical oil and gas production, and an expansion of oil and gas activities to new regions of the country.

Scope of the Assessment

We defined the scope of this assessment by the following activities involving water that support hydraulic fracturing (i.e., the hydraulic fracturing water cycle; see Figure ES-2):[1]

- **Water acquisition:** the withdrawal of ground or surface water needed for hydraulic fracturing fluids;
- **Chemical mixing:** the mixing of water, chemicals, and proppant on the well pad to create the hydraulic fracturing fluid;
- **Well injection:** the injection of hydraulic fracturing fluids into the well to fracture the geologic formation;
- **Flowback and produced water:** the return of injected fluid and water produced from the formation (collectively referred to as produced water in this report) to the surface, and subsequent transport for reuse, treatment, or disposal; and
- **Wastewater treatment and waste disposal:** the reuse, treatment and release, or disposal of wastewater generated at the well pad, including produced water.

This assessment reviews, analyzes, and synthesizes information relevant to the potential impacts of hydraulic fracturing on drinking water resources at each stage of the hydraulic fracturing water cycle. Impacts are defined as any change in the quality or quantity of drinking water resources. Where possible, we identify the mechanisms responsible or potentially responsible for any impacts. For example, a spill of hydraulic fracturing fluid is a mechanism by which drinking water resources could be impacted.

Drinking water resources are defined within this report as any body of ground water or surface water that now serves, or in the future could serve, as a source of drinking water for public or private use. This is broader than most federal and state regulatory definitions of drinking water and encompasses both fresh and non-fresh bodies of water. Trends indicate that both types of water bodies are currently being used, and will continue to be used in the future, as sources of drinking water.

This assessment focuses on the potential impacts from activities in the hydraulic fracturing water cycle on drinking water resources. We do this so federal, tribal, state, and local officials; industry; and the public can better understand and address any vulnerabilities of drinking water resources to hydraulic fracturing activities. We do not address other concerns raised about hydraulic fracturing specifically or about oil and gas exploration and production activities more generally. Activities that

[1] In this assessment, we refer to the "EPA" when referencing other EPA studies. If a conclusion or analysis was done specifically by the authors of this assessment, we refer to it and its findings in the first person.

are not considered include: acquisition and transport of constituents of hydraulic fracturing fluids besides water (e.g., sand mining and chemical production) outside of the stated water cycle; site selection and well pad development; other infrastructure development (e.g., roads, pipelines, compressor stations); site reclamation; and well closure. A summary and evaluation of current or proposed regulations and policies is beyond the scope of this report. Additionally, this report does not discuss the potential impacts of hydraulic fracturing on other water users (e.g., agriculture or industry), other aspects of the environment (e.g., seismicity, air quality, or ecosystems), worker health or safety, or communities. Furthermore, this report is not a human health risk assessment. It does not identify populations that are exposed to chemicals, estimate the extent of exposure, or estimate the incidence of human health impacts.

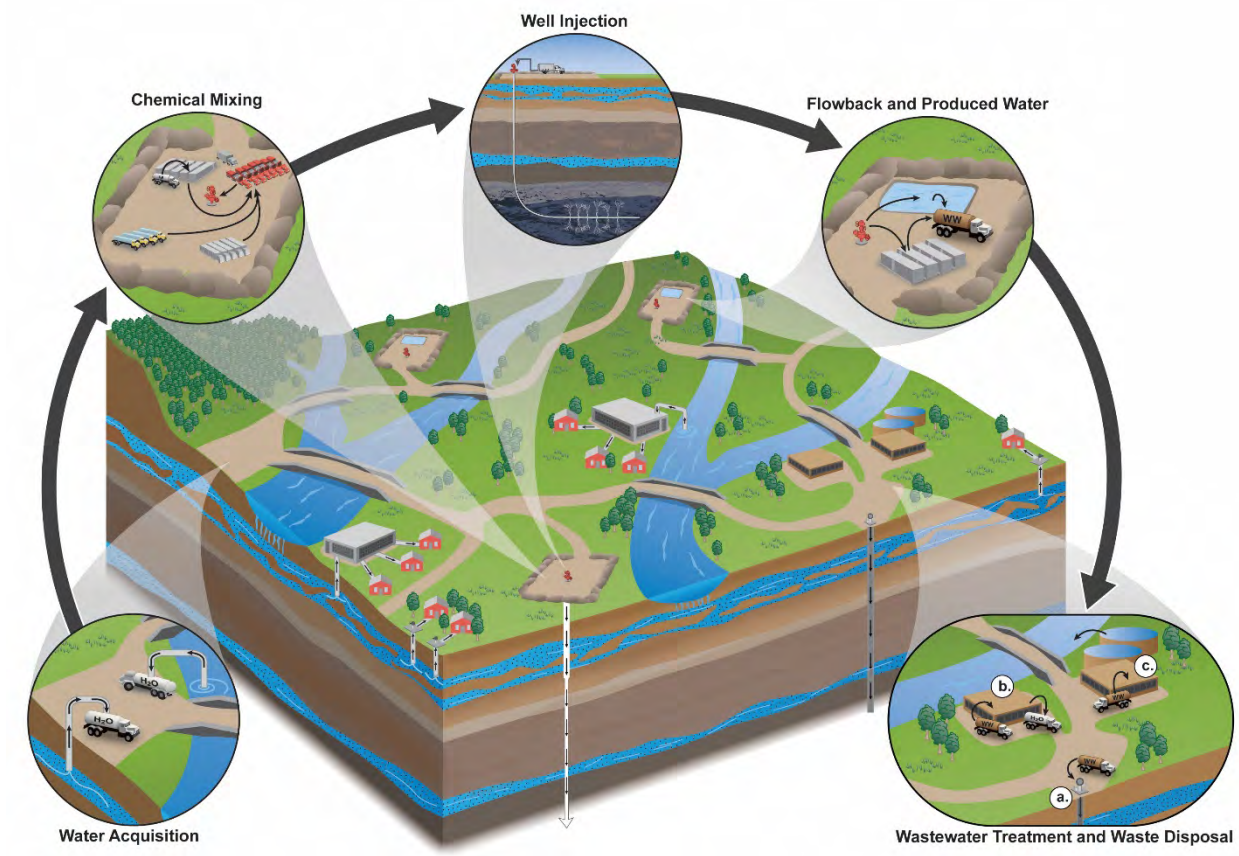

Figure ES-2. The stages of the hydraulic fracturing water cycle.

Shown here is a generalized landscape depicting the activities of the hydraulic fracturing water cycle and their relationship to each other, as well as their relationship to drinking water resources. Arrows depict the movement of water and chemicals. Specific activities in the "Wastewater Treatment and Waste Disposal" inset are (a)underground injection control (UIC) well disposal, (b) wastewater treatment and reuse, and (c) wastewater treatment and discharge at a centralized waste treatment (CWT) facility. Note: Figure not to scale.

Approach

This assessment relies on relevant scientific literature and data. Literature evaluated included articles published in science and engineering journals, federal and state government reports, non-governmental organization (NGO) reports, and industry publications. Data sources examined included federal- and state-collected data sets, databases maintained by federal and state government agencies, other publicly-available data and information, and data, including confidential and non-confidential business information, submitted by industry 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* (hereafter referred to as the "Study Plan") and published by scientific journals or as peer-reviewed EPA reports; those articles and reports are cited throughout this assessment. The research topic areas and projects described in the Study Plan were designed to meet the data and information needs of this assessment and were developed with substantial expert and public input.

Proximity of Current Activity and Drinking Water Resources

Thousands of wells are drilled and fractured every year in the United States, with activities concentrated in specific locations. We estimate 25,000-30,000 new wells were drilled and hydraulically fractured annually in the United States between 2011 and 2014. Additional, pre-existing wells (wells more than one year old that may or may not have been hydraulically fractured in the past) were also likely fractured. Hydraulic fracturing took place in at least 25 states between 1990 and 2013. The EPA's analysis of disclosures made to FracFocus 1.0 (hereafter "FracFocus") contained wells from 20 of these states.[2] Almost half of these wells were in Texas. Colorado was a distant second, while Pennsylvania and North Dakota were third and fourth, respectively. Hydraulic fracturing activities were further localized within the 20 states. Of the approximately 1,500 counties or county equivalents in these 20 states, slightly over 400 contained all of the wells disclosed to FracFocus during this time period. In Colorado, over 85% of the hydraulically fractured wells disclosed were located in two counties. The price of gas and oil may cause short term volatility in the number of wells drilled and fractured per year, yet hydraulic fracturing is expected to continue to expand and drive an increase in domestic oil and gas production in coming decades.

Hydraulically fractured wells can be located near residences and drinking water resources. Between 2000 and 2013, approximately 9.4 million people lived within one mile of a hydraulically

[1] Some information provided to the EPA in response to two separate information requests to service companies and well operators was claimed as confidential business information.

[2] FracFocus is a publicly accessible website (www.fracfocus.org) managed by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission where oil and gas production well operators may disclose information voluntarily or pursuant to state requirements about the ingredients used in hydraulic fracturing fluids at individual wells. The EPA analyzed disclosures from FracFocus 1.0 for over 38,000 oil and gas production wells hydraulically fractured between January 1, 2011 and February 28, 2013. A disclosure refers to data submitted for a specific oil and gas production well for a specific fracture date. Most wells had only one disclosure, but a small number of wells (876 wells) had multiple disclosures. For the purposes of this Executive Summary, we equate disclosures with wells when discussing this study.

fractured well. Approximately 6,800 sources of drinking water for public water systems were located within one mile of at least one hydraulically fractured well during the same period. These drinking water sources served more than 8.6 million people year-round in 2013.

Although proximity of hydraulic fracturing activities to a drinking water resource is not in of itself sufficient for an impact to occur,, it does increase the potential for impacts. Residents and drinking water resources in areas experiencing hydraulic fracturing activities are most likely to be affected by any potential impacts, should they occur. However, hydraulic fracturing can also affect drinking water resources outside the immediate vicinity of a hydraulically fractured well; a truck carrying wastewater could spill or a release of inadequately treated wastewater could have downstream effects.

Major Findings

From our assessment, we conclude there are above and below ground mechanisms by which hydraulic fracturing activities have the potential to impact drinking water resources. These mechanisms include water withdrawals in times of, or in areas with, low water availability; spills of hydraulic fracturing fluids and produced water; fracturing directly into underground drinking water resources; below ground migration of liquids and gases; and inadequate treatment and discharge of wastewater.

We did not find evidence that these mechanisms have led to widespread, systemic impacts on drinking water resources in the United States. Of the potential mechanisms identified in this report, we found specific instances where one or more mechanisms led to impacts on drinking water resources, including contamination of drinking water wells. The number of identified cases, however, was small compared to the number of hydraulically fractured wells.

This finding could reflect a rarity of effects on drinking water resources, but may also be due to other limiting factors. These factors include: insufficient pre- and post-fracturing data on the quality of drinking water resources; the paucity of long-term systematic studies; the presence of other sources of contamination precluding a definitive link between hydraulic fracturing activities and an impact; and the inaccessibility of some information on hydraulic fracturing activities and potential impacts.

Below, we provide a synopsis of the assessment's key findings, organized by each stage of the hydraulic fracturing water cycle. We provide answers to the research questions presented in the Study Plan and Chapter 1. While come citations are provided here, individual chapters should be consulted for additional detail and citations.

Water Acquisition

Water is a major component of nearly all hydraulic fracturing operations. It typically makes up almost 90% or more of the fluid volume injected into a well, and each hydraulically fractured well requires thousands to millions of gallons of water. Cumulatively, hydraulic fracturing activities in the United States used on average 44 billion gal of water a year in 2011 and 2012, according to the

EPA's analysis of FracFocus disclosures. Although this represents less than 1% of total annual water use and consumption at this scale, water withdrawals could potentially impact the quantity and quality of drinking water resources at more local scales.[1]

Research Questions: Water Acquisition

- ***What are the types of water used for hydraulic fracturing?***

Water for hydraulic fracturing typically comes from surface water, ground water, or reused hydraulic fracturing wastewater. Hydraulic fracturing operations in the eastern United States generally rely on surface water, while operations in the more semi-arid to arid western states generally use mixed supplies of surface and ground water. In the Marcellus Shale in Pennsylvania, for example, most water used for hydraulic fracturing originates from surface water, whereas surface and ground water are used in approximately equal proportions in the Barnett Shale in Texas (see Figure ES-3a,b). In areas that lack available surface water (e.g., western Texas), ground water supplies most of the water needed for hydraulic fracturing.

Across the United States, the vast majority of water used in hydraulic fracturing is fresh, although operators also make use of lower-quality water, including reused hydraulic fracturing wastewater.[2] Based on available data, the median reuse of wastewater as a percentage of injected volumes is 5% nationally, with the percentage varying by location.[3] Available data on reuse trends indicate increased reuse of wastewater over time in both Pennsylvania and West Virginia. Reuse as a percentage of injected volumes is lower in other areas, including regions with more water stress, likely because of the availability of disposal wells. For example, reused wastewater is approximately 18% of injected volumes in the Marcellus Shale in Pennsylvania's Susquehanna River Basin, whereas it is approximately 5% in the Barnett Shale in Texas (see Figure ES-3a,b).

[1] Water use is water withdrawn from ground- or surface water for a specific purpose, part or all of which may be returned to the local hydrologic cycle. If no water is returned, water use equals water consumption. 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). In the case of hydraulic fracturing, water can be consumed by the loss of injected water to subsurface zones or via underground disposal of wastewaters, among other means.

[2] In this assessment, hydraulic fracturing "wastewater" refers to both produced water and any other water generated as a hydraulic fracturing site. As used in this assessment, the term "wastewater" is not intended to constitute a term of art for legal or regulatory purposes.

[3] Reused wastewater as a percentage of injected water differs from the percentage of wastewater that is managed through reuse, as opposed to other wastewater management options. For example, in the Marcellus in Pennsylvania, approximately 18% of injected water is reused produced water, while approximately 70% of wastewater or more is managed through reuse (Figure ES-3a).

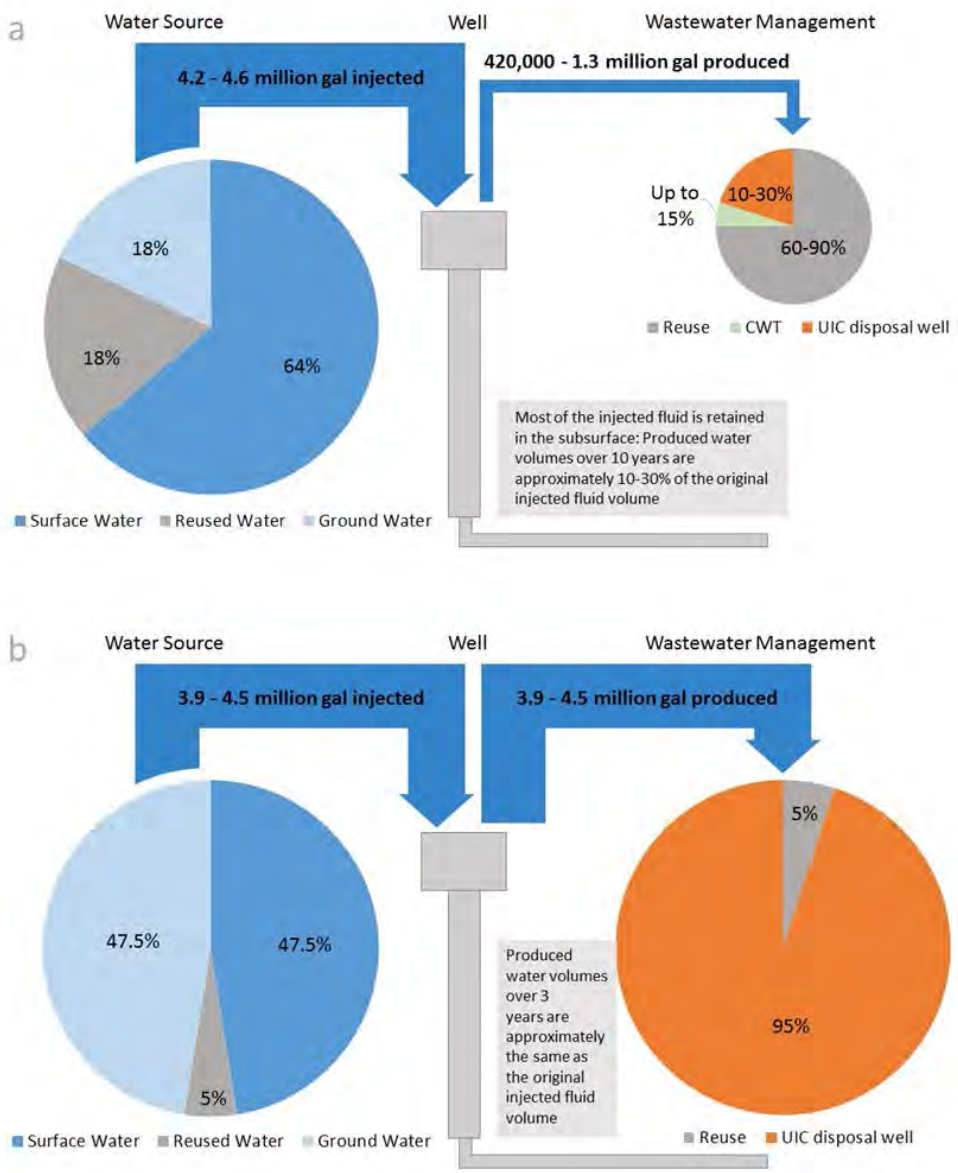

Figure ES-3. Water budgets representative of practices in the Marcellus Shale in the Susquehanna River Basin in Pennsylvania (a) and the Barnett Shale in Texas (b).

Pie size and arrow thickness represent the relative volume of water as it flows through the hydraulic fracturing water cycle. Wastewater going to a centralized waste treatment (CWT) facility may be either discharged to surface water or reused. Wastewater going to an underground injection control (UIC) well is disposed of below ground. These examples represent typical water management practices as depicted for the most recent time period reviewed by this assessment. They do not represent any specific well. Note: Values for Marcellus Shale are specific to the Susquenhanna River Basin, except for the produced water volumes. The longest-term measurement available was from the West Virginia portion of the the Marcellus Shale.

- ***How much water is used per well?***

The national median volume of water used per hydraulically fractured well is approximately 1.5 million gal (5.7 million L), according to the EPA's analysis of FracFocus disclosures. This estimate likely represents a wide variety of fractured well types, including vertical wells that generally use much less water per well than horizontal wells. Thus, published estimates for horizontal shale gas wells are typically higher (e.g., approximately 4 million gallons (Vengosh et al., 2014)). There is also wide variation within and among states and basins in the median water volumes used per well, from more than 5 million gal (19 million L) in Arkansas, Louisiana and West Virginia to less than 1 million gal (3.8 million L) in California, New Mexico, and Utah, among others. This variation results from several factors, including well length, formation geology, and fracturing fluid formulation.

- ***How might cumulative water withdrawals for hydraulic fracturing affect drinking water quantity?***

Cumulatively, hydraulic fracturing uses billions of gallons of water each year at the national and state scales, and even in some counties. As noted above, hydraulic fracturing water use and consumption are generally less than 1% of total annual water use and consumption at these scales. However, there are a few counties in the United States where these percentages are higher. For 2011 and 2012, annual hydraulic fracturing water use was 10% or more compared to 2010 total annual water use in 6.5% of counties with FracFocus disclosures analyzed by the EPA, 30% or more in 2.2% of counties, and 50% or more in 1.0% of counties. Consumption estimates followed the same general pattern. In these counties, hydraulic fracturing is a relatively large user and consumer of water.

High fracturing water use or consumption alone does not necessarily result in impacts to drinking water resources. Rather, impacts result from the combination of water use or consumption and water availability at local scales. In our survey of published literature, we did not find a case where hydraulic fracturing water use or consumption alone caused a drinking water well or stream to run dry. This could indicate an absence of effects or a lack of documentation in the literature we reviewed. Additionally, water availability is rarely impacted by just one use or factor alone. In Louisiana, for example, the state requested hydraulic fracturing operations switch from ground to surface water, due to concerns that ground water withdrawals for fracturing could, in combination with other uses, adversely affect drinking water supplies.

The potential for impacts to drinking water resources from hydraulic fracturing water withdrawals is highest in areas with relatively high fracturing water use and low water availability. Southern and western Texas are two locations where hydraulic fracturing water use, low water availability, drought, and reliance on declining ground water has the potential to affect the quantity of drinking water resources. Any impacts are likely to be realized locally within these areas. In a detailed case study of southern Texas, Scanlon et al. (2014) observed generally adequate water supplies for hydraulic fracturing, except in specific locations. They found excessive drawdown of local ground water in a small proportion (approximately 6% of the area) of the Eagle Ford Shale. They suggested water management, particularly a shift towards brackish water use, could minimize potential future impacts to fresh water resources.

The potential for impacts to drinking water quantity due to hydraulic fracturing water use appears to be lower—but not eliminated—in other areas of the United States. Future problems could arise if hydraulic fracturing increases substantially in areas with low water availability, or in times of water shortages. In detailed case studies in western Colorado and northeastern Pennsylvania, the EPA did not find current impacts, but did conclude that streams could be vulnerable to water withdrawals from hydraulic fracturing. In northeast Pennsylvania, water management, such as minimum stream flow requirements, limits the potential for impacts, especially in small streams. In western North Dakota, ground water is limited, but the industry may have sufficient supplies of surface water from the Missouri River system. These location-specific examples emphasize the need to focus on regional and local dynamics when considering potential impacts of hydraulic fracturing water acquisition on drinking water resources.

- ***What are the possible impacts of water withdrawals for hydraulic fracturing on water quality?***

Water withdrawals for hydraulic fracturing, similar to all water withdrawals, have the potential to alter the quality of drinking water resources. Ground water withdrawals exceeding natural recharge rates decrease water storage in aquifers, potentially mobilizing contaminants or allowing the infiltration of lower quality water from the land surface or adjacent formations. Withdrawals could also decrease ground water discharge to streams, potentially affecting surface water quality. Areas with large amounts of sustained ground water pumping are most likely to experience impacts, particularly drought-prone regions with limited ground water recharge.

Surface water withdrawals also have the potential to affect water quality. Withdrawals may lower water levels and alter stream flow, potentially decreasing a stream's capacity to dilute contaminants. Case studies by the EPA show that streams can be vulnerable to changes in water quality due to water withdrawals, particularly smaller streams and during periods of low flow. Management of the rate and timing of surface water withdrawals has been shown to help mitigate potential impacts of hydraulic fracturing withdrawals on water quality.

Chemical Mixing

Hydraulic fracturing fluids are developed to perform specific functions, including: create and extend fractures, transport proppant, and place proppant in the fractures. The fluid generally consists of three parts: (1) the base fluid, which is the largest constituent by volume and is typically water; (2) the additives, which can be a single chemical or a mixture of chemicals; and (3) the proppant. Additives are chosen to serve a specific purpose (e.g., adjust pH, increase viscosity, limit bacterial growth). Chemicals generally comprise a small percentage (typically 2% or less) of the overall injected fluid volume. Because over one million gallons of fluids are typically injected per well, thousands of gallons of chemicals can be potentially stored on-site and used during hydraulic fracturing activities.

On-site storage, mixing, and pumping of chemicals and hydraulic fracturing fluids have the potential to result in accidental releases, such as spills or leaks. Potential impacts to drinking water resources from spills of hydraulic fracturing fluids and chemicals depend on the characteristics of the spills, and the fate, transport, and the toxicity of chemicals spilled.

Research Questions: Chemical Mixing

- ***What is currently known about the frequency, severity, and causes of spills of hydraulic fracturing fluids and additives?***

The frequency of on-site spills from hydraulic fracturing could be estimated for two states, but not for operations nationally or for other areas. Frequency estimates from data and literature ranged from one spill for every 100 wells in Colorado to between approximately 0.4 and 12.2 spills for every 100 wells in Pennsylvania.[1] These estimates include spills of hydraulic fracturing fluids and chemicals, and produced water reported in state databases. Available data generally precluded estimates of hydraulic fracturing fluid and/or chemical spill rates separately from estimates of an overall spill frequency. It is unknown whether these spill estimates are representative of national occurrences. If the estimates are representative, the number of spills nationally could range from approximately 100 to 3,700 spills annually, assuming 25,000 to 30,000 new wells are fractured per year.

The EPA characterized volumes and causes of hydraulic fracturing-related spills identified from selected state and industry data sources. The spills occurred between January 2006 and April 2012 in 11 states and included 151 cases in which fracturing fluids or chemicals spilled on or near a well pad. Due to the methods used for the EPA's characterization of spills, these cases were likely a subset of all fracturing fluid and chemical spills during the study's time period. The reported volume of fracturing fluids or chemicals spilled ranged from 5 gal to more than 19,000 gal (19 to 72,000 L), with a median volume of 420 gal (1,600 L) per spill. Spill causes included equipment failure, human error, failure of container integrity, and other causes (e.g., weather and vandalism). The most common cause was equipment failure, specifically blowout preventer failure, corrosion, and failed valves. More than 30% of the 151 fracturing fluid or chemical spills were from fluid storage units (e.g., tanks, totes, and trailers).

- ***What are the identities and volumes of chemicals used in hydraulic fracturing fluids, and how might this composition vary at a given site and across the country?***

In this assessment, we identified a list of 1,076 chemicals used in hydraulic fracturing fluids. This is a cumulative list over multiple wells and years. These chemicals include acids, alcohols, aromatic hydrocarbons, bases, hydrocarbon mixtures, polysaccharides, and surfactants. According to the EPA's analysis of disclosures to FracFocus, the number of unique chemicals per well ranged from 4 to 28, with a median of 14 unique chemicals per well.

Our analysis indicates that chemical use varies and that no single chemical is used at all well sites across the country, although several chemicals are widely used. Methanol, hydrotreated light petroleum distillates, and hydrochloric acid were reported as used in 65% or more of wells, according to FracFocus disclosures analyzed by the EPA. Only 32 chemicals, excluding water, quartz, and sodium chloride, were used in more than 10% of wells according to the EPA's analysis

[1] Spill frequency estimates are for a given number of wells over a given period of time. These are not annual estimates nor are they for the lifetime of a well.

of FracFocus disclosures. The composition of hydraulic fracturing fluids varies by state, by well, and within the same service company and geologic formation. This variability likely results from several factors, including the geology of the formation, the availability and cost of different chemicals, and operator preference.

Estimates from the EPA's database developed from FracFocus suggest median volumes of individual chemicals injected per well ranged from a few gallons to thousands of gallons, with an overall median of 650 gal (2,500 L) per chemical per well. Based on this overall median and assuming 14 unique chemicals are used per well, an estimated 9,100 gal (34,000 L) of chemicals may be injected per well. Given that the number of chemicals per well ranges from 4 to 28, the estimated volume of chemicals injected per well may range from approximately 2,600 to 18,000 gal (9,800 to 69,000 L).

- ***What are the chemical, physical, and toxicological properties of hydraulic fracturing chemical additives?***

Measured or estimated physicochemical properties were obtained for 453 chemicals of the total 1,076 chemicals reported in hydraulic fracturing fluids. We could not estimate physicochemical properties for the inorganic chemicals or mixtures. The 453 chemicals have a wide range of physicochemical properties.

Properties affecting the likelihood of a spilled chemical reaching and impacting a drinking water resource include mobility, solubility, and volatility. Of the 453 chemicals for which physicochemical properties were available, 18 of the top 20 most mobile ones were reported in the EPA's FracFocus database for 2% or less of wells. Choline chloride and tetrakis (hydroxymethyl) phosphonium were exceptions and were reported in 14% and 11% of wells, respectively. These two chemicals appear to be relatively more common, and, if spilled, would move quickly through the environment with the flow of water. The majority of the 453 chemicals associate strongly with soils and organic materials, suggesting the potential for these chemicals to persist in the environment as long-term contaminants. Many of the 453 chemicals fully dissolve in water, but their aqueous solubility varies greatly. Few of the chemicals volatilize, and thus a large proportion of most hydraulic fracturing chemicals tend to remain in water.

Oral reference values and oral slope factors meeting the criteria used in this assessment were not available for the majority of chemicals used in hydraulic fracturing fluids, representing a significant data gap for hazard identification.[1,2] Reference values and oral slope factors are important for understanding the potential human health effects resulting from exposure to a chemical. Chronic oral reference values and/or oral slope factors from selected federal, state, and international sources were available for 90 (8%) of the 1,076 chemicals used in hydraulic fracturing fluids. From

[1] A reference value is an estimate of an exposure to the human population (including susceptible subgroups) for a given duration that is likely to be without an appreciable risk of adverse health effects over a lifetime. Reference value is a generic term not specific to a given route of exposure.
[2] An oral slope factor is an upper-bound, approximating 95% confidence limit, on the increased cancer risk from a lifetime oral exposure to an agent.

U.S. federal sources alone, chronic oral reference values were available for 73 chemicals (7%) of the 1,076 chemicals, and oral slope factors were available for 15 chemicals (1%). Of the 32 chemicals reported as used in at least 10% of wells in the EPA's FracFocus database (excluding water, quartz, and sodium chloride), seven (21%) have a federal chronic oral reference value. Oral reference values and oral slope factors are a key component of the risk assessment process, although comprehensive risk assessments that characterize the health risk associated with exposure to these chemicals are not available.

Of the chemicals that had values available, the health endpoints associated with those values include the potential for carcinogenesis, immune system effects, changes in body weight, changes in blood chemistry, cardiotoxicity, neurotoxicity, liver and kidney toxicity, and reproductive and developmental toxicity. However, it is important to note that evaluating any potential risk to human populations would require knowledge of the specific chemicals that are present at a particular site, whether or not humans are exposed to those chemicals and, if so, at what levels and for what duration, and the toxicity of the chemicals. Since most chemicals are used infrequently on a nationwide basis, potential exposure is likely to be a local or regional issue, rather than a national issue. Accordingly, consideration of hazards and risks associated with these chemical additives would be most useful on a site-specific basis and is beyond the scope of this assessment.

- ***If spills occur, how might hydraulic fracturing chemical additives contaminate drinking water resources?***

There are several mechanisms by which a spill can potentially contaminate drinking water resources. These include overland flow to nearby surface water, soil contamination and eventual transport to surface water, and infiltration and contamination of underlying ground water. Of the 151 spills characterized by the EPA, fluids reached surface water in 13 (9% of 151) cases and soil in 97 (64%) cases. None of the spills of hydraulic fracturing fluid were reported to have reached ground water. This could be due to an absence of impact; however, it can take several years for spilled fluids to infiltrate soil and leach into ground water. Thus, it may not be immediately apparent whether a spill has reached ground water or not.

Based on the relative importance of each of these mechanisms, impacts have the potential to occur quickly, be delayed short or long periods, or have a continual effect over time. In Kentucky, for example, a spill impacted a surface water body relatively quickly when hydraulic fracturing fluid entered a creek, significantly reducing the water's pH and increasing its conductivity (Papoulias and Velasco, 2013).

Well Injection

Hydraulic fracturing fluids are injected into oil or gas wells under high pressures. The fluids flow through the well (commonly thousands of feet below the surface) into the production zone (i.e., the geologic formation being fractured) where the fluid injection pressures are sufficient to create fractures in the rock.

There are two major subsurface mechanisms by which the injection of fluid and the creation and propagation of fractures can lead to contamination of drinking water resources: (1) the unintended

movement of liquids or gases out of the production well or along the outside of the production well into a drinking water resource via deficiencies in the well's casing or cement, and (2) the unintended movement of liquids or gases from the production zone through subsurface geologic formations into a drinking water resource. Combinations of these two mechanisms are also possible.

Research Questions: Well Injection

- ***How effective are current well construction practices at containing fluids—both liquids and gases—before, during, and after fracturing?***

Production wells are constructed to access and convey hydrocarbons from the formations in which they are found to the surface, and to isolate fluid-bearing zones (containing oil, gas, or water) from each other. Typically, multiple casings are emplaced and cemented along the wellbore to protect and isolate the oil and/or natural gas from the formations it must travel through to reach the surface.

Below ground drinking water resources are often separated from the production well using casing and cement. Cemented surface casing, in particular, is an important well construction feature for isolating drinking water resources from liquids and gases that may move through the subsurface. A limited risk modeling study of selected injection wells in the Williston Basin in North Dakota suggests that the risk of aquifer contamination from leaks inside the well to the drinking water resource decreases by a factor of approximately one thousand when surface casing extends below the bottom of the drinking water resource (Michie and Koch, 1991). Most wells used in hydraulic fracturing operations have casing and a layer of cement to protect drinking water resources, but there are exceptions: a survey conducted by the EPA of oil and gas production wells hydraulically fractured by nine oil and gas service companies in 2009 and 2010 estimated that at least 3% of the wells (600 out of 23,000 wells) did not have cement across a portion of the casing installed through the protected ground water resource identified by well operators. The absence of cement does not in and of itself lead to an impact. However, it does reduce the overall number of casing and cement barriers fluids must travel through to reach ground water resources.

Impacts to drinking water resources from subsurface liquid and gas movement may occur if casing or cement are inadequately designed or constructed, or fail. There are several examples of these occurrences in hydraulically fractured wells that have or may have resulted in impacts to drinking water resources. In one example, an inner string of casing burst during hydraulic fracturing, which resulted in a release of fluids on the land surface and possibly into the aquifer near Killdeer, North Dakota. The EPA found that, based on the data analysis performed for the study, the only potential source consistent with conditions observed in two impacted monitoring wells was the blowout that occurred during hydraulic fracturing (U.S. EPA, 2015j). In other examples, inadequately cemented casing has contributed to impacts to drinking water resources. In Bainbridge, Ohio, inadequately cemented casing in a hydraulically fractured well contributed to the buildup of natural gas and high pressures along the outside of a production well. This ultimately resulted in movement of natural gas into local drinking water aquifers (Bair et al., 2010; ODNR, 2008). In the Mamm Creek gas field

in Colorado, inadequate cement placement in a production well allowed methane and benzene to migrate along the production well and through natural faults and fractures to drinking water resources (Science Based Solutions LLC, 2014; Crescent, 2011; COGCC, 2004). These cases illustrate how construction issues, sustained casing pressure, and the presence of natural faults and fractures can work together to create pathways for fluids to migrate toward drinking water resources.

Fracturing older wells may also increase the potential for impacts to drinking water resources via movement of gases and liquids from the inside of the production well or along the outside of the production well to ground water resources. The EPA estimated that 6% of 23,000 oil and gas production wells were drilled more than 10 years before being hydraulically fractured in 2009 or 2010. Although new wells can be designed to withstand the stresses associated with hydraulic fracturing operations, older wells may not have been built or tested to the same specifications and their reuse for this purpose could be of concern. Moreover, aging and use of the well can contribute to casing degradation, which can be accelerated by exposure to corrosive chemicals, such as hydrogen sulfide, carbonic acid, and brines.

- ***Can subsurface migration of fluids—both liquids and gases—to drinking water resources occur, and what local geologic or artificial features might allow this?***

Physical separation between the production zone and drinking water resources can help protect drinking water. Many hydraulic fracturing operations target deep formations such as the Marcellus Shale or the Haynesville Shale (Louisiana/Texas), where the vertical distance between the base of drinking water resources and the top of the shale formation may be a mile or greater. Numerical modeling and microseismic studies based on a Marcellus Shale-like environment suggest that fractures created during hydraulic fracturing are unlikely to extend upward from these deep formations into shallow drinking water aquifers.

Not all hydraulic fracturing is performed in zones that are deep below drinking water resources. For example, operations in the Antrim Shale (Michigan) and the New Albany Shale (Illinois/Indiana/Kentucky) take place at shallower depths (100 to 1,900 ft or 30 to 579 m), with less vertical separation between the formation and drinking water resources. The EPA's survey of oil and gas production wells hydraulically fractured by nine service companies in 2009 and 2010 estimated that 20% of 23,000 wells had less than 2,000 ft (610 m) of measured distance between the point of shallowest hydraulic fracturing and the base of the protected ground water resources reported by well operators.

There are also places in the subsurface where oil and gas resources and drinking water resources co-exist in the same formation. Evidence indicates that hydraulic fracturing occurs within these formations. This results in the introduction of fracturing fluids into formations that may currently serve, or in the future could serve, as a source of drinking water for public or private use. According to the data examined, the overall frequency of occurrence of this practice appears to be low, with the activity generally concentrated in some areas in the western United States. The practice of injecting fracturing fluids into a formation that also contains a drinking water resource directly affects the quality of that water, since some of the fluid likely remains in the formation following hydraulic fracturing. Hydraulic fracturing in a drinking water resource is a concern in the short-

term (should there be people currently using these zones as a drinking water supply) and the long-term (if drought or other conditions necessitate the future use of these zones for drinking water).

Liquid and gas movement from the production zone to underground drinking water resources may also occur via other production wells or injection wells near hydraulic fracturing operations. Fractures created during hydraulic fracturing can intersect nearby wells or their fracture networks, resulting in the flow of fluids into those wells. These well communications, or "frac hits," are more likely to occur if wells are close to each other or on the same well pad. In the Woodford Shale in Oklahoma, the likelihood of well communication was less than 10% between wells more than 4,000 ft (1,219 m) apart, but rose to nearly 50% between wells less than 1,000 ft (305 m) apart (Ajani and Kelkar, 2012). If an offset well is not able to withstand the stresses applied during the hydraulic fracturing of a neighboring well, well components may fail, which could result in a release of fluids at the surface from the offset well. The EPA identified incidents in which surface spills of hydraulic fracturing-related fluids were attributed to well communication events.

Older or inactive wells—including oil and gas wells, injection wells, or drinking water wells—near a hydraulic fracturing operation may pose an even greater potential for impacts. A study in Oklahoma found that older wells were more likely to be negatively affected by the stresses applied by hydraulic fracturing in neighboring wells (Ajani and Kelkar, 2012). In some cases, inactive wells in the vicinity of hydraulic fracturing activities may not have been plugged properly—many wells plugged before the 1950s were done so with little or no cement. The Interstate Oil and Gas Compact Commission estimates that over one million wells may have been drilled in the United States prior to a formal regulatory system being in place, and the status and location of many of these wells are unknown (IOGCC, 2008). State programs exist to plug identified inactive wells, and work is on-going to identify and address such wells.

Flowback and Produced Water

Water, of variable quality, is a byproduct of oil and gas production. After hydraulic fracturing, the injection pressure is released and water flows back from the well. Initially this water is similar to the hydraulic fracturing fluid, but as time goes on the composition is affected by the characteristics of the formation and possible reactions between the formation and the fracturing fluid. Water initially produced from the well after hydraulic fracturing is sometimes called flowback in the literature, and the term appears in this assessment. However, hydraulic fracturing fluids and any formation water returning to the surface are often referred to collectively as produced water. This definition of produced water is used in this assessment.

The amount of produced water varies, but typically averages 10% to 25% of injected volumes, depending upon the amount of time since fracturing and the particular well (see Figure ES-3a). However, there are exceptions to this, such as in the Barnett Shale in Texas where the total volume of produced water can equal or exceed the injected volume of hydraulic fracturing fluid (see Figure ES-3b). Flow rates are generally high initially, and then decrease over time throughout oil or gas production.

Impacts on drinking water resources have the potential to occur if produced water is spilled and enters surface water or ground water. Environmental transport of chemical constituents in produced water depends on the characteristics of the spill (e.g., volume and duration), the composition of spilled fluids, and the characteristics of the surrounding environment.

Research Questions: Flowback and Produced Water

- ***What is currently known about the frequency, severity, and causes of spills of flowback and produced water?***

Surface spills of produced water from hydraulically fractured wells have occurred. As noted in the Chemical Mixing section above, the frequency of on-site spills from hydraulic fracturing activities could be estimated for two states, but not nationally. Estimates of spill frequencies at hydraulic fracturing sites in Colorado and Pennsylvania, including spills of produced water, ranged from approximately 0.4 to 12.2 spills per 100 wells. Available data generally precluded estimates of produced water spill rates separately from estimates of overall spill frequency. Away from the well, produced water spills from pipelines and truck transport also have the potential to impact drinking water resources.

The EPA characterized spill volumes and causes for 225 cases in which produced water spilled on or near a well pad. These spills occurred between January 2006 and April 2012 in 11 states. The median reported volume per produced water spill was 990 gallons (3,750 L), more than double that for spills of hydraulic fracturing fluids and chemicals. The causes of produced water spills were reported as human error, equipment failure, container integrity failure, miscellaneous causes (e.g., well communication), and unknown causes. Most of the total volume spilled (74%) for all 225 cases combined was caused by a failure of container integrity.

- ***What is the composition of hydraulic fracturing flowback and produced water, and what factors might influence this composition?***

A combination of factors influence the composition of produced water, including: the composition of injected hydraulic fracturing fluids, the type of formation fractured, subsurface processes, and residence time. The initial chemical composition of produced water primarily reflects the chemistry of the injected fluids. At later times, the chemical composition of produced water reflects the geochemistry of the fractured formation.

Produced water varies in quality from fresh to highly saline, and can contain high levels of major anions and cations, metals, organics, and naturally occurring radionuclides. Produced water from shale and tight gas formations typically contains high levels of total dissolved solids (TDS) and ionic constituents (e.g., bromide, calcium, chloride, iron, potassium, manganese, magnesium, and sodium). Produced water also may contain metals (e.g., barium, cadmium, chromium, lead, and mercury), and organic compounds such as benzene. Produced water from coalbed methane typically has much lower TDS levels compared to other produced water types, particularly if the coalbed was deposited under fresh water conditions..

We identified 134 chemicals that have been detected in hydraulic fracturing produced water. These include chemicals added during the chemical mixing stage, as well as naturally occurring organic chemicals and radionuclides, metals, and other constituents of subsurface rock formations mobilized by the hydraulic fracturing process. Data on measured chemical concentrations in produced water were available for 75 of these 134 chemicals.

Most of the available data on produced water content are for shale and coalbed methane formations, while less data are available for tight formations, such as sandstones. The composition of produced water must be determined through sampling and analysis, both of which have limitations—the former due to challenges in accessing production equipment, and the latter due to difficulties identifying target analytes before analysis and the lack of appropriate analytical methods. Most current data are for inorganic chemicals, while less data exist for organic chemicals. Many more organic chemicals were reported as used in hydraulic fracturing fluid than have been identified in produced water. The difference may be due to analytical limitations, limited study scopes, and undocumented subsurface reactions.

- ***What are the chemical, physical, and toxicological properties of hydraulic fracturing flowback and produced water constituents?***

The identified constituents of produced water include inorganic chemicals (cations and anions, i.e., metals, metalloids, non-metals, and radioactive materials), organic chemicals and compounds, and unidentified materials measured as total organic carbon and dissolved organic carbon. Some constituents are readily transported with water (i.e., chloride and bromide), while others depend strongly on the geochemical conditions in the receiving water body (i.e., radium and barium), and assessment of their transport is based on site-specific factors. We were able to obtain actual or estimated physicochemical properties for 86 (64%) of the 134 chemicals identified in produced water.

As in the case of chemicals in hydraulic fracturing fluid, chemical properties that affect the likelihood of an organic chemical in produced water reaching and impacting drinking water resources include: mobility, solubility, and volatility. In general, physicochemical properties suggest that organic chemicals in produced water tend to be less mobile in the environment. Consequently, if spilled, these chemicals may remain in soils or sediments near spill sites. Low mobility may result in smaller dissolved contaminant plumes in ground water, although these chemicals can be transported with sediments in surface water or small particles in ground water. Organic chemical properties vary with salinity, and effects depend on the nature of the chemical.

Oral reference values and/or oral slope factors from selected federal, state, and international sources were available for 83 (62%) of the 134 chemicals detected in produced water. From U.S. federal sources alone, chronic oral reference values were available for 70 (52%) of the 134 chemicals, and oral slope factors were available for 20 chemicals (15%). Of the chemicals that had values available, noted health effects include the potential for carcinogenesis, immune system effects, changes in body weight, changes in blood chemistry, pulmonary toxicity, neurotoxicity, liver and kidney toxicity, and reproductive and developmental toxicity. As noted above, evaluating any potential risk to human populations would require knowledge of the specific chemicals that are

present at a particular site, whether or not humans are exposed to those chemicals and, if so, at what levels and for what duration, and the toxicity of the chemicals. The chemicals present in produced water can vary based on the formation and specific well, due to differences in fracturing fluid formulation and formation geology. Accordingly, consideration of hazards and risks associated with these chemicals would be most useful on a site-specific basis and is beyond the scope of this assessment.

- ***If spills occur, how might hydraulic fracturing flowback and produced water contaminate drinking water resources?***

Impacts to drinking water resources from spills or releases of produced water depend on the volume, timing, and composition of the produced water. Impacts are more likely the greater the volume of the spill, the longer the duration of the release, and the higher the concentration of produced water constituents (i.e., salts, naturally occurring radioactive material, and metals).

The EPA characterization of hydraulic fracturing-related spills found that 8% of the 225 produced water spills included in the study reached surface water or ground water. These spills tended to be of greater volume than spills that did not reach a water body. A well blowout in Bradford County, Pennsylvania spilled an estimated 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 and ground water.

Chronic releases can and do occur from produced water disposed in unlined pits or impoundments, and can have long-term impacts. Ground water impacts may persist longer than surface water impacts because of lower flow rates and decreased mixing. Plumes from unlined pits used for produced water have been shown to persist for long periods and extend to nearby surface water bodies.

Wastewater Management and Waste Disposal

Hydraulic fracturing generates large volumes of produced water that require management. In this section we refer to produced water and any other waters generated onsite by the single term "wastewater." Clark and Veil (2009) estimated that, in 2007, approximately one million active oil and gas wells in the United States generated 2.4 billion gal per day (9.1 billion L per day) of wastewater. There is currently no reliable way to estimate what fraction of this total volume can be attributed to hydraulically fractured wells. Wastewater volumes in a region can increase sharply as hydraulic fracturing activity increases.

Wastewater management and disposal could affect drinking water resources through multiple mechanisms, including: inadequate treatment of wastewater prior to discharge to a receiving water, accidental releases during transport or leakage from wastewater storage pits, unpermitted discharges, migration of constituents in wastewaters following land application, inappropriate management of residual materials from treatment, or accumulation of wastewater constituents in sediments near outfalls of centralized waste treatment facilities (CWTs) or publicly owned treatment works (POTWs) that have treated hydraulic fracturing wastewater. The scope of this

assessment excludes potential impacts to drinking water from the disposal of hydraulic fracturing wastewater in underground injection control (UIC) wells.

Research Questions: Wastewater Management and Waste Disposal

- ***What are the common treatment and disposal methods for hydraulic fracturing wastewater, and where are these methods practiced?***

Hydraulic fracturing wastewater is managed using several options, including: disposal in UIC wells (also called disposal wells); through evaporation ponds; treatment at CWTs, followed by reuse or by discharge to either surface waters or POTWs; reuse with minimal or no treatment; and land application or road spreading. Treatment of hydraulic fracturing wastewater by POTWs was used in the past in Pennsylvania. This decreased sharply following new state-level requirements and a request by the Pennsylvania Department of Environmental Protection (PA DEP) for well operators to stop sending Marcellus Shale wastewater to POTWs (and 15 CWTs) discharging to surface waters.

Wastewater management decisions are generally based on the availability and associated costs (including transportation) of disposal or treatment facilities. A survey of state agencies found that, in 2007, more than 98% of produced water from the oil and gas industry was managed via underground injection (Clark and Veil, 2009). Available information suggests that disposal wells are also the primary management practice for hydraulic fracturing wastewater in most regions in the United States (e.g., the Barnett Shale; see Figure ES-3b). The Marcellus Shale region is a notable exception, where most wastewater is reused because of the small number of disposal wells in Pennsylvania (see Figure ES-3a). Although this assessment does not address potential effects on drinking water resources from the use of disposal wells, any changes in cost of disposal or availability of disposal wells would likely influence wastewater management decisions.

Wastewater from some hydraulic fracturing operations is sent to CWTs, which may discharge treated wastewater to surface waters, POTWs, or back to well operators for reuse in other hydraulic fracturing operations. Available data indicate that the use of CWTs for treating hydraulic fracturing wastewater is greater in the Marcellus Shale region than other parts of the country. Most of the CWTs accepting hydraulic fracturing wastewater in Pennsylvania cannot significantly reduce TDS, and many of these facilities provide treated wastewater to well operators for reuse and do not currently discharge treated wastewater to surface water.

Reuse of wastewater for subsequent hydraulic fracturing operations may require no treatment, minimal treatment, or more extensive treatment. Operators reuse a substantial amount (ca. 70-90%) of Marcellus Shale wastewater in Pennsylvania (see Figure ES-3a). Lesser amounts of reuse occur in other areas (e.g., the Barnett Shale; see Figure ES-3b). In certain formations, such as the Bakken Shale in North Dakota, there is currently no indication of appreciable reuse.

In some cases, wastewater is used for land applications such as irrigation or road spreading for deicing or dust suppression. Land application has the potential to introduce wastewater constituents into surface water and ground water due to runoff and migration of brines. Studies of

road spreading of conventional oil and gas brines have found elevated levels of metals in soils and chloride in ground water.

- ***How effective are conventional POTWs and commercial treatment systems in removing organic and inorganic contaminants of concern in hydraulic fracturing wastewater?***

Publicly owned treatment works using basic treatment processes are not designed to effectively reduce TDS concentrations in highly saline hydraulic fracturing wastewater—although specific constituents or constituents groups can be removed (e.g., metals, oil, and grease by chemical precipitation or other processes). In some cases, wastewater treated at CWTs may be sent to a POTW for additional treatment and discharge. It is blended with POTW influent to prevent detrimental effects on biological processes in the POTW that aid in the treatment of wastewater.

Centralized waste treatment facilities with advanced wastewater treatment options such as reverse osmosis, thermal distillation, or mechanical vapor recompression, reduce TDS concentrations and can treat contaminants currently known to be in hydraulic fracturing wastewater. However, there are limited data on the composition of hydraulic fracturing wastewater, particularly for organic constituents. It is unknown whether advanced treatment systems are effective at removing constituents that are generally not tested for.

- ***What are the potential impacts from surface water disposal of treated hydraulic fracturing wastewater on drinking water treatment facilities?***

Potential impacts to drinking water resources may occur if hydraulic fracturing wastewater is inadequately treated and discharged to surface water. Inadequately treated hydraulic fracturing wastewater may increase concentrations of TDS, bromide, chloride, and iodide in receiving waters. In particular, bromide and iodide are precursors of disinfection byproducts (DBPs) that can form in the presence of organic carbon in drinking water treatment plants or wastewater treatment plants. Drinking water treatment plants are required to monitor for certain types of DBPs, because some are toxic and can cause cancer.

Radionuclides can also be found in inadequately treated hydraulic fracturing wastewater from certain shales, such as the Marcellus. A recent study by the PA DEP (2015b) found elevated radium concentrations in the tens to thousands of picocuries per liter and gross alpha and gross beta in the hundreds to thousands of picocuries per liter in effluent samples from some CWTs receiving oil and gas wastewater. Radium, gross alpha, and gross beta were also detected in effluents from POTWs receiving oil and gas wastewater (mainly as effluent from CWTs), though at lower concentrations than from the CWTs. Research in Pennsylvania also indicates the accumulation of radium in sediments and soils affected by the outfalls of some treatment plants that have handled oil and gas wastewater, including Marcellus Shale wastewater, and other wastewaters (PA DEP, 2015b; Warner et al., 2013a). Mobilization of radium from sediments and potential impacts on downstream water quality depend upon how strongly the radium has sorbed to sediments. Impacts may also occur if sediment is resuspended (e.g., following storm events). There is no evidence of radionuclide contamination in drinking water intakes due to inadequately treated hydraulic fracturing wastewater.

Hydraulic fracturing wastewaters contain other constituents such as barium, boron, and heavy metals. Barium in particular has been documented in some shale gas produced waters. Little data exist on metal and organic compound concentrations in untreated and treated wastewaters in order to evaluate whether treatment is effective, and whether there are potential downstream effects on drinking water resources when wastewater is treated and discharged.

Key Data Limitations and Uncertainties

This assessment used available data and literature to examine the potential impacts of hydraulic fracturing from oil and gas on drinking water resources nationally. As part of this effort, we identified data limitations and uncertainties associated with current information on hydraulic fracturing and its potential to affect drinking water resources. In particular, data limitations preclude a determination of the frequency of impacts with any certainty. These limitations and uncertainties are discussed in brief below.

Limitations in Monitoring Data and Chemical Information

While many activities conducted as part of the hydraulic fracturing water cycle take place above ground, hydraulic fracturing itself occurs below ground and is not directly observable. Additionally, potential mechanisms identified in this assessment may result in impacts to drinking water resources that are below ground (e.g., spilled fluids leaching into ground water). Data that could be used to characterize the presence, migration, or transformation of chemicals in the subsurface before, during, and after hydraulic fracturing were found to be scarce relative to the number of hydraulically fractured oil and gas production wells. Specifically, local water quality data needed to compare pre- and post-hydraulic fracturing conditions are not consistently collected or readily available. The limited amount of data collected before and during hydraulic fracturing activities reduces the ability to determine whether hydraulic fracturing affected drinking water resources in cases of alleged contamination.

Information (identity, frequency of use, physicochemical and toxicological properties, etc.) on the chemicals associated with the hydraulic fracturing water cycle is not complete and limits understanding of potential impacts on drinking water resources. Well operators claimed at least one chemical as confidential at more than 70% of wells reported to FracFocus and analyzed by the EPA. The identity of these chemicals, and other chemicals in produced water, are needed to understand their properties and would also help inform what chemicals to test for to establish baseline conditions and to test for in the event of a suspected drinking water impact. Of the 1,173 total chemicals identified by the EPA in hydraulic fracturing fluid and flowback and produced water, 147 have chronic oral reference values and/or oral slope factors from the sources that met the selection criteria for inclusion in this assessment. Because the majority of chemicals identified in this report do not have chronic oral reference values and/or oral slope factors, risk assessors at the local and regional level may need to use alternative sources of toxicity information that could introduce greater uncertainties.

Other Contributing Limitations

We found other limitations that hamper the ability to fully assess the potential impacts of hydraulic fracturing on drinking water resources nationally. These include the number and location of hydraulically fractured wells, the location of drinking water resources, and information on changes in industry practices. The lack of a definitive well count particularly contributes to uncertainties regarding total water use or total wastewater volume estimates, and would limit any kind of cumulative impact assessment. Lack of specific information about private drinking water well locations and the depths of drinking water resources in relation to hydraulically fractured rock formations and well construction features (e.g., casing and cement) limits the ability to assess whether subsurface drinking water resources are isolated from hydraulically fractured oil and gas production wells. Finally, this assessment is a snapshot in time, and the industry is rapidly changing (e.g., the number of wells fractured, the location of activities, and the chemicals used). It is unclear how changes in industry practices could affect potential drinking water impacts in the future. Consideration of future development scenarios was not a part of this assessment, but such an evaluation could help establish potential short- and long-term impacts to drinking water resources and how to assess them.

Conclusions

Through this national-level assessment, we have identified potential mechanisms by which hydraulic fracturing could affect drinking water resources. Above ground mechanisms can affect surface and ground water resources and include water withdrawals at times or in locations of low water availability, spills of hydraulic fracturing fluid and chemicals or produced water, and inadequate treatment and discharge of hydraulic fracturing wastewater. Below ground mechanisms include movement of liquids and gases via the production well into underground drinking water resources and movement of liquids and gases from the fracture zone to these resources via pathways in subsurface rock formations.

We did not find evidence that these mechanisms have led to widespread, systemic impacts on drinking water resources in the United States. Of the potential mechanisms identified in this report, we found specific instances where one or more of these mechanisms led to impacts on drinking water resources, including contamination of drinking water wells. The cases occurred during both routine activities and accidents and have resulted in impacts to surface or ground water. Spills of hydraulic fracturing fluid and produced water in certain cases have reached drinking water resources, both surface and ground water. Discharge of treated hydraulic fracturing wastewater has increased contaminant concentrations in receiving surface waters. Below ground movement of fluids, including gas, most likely via the production well, have contaminated drinking water resources. In some cases, hydraulic fracturing fluids have also been directly injected into drinking water resources, as defined in this assessment, to produce oil or gas that co-exists in those formations.

The number of identified cases where drinking water resources were impacted are small relative to the number of hydraulically fractured wells. This could reflect a rarity of effects on drinking water

resources, or may be an underestimate as a result of several factors. There is insufficient pre- and post-hydraulic fracturing data on the quality of drinking water resources. This inhibits a determination of the frequency of impacts. Other limiting factors include the presence of other causes of contamination, the short duration of existing studies, and inaccessible information related to hydraulic fracturing activities.

This state-of-the-science assessment contributes to the understanding of the potential impacts of hydraulic fracturing on drinking water resources and the factors that may influence those impacts. The findings in this assessment can be used by federal, state, tribal, and local officials; industry; and the public to better understand and address any vulnerabilities of drinking water resources to hydraulic fracturing activities. This assessment can also be used to help facilitate and inform dialogue among interested stakeholders, and support future efforts, including: providing context to site-specific exposure or risk assessments, local and regional public health assessments, and 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 advances the scientific basis for 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 1

Introduction

1. Introduction

1.1. Background

Since the early 2000s, oil and natural gas production in the United States has been transformed through the technological innovations of hydraulic fracturing and directional drilling. Hydraulic fracturing is a stimulation technique used to increase production of oil and gas. It involves the injection of fluids under pressures great enough to fracture the oil- and gas-production formations. Hydraulic fracturing in combination with advanced directional drilling techniques has made it possible to economically extract hydrocarbons from unconventional resources, such as shale, tight formations, and coalbeds.[1] It can also enhance production from conventional resources. The surge in use of hydraulic fracturing and associated technologies has significantly increased domestic energy supplies (see Chapter 2) and brought economic benefits to many areas of the United States.

The growth in domestic oil and gas exploration and production– the direct result of the expanded use of hydraulic fracturing– has also raised concerns about its potential for impacts to human health and the environment. Specific concerns have been raised by the public about the effects of hydraulic fracturing on the quality and quantity of drinking water resources. Some residents living close to oil and gas production well sites report changes in the quality of ground water resources used for drinking water and assert that hydraulic fracturing is responsible for these changes. Other concerns include competition for water between hydraulic fracturing operations and other water users, especially in areas of the country experiencing drought, and the disposal of wastewater generated from 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, 2011c; hereafter Study Plan). The research described in the Study Plan began the same year. In 2012, the EPA issued *Potential Impacts of Hydraulic Fracturing on Drinking Water Resources: Progress Report* (U.S. EPA, 2012f; hereafter Progress Report) in order to update the public on the status of the research being conducted under the Study Plan. In this report, we review and synthesize scientific literature, including the publications resulting from the EPA's research and information provided by stakeholders, to assess the potential for hydraulic fracturing for oil and gas to change the quality or quantity of drinking water resources. This report also identifies factors affecting the frequency or severity of any potential impacts.

1.2. Scope

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

[1] Unconventional resources is an umbrella term for oil and natural gas that is produced by means that do not meet the criteria for conventional production. What has qualified as unconventional at any particular time is a complex function of resource characteristics, the available exploration and production technologies, the economic environment, and the scale, frequency, and duration of production from the resource (see Text Box 2-2).

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 reservoirs. It tends to focus on hydraulic fracturing in shale, which reflects the relatively large amount of literature and available data on hydraulic fracturing in this type of geologic formation.

The scope of activities examined in this assessment is defined by the hydraulic fracturing water cycle. This cycle encompasses activities involving water that support hydraulic fracturing and consists of five stages: (1) acquisition of water needed to create hydraulic fracturing fluids; (2) mixing of water and chemicals on the well pad to create hydraulic fracturing fluids; (3) injection of hydraulic fracturing fluids into the well to fracture the geologic formation; (4) management of flowback and produced water on the well pad and in transit for reuse, treatment, or disposal; and (5) reuse, treatment and discharge, or disposal of hydraulic fracturing wastewater (see Figure 1-1).[1,2,3,4]

Activities within the hydraulic fracturing water cycle can take place on or near the well pad or some distance away. On-site activities include mixing and injecting hydraulic fracturing fluids and capturing flowback and produced water. Water withdrawals and wastewater treatment and disposal may occur in the same watershed, adjacent watersheds, or watersheds many miles away from the production site.

This assessment focuses on impacts on drinking water resource quantity and quality. Consistent with the Study Plan (U.S. EPA, 2011c), drinking water resources are defined broadly within this report as any body of ground water or surface water that now serves, or in the future could serve, as a source of drinking water for public or private use. This is broader than most regulatory definitions of "drinking water" and encompasses both fresh and non-fresh bodies of water, since trends indicate both types of water bodies are now and in the future will be used as sources of drinking water (see Chapter 3). 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.

We assess potential effects on drinking water resources from business-as-usual operations as well as from accidents and unintended releases that may occur during the hydraulic fracturing water cycle (see Table 1-1).

[1] Hydraulic fracturing fluids are engineered fluids, typically consisting of a base fluid, additives, and proppants, that are pumped under high pressure into the well to create and hold open fractures in the formation.
[2] Flowback is defined multiple ways in the literature. In general, it is either fluids predominantly containing hydraulic fracturing fluid that return from a well to the surface or a process used to prepare the well for production (see Chapter 7).
[3] Produced water is water that flows from oil and gas wells.
[4] Hydraulic fracturing wastewater is flowback and 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 (see Chapter 8).

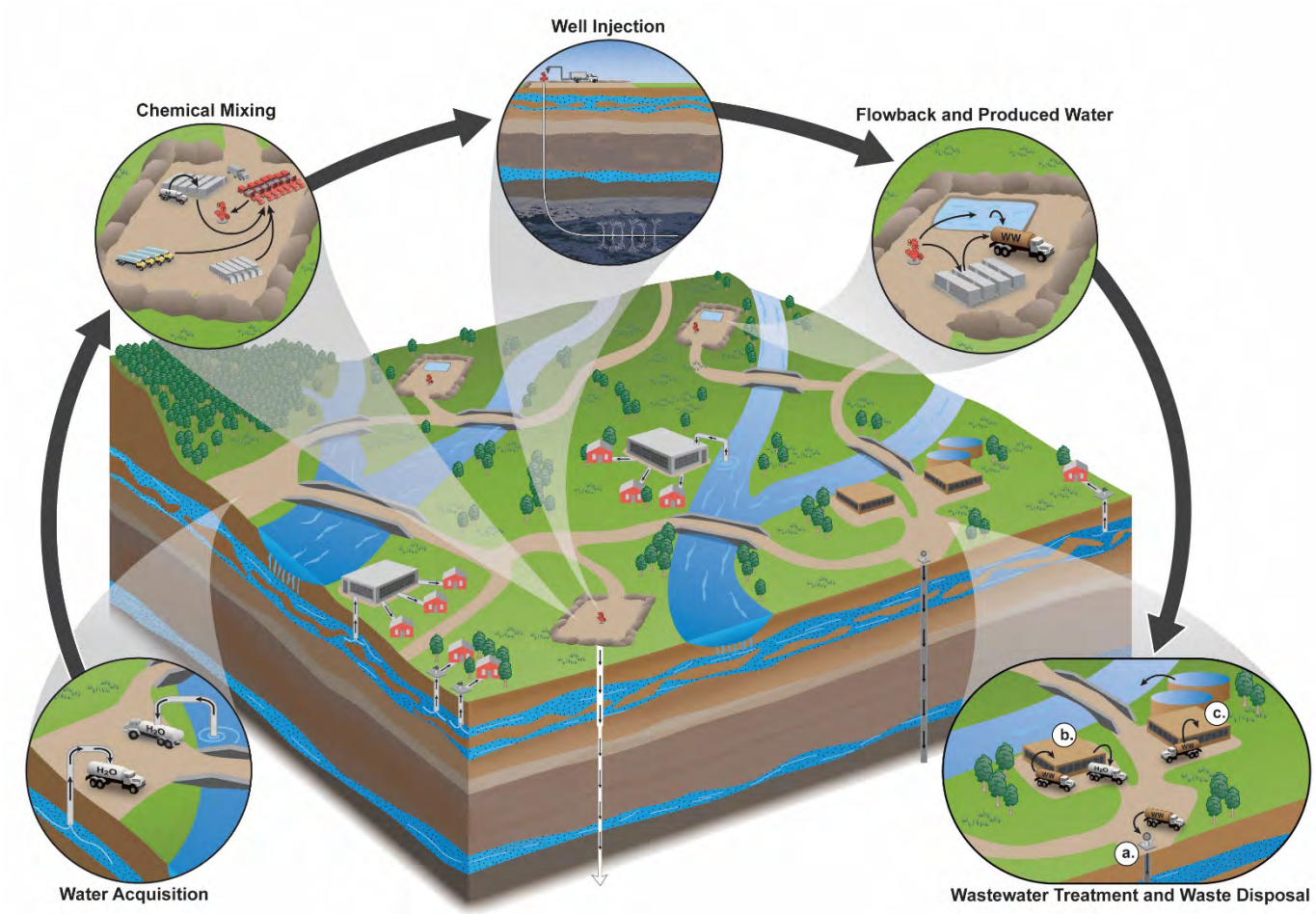

Figure 1-1. Conceptualized view of the stages of the hydraulic fracturing water cycle.

Shown here is a generalized landscape depicting the activities of the hydraulic fracturing water cycle and their relationship to each other, as well as 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 body of ground water 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 Treatment and Waste Disposal" inset are (a) underground injection control (UIC) well disposal, (b) wastewater treatment and reuse, and (c) wastewater treatment and discharge at a centralized waste treatment (CWT) facility. Note: Figure not to scale.

Table 1-1. Stages of the hydraulic fracturing water cycle have various potential effects on drinking water resources.

The potential effects addressed in this assessment, and how they are related to the activities within each stage, are summarized here.

Water cycle stage	Activities or processes potentially affecting drinking water resources	Potential drinking water effects addressed in this assessment			
		Quality		Quantity	
		Ground water	Surface water	Ground water	Surface water
Water acquisition	Water withdrawals	X	X	X	X
Chemical mixing	Spills of hydraulic fracturing fluids	X	X		
Well injection	Subsurface migration of hydraulic fracturing fluids or formation fluids	X	X		
Flowback and produced water	Spills of flowback or produced water	X	X		
Wastewater treatment and waste disposal	Discharge of untreated or inadequately treated wastewater and inappropriate disposal of waste solids	X	X		

As part of the assessment, we evaluated immediate, near-term, and long-term effects on drinking water resources. For example, we considered how surface spills of hydraulic fracturing fluids may potentially have immediate or near-term impacts on neighboring surface water and shallow ground water quality (see Chapters 5 and 7). We also considered how the potential release of hydraulic fracturing fluids in the subsurface may take years to impact ground water resources, because liquids and gas often move slowly in the subsurface (see Chapter 6). Additionally, effects may be detected near the activity or at 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 (see Chapter 8).

This assessment focuses predominantly on activities supporting a single well or multiple wells on a single well pad, accompanied by a more limited discussion of cumulative activities and the effects 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 address *mechanisms* for impacts as well as *impacts* of hydraulic fracturing for oil and gas on drinking water resources. In general, a mechanism is the means or series of events that links an activity to an impact, while an impact is the end result of a mechanism and represents a change in the entity of interest. Specific definitions used in this assessment are provided below.

[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 **mechanism** is a means or series of events by which an activity within the hydraulic fracturing water cycle has been observed to change the quality or quantity of drinking water resources.
- A **suspected mechanism** is a means or series of events by which hydraulic fracturing activities could logically have resulted in an observed change in the quality or quantity of drinking water resources. Available evidence may or may not be sufficient to determine if it is the *only* mechanism that caused the observed change.
- A **potential mechanism** is a means or series of events by which hydraulic fracturing activities could logically or theoretically (for instance, based on modeling) change the quality or quantity of drinking water resources but one that has not yet been observed.
- An **impact** is any observed change in the quality or quantity of drinking water resources, regardless of severity, that results from a mechanism.
- A **potential impact** is any change in the quality or quantity of drinking water resources that could logically occur as the result of a mechanism or potential mechanism but has not yet been observed.

Potential mechanisms and impacts, as well as suspected mechanisms, are addressed because data required to document mechanisms and impacts may be inaccessible, incomplete, or nonexistent. In addition, evidence may be insufficient to isolate the contribution of hydraulic fracturing to changes in the quality or quantity of drinking water resources from other human activities occurring nearby. We anticipate that our understanding of mechanisms and impacts will be advanced as the scientific community continues to evaluate potential health and environmental effects of hydraulic fracturing.

In this assessment, we also identify and discuss factors affecting the frequency or severity of changes 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 effects 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 impacts of hydraulic fracturing activities as they have been reported in the scientific literature. A summary and evaluation of current or proposed regulations and policies is beyond the scope of this report.

For this assessment, we did not conduct site-specific predictive modeling to quantitatively estimate environmental concentrations of contaminants in drinking water resources, although modeling studies conducted by others are described. Further, this report 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 (see Chapter 9).

This assessment focuses on the potential 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 include acquisition and transport of constituents of hydraulic fracturing fluids besides water (e.g., sand mining and chemical production); site selection and well pad 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. 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 or ecosystems), worker health or safety, or communities.

1.3. 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 that have been published 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 including confidential and non-confidential business information submitted by industry to the EPA.[1]

1.3.1. 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 they were designed to meet the data and information needs of this assessment. As such, published, peer-reviewed results of the research conducted under the Study Plan are incorporated and cited 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 1.3.2. The articles and EPA reports themselves that give complete and detailed project results can be found on the EPA's hydraulic fracturing 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 articles and EPA reports that are referenced in this assessment can be found in Appendix H.

1.3.2. Literature and Data Search Strategy

The EPA used a broad search strategy to identify approximately 3,700 sources of scientific information that could be applicable to this assessment. This search strategy included both

[1] 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.

requesting input from scientists, stakeholders, and the public about relevant data and information, and thorough searching of published information and applicable data.[1]

Over 1,400 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 Science Advisory Board (SAB), the EPA's independent federal scientific advisory committee, from its review of the EPA's draft Study Plan; its consultation on the EPA's Progress Report (U.S. EPA, 2012f); and during an SAB briefing on new and emerging information related to hydraulic fracturing in fall 2013. 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 material to the SAB during the SAB review of the draft Study Plan, Progress Report, and briefing on emerging information, 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 input to the EPA.

Approximately 2,300 additional sources were identified by conducting searches for material that could be applicable to the assessment 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 fall 2014. After that time, we largely 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. In many cases, our searches uncovered the same material submitted by the public, but approximately 2,300 new sources were also identified.

1.3.3. Literature and Data Evaluation Strategy

We evaluated the literature and data identified in the search strategy above 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, 2003). The factors are (1) applicability and utility, (2) evaluation and review, (3) soundness, (4) clarity and completeness, and (5) uncertainty and variability. Table 1-2 lists these factors along with the specific criteria for each that were developed for this assessment. We first evaluated all materials for applicability. If "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, the preponderance of literature on some topics did not fully conform to some aspects of the outlined criteria. For instance, there were many white

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

papers and reports in technical areas in which independent peer review is not standard practice or is not well documented. Therefore, we included references in the assessment that were not peer-reviewed but that addressed topics not found in the peer-reviewed literature, that provided useful background information, or that corroborated conclusions in the peer-reviewed literature.

Table 1-2. Criteria developed for the five factors 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, 2003). Criteria are incorporated into the Quality Assurance Project Plans for this assessment (U.S. EPA, 2014g, 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.

1.3.4. 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. QA 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, 2014h) 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). For instance, 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 1.3.2 and 1.3.3 (U.S. EPA, 2014g, 2013d). A QA audit was conducted by the QA Manager during the preparation of this assessment in order 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), 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. The EPA often engages the SAB as an external 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, will also provide comment on 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.

1.4. Organization

This assessment begins with a general description of hydraulic fracturing activities and the role of hydraulic fracturing in the oil and gas industry in the United States (see Chapter 2). It follows with a characterization of drinking water resources in the continental United States, with a focus on areas in which we estimate hydraulic fracturing has taken place over the time period of 2000–2013 (see Chapter 3).

Chapters 4 through 8 are organized around the stages of the hydraulic fracturing water cycle (see Figure 1-1) and address the potential for activities conducted during those stages to change the quality or quantity of drinking water resources. Each of the stages is covered by a separate chapter. There is also a chapter devoted to an examination of the properties of chemicals and constituents that have been or may be used in hydraulic fracturing fluids or present in flowback and produced water (see Chapter 9).

Each chapter addresses research questions developed under the Study Plan, as data and information allow (see Table 1-3). Concise answers appear in text boxes at the end of each chapter. The final chapter provides major conclusions and a synthesis of information presented across the assessment. It also highlights significant gaps in information that contribute to uncertainties about those conclusions (see Chapter 10).

Table 1-3. Research questions addressed by this assessment.

Each chapter addresses research questions developed under the Study Plan. Chapters 2 and 3 develop background on hydraulic fracturing and drinking water resources, respectively.

Chapter and water cycle stage	Research questions

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

Chapter and water cycle stage	Research questions
Chapter 4 - Water Acquisition	• What are the types of water used for hydraulic fracturing? • How much water is used per well? • How might cumulative water withdrawals for hydraulic fracturing affect drinking water quantity? • What are the possible impacts of water withdrawals for hydraulic fracturing on water quality?
Chapter 5 - Chemical Mixing	• What is currently known about the frequency, severity, and causes of spills of hydraulic fracturing fluids and chemical additives? • What are the identities and volumes of chemicals used in hydraulic fracturing fluids, and how might this composition vary at a given site and across the country? • What are the chemical and physical properties of hydraulic fracturing chemical additives? • If spills occur, how might hydraulic fracturing chemical additives contaminate drinking water resources?
Chapter 6 - Well Injection	• How effective are current well construction practices at containing fluids- both liquids and gases- before, during, and after fracturing? • Can subsurface migration of fluids- both liquids and gases- to drinking water resources occur, and what local geologic or artificial features might allow this?
Chapter 7 - Flowback and Produced Water	• What is currently known about the frequency, severity, and causes of spills of flowback and produced water? • What is the composition of hydraulic fracturing flowback and produced water, and what factors might influence this composition? • What are the chemical and physical properties of hydraulic fracturing flowback and produced water constituents? • If spills occur, how might hydraulic fracturing flowback and produced water contaminate drinking water resources?

Chapter and water cycle stage	Research questions
Chapter 8 - Wastewater Treatment and Waste Disposal	• What are the common treatment and disposal methods for hydraulic fracturing wastewater, and where are these methods practiced? • How effective are conventional publicly owned treatment works and commercial treatment systems in removing organic and inorganic contaminants of concern in hydraulic fracturing wastewater? • What are the potential impacts from surface water disposal of treated hydraulic fracturing wastewater on drinking water treatment facilities?
Chapter 9 - Hazard Evaluation of Chemicals Across the Water Cycle Stages	• What are the toxicological properties of hydraulic fracturing chemical additives? • What are the toxicological properties of hydraulic fracturing flowback and produced water constituents?

1.5. Intended Use

We expect that this report, as a synthesis of the science, will contribute to the understanding of the potential impacts of hydraulic fracturing on drinking water resources and the factors that may influence those impacts. The data and findings in this report can be used by federal, tribal, state, and local officials; industry; and the public to better understand and address any 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.

We also expect this report may support future assessment efforts. For instance, 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 advances the scientific basis for 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.

1.6. References for Chapter 1

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Chapter 2

Hydraulic Fracturing, Oil and Gas Production, and the U.S. Energy Sector

2. Hydraulic Fracturing, Oil and Gas Production, and the U.S. Energy Sector

This chapter provides general background information useful for understanding the in-depth technical chapters that follow. We describe the process and purpose of hydraulic fracturing and the situations and settings in which it is used (Section 2.1). Then, to place hydraulic fracturing in the context of well site operations, we describe activities from site assessment and selection through production to site closure. This helps illustrate the intensive nature of activities during the relatively short hydraulic fracturing phase during the life of a production well (Section 2.2). Finally, we characterize the prevalence of hydraulic fracturing in the United States, its importance in the oil and gas industry today and into the future, and its role in the U.S. energy sector (Sections 2.3 and 2.4).

2.1. What is Hydraulic Fracturing?

Hydraulic fracturing is a stimulation technique used to increase production of oil and gas. Hydraulic fracturing involves the injection of fluids under pressures great enough to fracture the oil- and gas-production formations. Hydraulic fracturing fluid transfers the pressure generated by equipment at the surface into the subsurface to create fractures, and it carries and places the proppant into the fractures so that they remain "propped" open after the injection pumping pressure is terminated (Gupta and Valkó, 2007). Oil and gas can then flow through the fractures into the well and through the well to the surface. Hydraulic fracturing has been used since the late 1940s and for the first almost 50 years was used in vertical wells in conventional hydrocarbon reservoirs.[1] Hydraulic fracturing is still used in these settings, but the process has evolved; technological developments have led to the use of hydraulic fracturing in low-permeability (unconventional) hydrocarbon reservoirs that could not otherwise be profitably produced (see Text Box 2-1). Wells stimulated by hydraulic fracturing may be vertical, deviated, or horizontal in orientation (see Figure 2-1), and they may be newly drilled or older at the time the fracturing is done.

[1] A conventional reservoir is a reservoir in which buoyant forces keep hydrocarbons in place below a sealing caprock. Reservoir and fluid characteristics of conventional reservoirs typically permit oil or natural gas to flow readily into wellbores. The term is used to make a distinction from shale and other unconventional reservoirs, in which gas might be distributed throughout the reservoir at the basin scale, and in which buoyant forces or the influence of a water column on the location of hydrocarbons within the reservoir are not significant.

Text Box 2-1. Is Hydraulic Fracturing "New"?

Hydraulic fracturing in one form or another has been in use since the late 1940s, when a fracturing technique was patented by the Stanolind Oil and Gas Company and licensed to the Halliburton Oil Well Cementing Company. There are precedents that go back even further: reports from the early days of the oil and gas industry in the mid-19th century show producers trying to increase production by pumping fluids or dropping explosives into wells (Montgomery and Smith, 2010). Throughout its history, hydraulic fracturing has been used as a production technique to increase, or "stimulate," production from a well (some hydraulic fracturing methods are used to stimulate production in water wells, which is outside the scope of this report).

The groundwork for the transformation to modern hydraulic fracturing was laid in the 1970s and early 1980s, when a coalition of private companies, government agencies, and industry groups began sponsoring research into shale gas development technologies. During that period, Congress began to offer tax incentives to induce producers to apply the developing technologies in the field (Wang and Krupnick, 2013; EIA, 2011a; Yergin, 2011). The first horizontal wells were drilled in the mid-1980s in the Austin Chalk oil-bearing formation in Texas (Pearson, 2011; Haymond, 1991). Directional drilling and other emerging technologies matured in the late 1990s. In 2001, the Mitchell Energy company found a way to economically fracture the Barnett Shale in Texas. The company was bought by Devon Energy, a company with advanced experience in horizontal drilling. In 2002, seven wells were drilled and developed in the Barnett Shale using both 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. By 2003/2004, modern hydraulic fracturing in the Barnett Shale was producing more gas than all other shale gas wells in the rest of the country (mostly shallow shale gas production in the Appalachian and Michigan Basins, see Section 2.4.1) (DOE, 2011b; Montgomery and Smith, 2010). By 2005, the new techniques were being used in low-permeability hydrocarbon plays outside of Texas, and modern hydraulic fracturing soon became the industry standard, driving the surge in U.S. production of natural gas.

Despite the long history of hydraulic fracturing, the culmination of technical innovations in the early 2000s represent an appreciable change. These innovations have made hydraulic fracturing economical enough to become standard practice in the oil and gas industry. Modern hydraulic fracturing (sometimes referred to as high-volume hydraulic fracturing) is characterized by the use of long horizontal wells and higher volumes of more complex mixtures of water, proppants, and chemical additives for injection as compared to earlier fracturing practices. Wells are often deep and long: shale gas production wells are commonly 5,000 to 13,500 ft (1,524 to 4,115 m) deep with long horizontal sections of 2,000 to 5,000 ft (610 to 1,524 m) or more in length. Other important advances occurred in oil and gas geophysical survey techniques (such as downhole telemetry and 3D seismic imaging) (Wang and Krupnick, 2013; EIA, 2011a). Hydraulic fracturing continues to be conducted in vertical production wells as well as conventional reservoirs using some of these newer techniques. Modern hydraulic fracturing has made it possible to extract resources in previously untapped hydrocarbon-bearing geologic settings, altering and expanding the geographic range of oil and gas production activities.

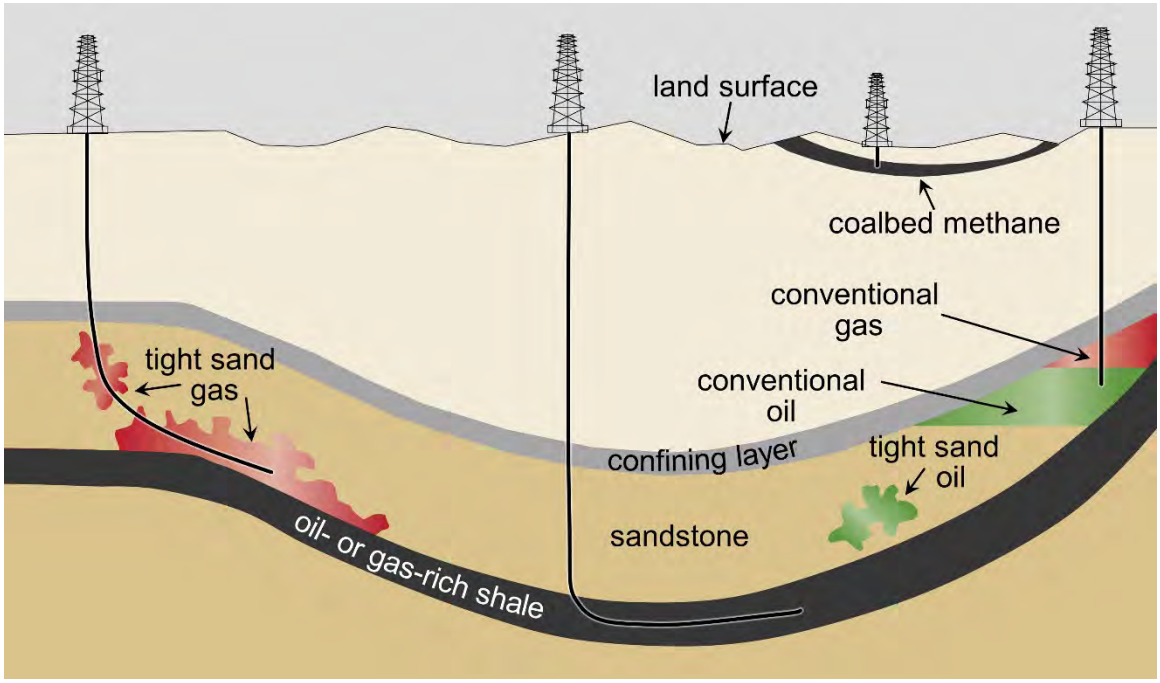


Figure 2-1. Schematic cross-section of general types of oil and gas resources and the orientations of production wells used in hydraulic fracturing.

Shown are conceptual illustrations of types of oil and gas wells. A vertical well is producing from a conventional oil and gas deposit (right). In this case, a thin, gray confining layer serves to "trap" oil (green) or gas (red). Also shown are wells producing from unconventional formations: a vertical coalbed methane well (second from right); a horizontal well producing from a shale formation (center); and a deviated well producing from a tight sand formation (left). Note: Figure not to scale. Modified from USGS (2002) and Newell (2011).

Historically, oil and gas have been extracted from conventional reservoirs that develop when hydrocarbons formed in deeper geologic source formations migrate until they accumulate underneath an impermeable layer (see Figure 2-1). Extraction practices vary. In settings where a reservoir is permeable enough and under enough pressure to yield a relatively high rate of hydrocarbon flow into a well, the economic extraction of oil and/or gas may be as simple as using a drilled well to enable hydrocarbons to flow to the surface under the natural pressure of the reservoir. In other cases, producers may inject water and/or carbon dioxide under pressure into the reservoir via one or more nearby wells to help move and enhance production of the oil and gas. But essentially, producers are drawing on hydrocarbons that have already accumulated in a relatively accessible form.

Hydraulic fracturing is one of several methods used to enhance production from oil and gas reservoirs. It is distinct from other methods of hydrocarbon extraction (known generally as enhanced recovery techniques) that involve injecting fluids to influence either reservoir pressure, fluid viscosity, or both. The primary purpose of hydraulic fracturing is to increase the surface area of the reservoir rock by creating fractures that are propped open, allowing the hydrocarbon to flow from the rock through the fractures to the well and through the well up to the surface.

Hydraulic fracturing, in conjunction with horizontal and directional drilling, has made it possible to economically extract oil and gas from "unconventional" geologic formations (see Text Box 2-2), such as the relatively low permeability shales in which oil and gas form (see Figure 2-1). With modern horizontal drilling techniques, producers can, for example, drill a single well that follows the contours of a relatively thin, horizontal shale formation. Such drilling allows fracturing to be conducted in a long horizontal section of the well that accesses an extensive portion of the oil- or gas-bearing formation. Unconventional formations include:

- ***Shales.*** Organic-rich black shales are the source rocks in which oil and gas form on geologic timescales. Shales have very low permeability, and the hydrocarbons are contained in the pore space in the shales. Some shales produce predominantly gas and others predominantly oil; often there will be some coproduction of gas from oil wells and coproduction of liquid hydrocarbons from gas wells (USGS, 2013a; EIA, 2011a).
- ***Tight formations.*** "Tight" sands (sandstones), siltstone, carbonates, etc., are relatively low permeability, non-shale, sedimentary formations that can contain hydrocarbons. The hydrocarbons are contained in the pore space of the formations. There is a continuum in permeability between "tight" formations which require hydraulic fracturing to be produced economically and sandstone (and other) formations that do not. In the literature, "tight gas" is generally distinguished from "shale gas," while oil resources from shale and tight formations are frequently lumped together under the label "shale oil" or "tight oil" (Schlumberger, 2014; USGS, 2014a).
- ***Coalbeds.*** Hydraulic fracturing can be used to extract methane (the primary component of natural gas) from coal seams. In coalbeds, the methane is adsorbed to the coal surface rather than contained in pore space or structurally trapped in the formation. Pumping the injected and formation water out of the coalbeds after fracturing serves to depressurize the coal, thereby allowing the methane to desorb and flow into the well and to the surface (USGS, 2000).

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

The terms "conventional" and "unconventional" are widely used in the literature to distinguish types of oil and gas reservoirs, plays, wells, production techniques, and more. In this report, the terms are used to distinguish different types of hydrocarbon resources: "conventional" resources are those that can economically be extracted using long-established technologies, and "unconventional" resources are those whose extraction has become economical only with the advances that have occurred in modern hydraulic fracturing (often coupled with directional drilling) in recent years.

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

Although the goal of stimulation by hydraulic fracturing is the same wherever it is employed, the way it is accomplished varies due to a number of factors. General location and geologic conditions,

whether the well is existing or newly drilled, the proximity of the well to infrastructure and raw materials, operator preferences, and other factors can affect how a hydraulic fracturing operation is designed and carried out. Technological advances have made it possible to drill deeper and longer horizontal wells, to conduct fracturing through longer portions of the well, and to place multiple wells on a single well pad (NETL, 2013; Montgomery and Smith, 2010). Many facets of hydraulic fracturing-related technology have changed since they were first pioneered (see Text Box 2-1). How hydraulic fracturing is practiced now (especially in the long horizontal wells) is different from how it was conducted during the first decades of its use. As operators gain experience with both evolving and new technologies, practices will continue to change.

The following three maps show the locations of major shale oil and gas resources, tight gas resources, and coalbed methane resources, respectively, in the continental United States (see Figure 2-2, Figure 2-3, and Figure 2-4). These maps represent resources that are being exploited now or could be exploited in the future. Hydraulic fracturing continues to be used to enhance production in conventional reservoirs (not shown), although it is uncertain how often this occurs.

The formations hydraulically fractured for gas or oil vary in their depth below the surface. For example, the Marcellus Shale (found primarily in Pennsylvania, New York, and West Virginia) is found at depths of 4,000 to 8,500 ft (1,200 to 2,600 m), the Barnett Shale (Texas) is found at depths of 6,500 to 8,500 ft (2,000 to 2,600 m), and the Haynesville-Bossier Shale (Louisiana and Texas) is found at depths of 10,500 to 13,500 ft (3,200 to 4,100 m) (NETL, 2013). These represent some of the largest gas-producing shale formations or shale plays. However, some other plays are shallower. Parts of the Antrim (Michigan), Fayetteville (Arkansas), and New Albany (Indiana and Kentucky) shale plays, for example, are less than 2,000 ft (600 m) deep (NETL, 2013; GWPC and ALL Consulting, 2009). Exploitation of thin coal seams often takes place close to the surface as well. In the San Juan Basin (New Mexico), coal seams are 550 to 4,000 ft (170 to 1,200 m) deep; in the Powder River Basin (Wyoming and Montana) they are 450 to greater than 6,500 ft (140 to 2,000 m) deep, and in the Black Warrior Basin (Alabama and Mississippi) depths can range from the ground surface to 3,500 ft (1,100 m) (ALL Consulting, 2004). See Chapter 6 for more information on the depths of these formations and plays.

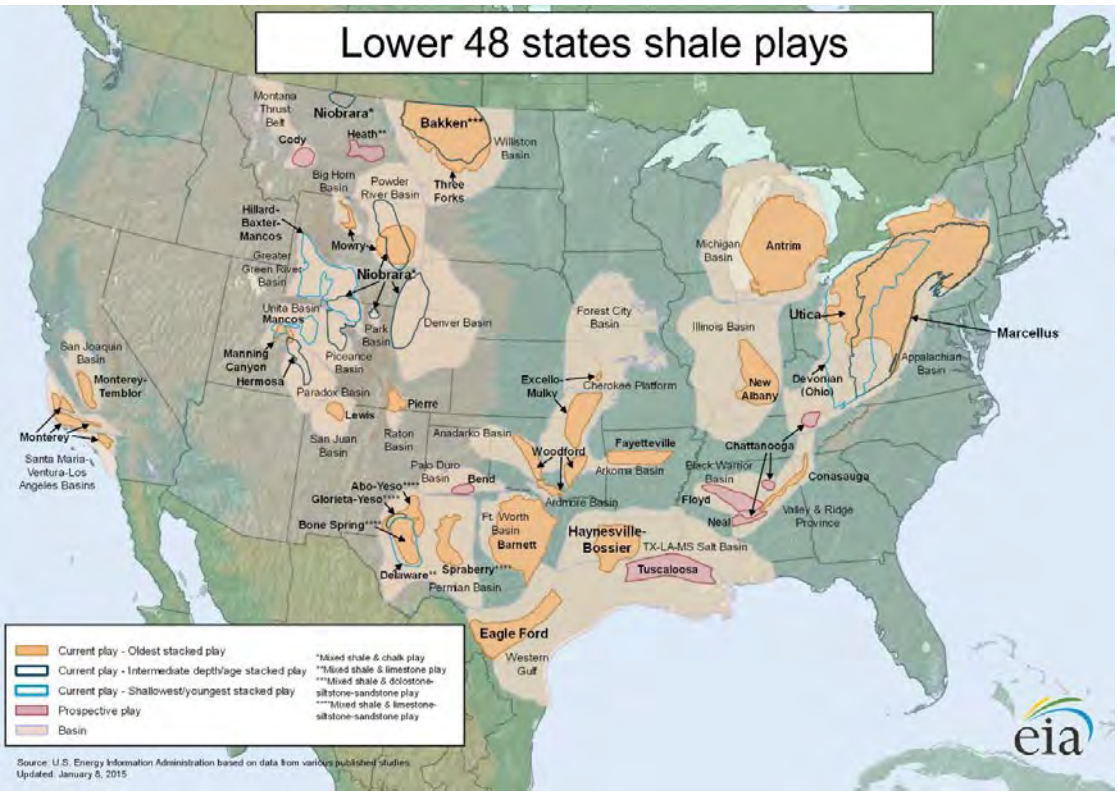
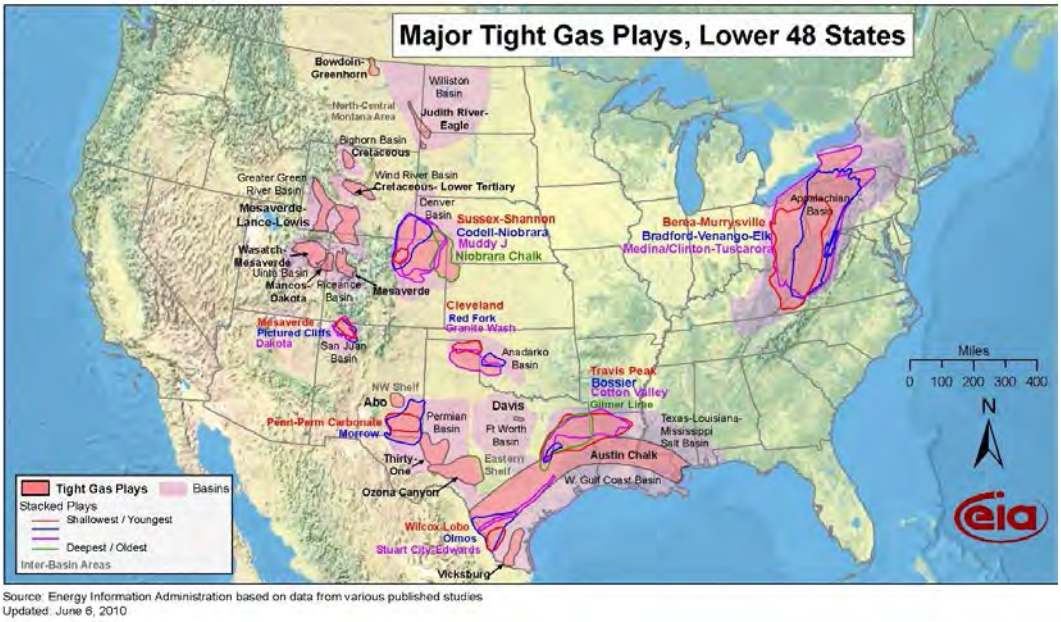


Figure 2-2. Shale gas and oil plays in the lower 48 United States.

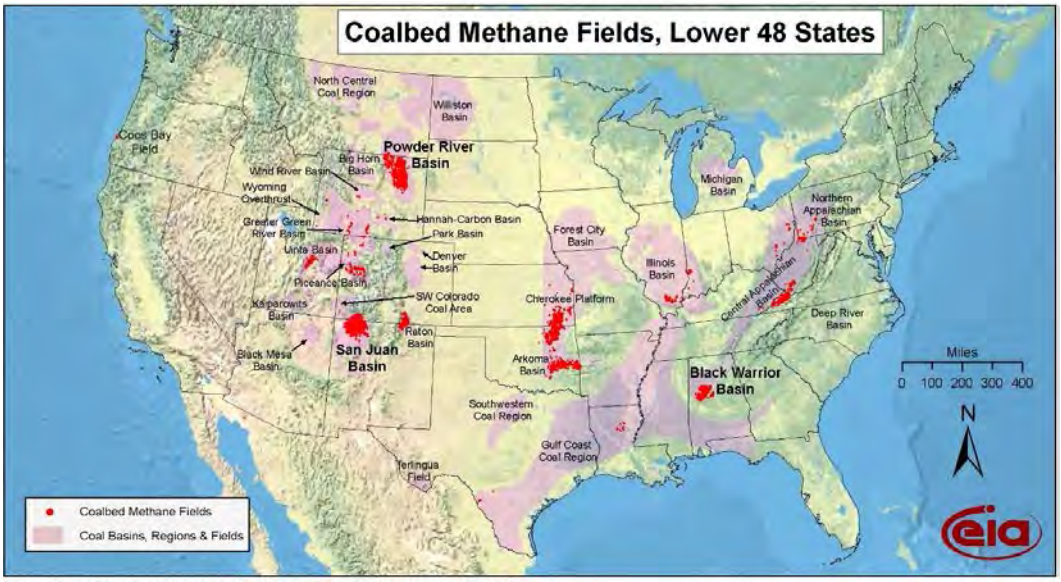
Source: EIA (2015b).



Source: Energy Information Administration based on data from various published studies
Updated: June 6, 2010

Figure 2-3. Tight gas plays in the lower 48 United States.

Source: EIA (2011b).



Source: Energy Information Administration based on data from USGS and various published studies
Updated: April 8, 2009

Figure 2-4. Coalbed methane fields in the lower 48 United States.

Source: EIA (2011b).

2.1. Hydraulic Fracturing and the Life of a Well

Hydraulic fracturing itself is a relatively short-term process, with the timeframe for a typical fracturing treatment being two to 10 days during which fluids are injected into the well to fracture the oil- and gas-bearing geologic formations (Halliburton, 2013; NYSDEC, 2011). However, it is a period of intense activity— the most activity that takes place at a well site during its existence.

In this section, we briefly describe some of the supporting and ancillary activities that take place at the well site, from initial site development through production and ultimately to closure (see Figure 2-5). This time period likely ranges from years to decades, depending on factors such as rate of depletion of the oil or gas, cost of production, and the price of oil and gas. The rate of oil and gas depletion in the reservoir is somewhat uncertain in unconventional formations because there is relatively little history on which to base predictions.

The overview of well operations presented in this section is broad and is provided to illustrate common activities and describe some specific operational details. The details of well preparation, operations, and closure vary from company to company, from play to play, from jurisdiction to jurisdiction, and from well to well. The various activities involved in well development and operations can be conducted by the well owner and/or operator, owner/operator representatives, service companies, or other third parties contractors working for the well owner.

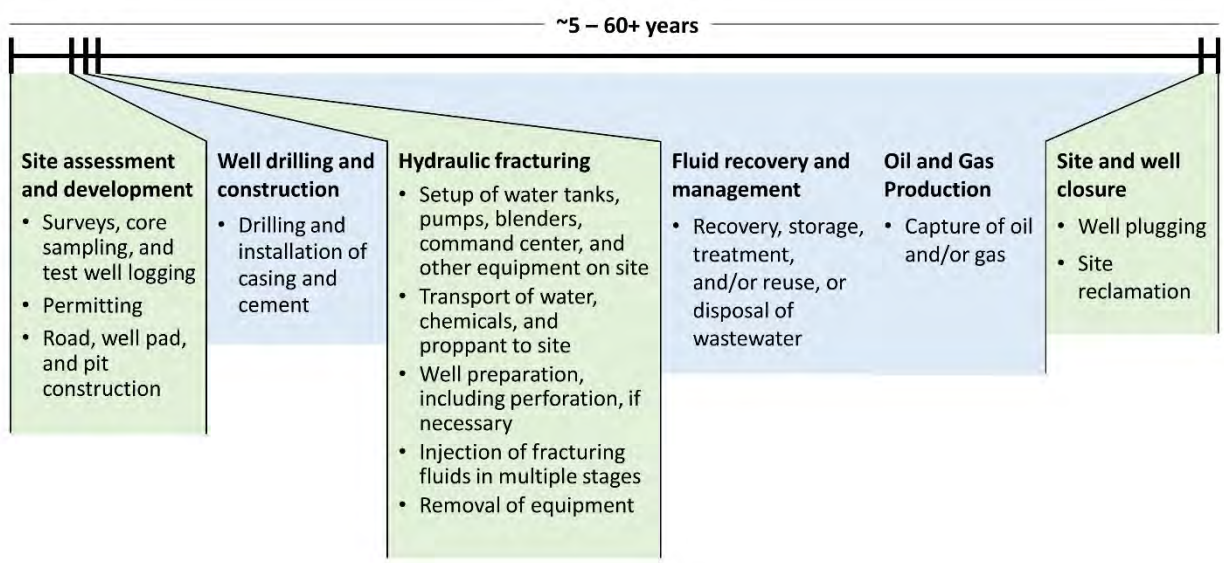


Figure 2-5. Generalized timeline and summary of activities that take place during the operational phases of an oil or gas well site operation in which hydraulic fracturing is used.

Relative duration of phases is approximate.

2.1.1. Site and Well Development

Numerous activities occur to assess and develop the site and to drill and construct the production well before hydraulic fracturing and production can occur.

2.1.1.1. Site Assessment and Development

Identifying a geologically suitable well site requires integrating data from geophysical surveys (including seismic surveys) that help to delineate subsurface features with other geologic information from rock core samples. Cores may be obtained while drilling exploratory wells or test holes. Core samples provide firsthand information on the characteristics of the oil- or gas-bearing formation, such as porosity, permeability, and details about the quantities and qualities of the hydrocarbon resource. Drilling rates and drill cuttings help identify the strata being drilled through and can help confirm and correlate stratigraphy and formation depths, including the depths of water-bearing formations.[1] Well logging (also known as wireline logging) is especially useful combined with core analysis for understanding the properties of formations (Kundert and Mullen, 2009).[2]

Logistical factors involved in the selection of the well drilling site include topography; proximity to facilities such as roads, pipelines, and water sources; well spacing considerations; well setback requirements; potential for site erosion; location relative to environmentally sensitive areas; and proximity to populated areas (Drohan and Brittingham, 2012; Arthur et al., 2009a). Before developing the site and initiating well drilling, the oil and gas company (or their representative) obtains a mineral rights lease, negotiates with landowners, and applies for a drilling permit from the appropriate state and local authorities. During the project, leases and permissions are also needed for other activities including performing seismic surveys and drilling exploratory holes (Hyne, 2012). This initial site assessment phase of the process may take several months (King, 2012).

Site preparation is necessary to enable equipment and supplies to reach the well area. Typically, the site is surveyed first, and then an access road may need to be built to accommodate truck traffic (Hyne, 2012). The operator then levels and grades the site to manage drainage and to allow equipment to be hauled to and placed on site. Next, the operator may excavate and grade several impoundments or storage pits near the well pad. In some cases, steel tanks may be used to hold fluids instead of, or in addition to, pits. The pits may hold water intended for drilling fluids, materials generated during drilling such as used drilling mud and drill cuttings, or the flowback and produced waters after fracturing (Hyne, 2012). Pit construction is generally governed by local regulations; federal regulations may also apply on federal and Indian Country. In some areas, regulations may require pits to be lined to prevent fluid seepage into the shallow subsurface or may

[1] Drill cuttings are ground rock produced by the drilling process.

[2] Well logging consists of a continuous measurement of physical properties in or around the well with electrically powered instruments to infer formation properties. Measurements may include electrical properties (resistivity and conductivity), sonic properties, active and passive nuclear measurements, measurements of the wellbore, pressure measurement, formation fluid sampling, sidewall coring tools and others. Measurements may be taken via a wireline, which is a wire or cable that is used to deploy tools and instruments downhole and that transmits data to the surface.

prohibit pits altogether. Some sites have piping along the surface of the well pad or in the shallow subsurface that delivers water used for hydraulic fracturing, removes flowback and produced water, or transports the oil and gas once production begins (Arthur et al., 2009a).

After site and well pad preparation, drill rigs and associated equipment (e.g., the drill rig platform, drilling mud system components, generators, chemical storage tanks, blowout preventer, fuel storage tanks, cement pumps, drill pipe, and casing) are moved on and off the pad at the different stages of well drilling and completion. During drilling and completion, 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).

Well Drilling and Construction

Construction of the production well involves the drilling of the hole (or wellbore), along with the installation and cementing of a series of casing strings to support the wellbore and isolate and protect both the hydrocarbons being produced and any water-bearing zones through which the well passes.[1] In certain settings, some portions of the well can be completed as open holes.[2] Details on these and other well construction activities are presented in Chapter 6 and Appendix D.

The operator begins drilling by lowering and rotating the drill string, which consists of the drill bit, drill pipe (see Figure 2-6), and drill collars (heavy pieces of pipe that add weight to the bit). The drill pipe attaches to the drill bit, rotating and advancing the bit; as drilling advances, new sections of pipe are added at the surface, enabling the drilling to proceed deeper (Hyne, 2012). A drilling fluid is circulated during drilling.[3] The drilling fluid, which may be water-based or oil-based, is pumped down to the drill bit, where it cools and lubricates the drill bit, counterbalances downhole pressures, and lifts the drill cuttings to the surface (King, 2012).

Although all wells are initially drilled vertically, finished well orientations include vertical, deviated, and horizontal. The operator selects the well orientation that will provide access to the targeted zone(s) within a formation and that will align the well with existing fractures and other geologic structures to optimize production. Deviated wells may be "S" shaped or continuously slanted. Horizontal wells have lateral sections oriented approximately 90 degrees from the vertical portion of the well. In wells completed horizontally, the lengths of these laterals can range from 2,000 to 5,000 ft (610 to 1,524 m) or more (Hyne, 2012; Miskimins, 2008; Bosworth et al., 1998).[4] Horizontal wells are instrumental in accessing productive areas of thin and laterally extensive oil- and gas-bearing shales. Although the portion of hydraulically fractured wells that are horizontal is growing, in some areas, such as California, hydraulic fracturing is still primarily conducted in vertical wells (CCST, 2015).

[1] Casing is steel pipe that is lowered into a wellbore. Casing extends from the bottom of the hole to the surface.
[2] An open hole completion is a well completion that has no casing or liner set across the reservoir formation, allowing the produced fluids to flow directly into the wellbore.
[3] Drilling fluid is any of a number of liquid and gaseous fluids and mixtures of fluids and solids (as solid suspensions, mixtures, and emulsions of liquids, gases, and solids) used when drilling boreholes (Schlumberger, 2014).
[4] A lateral is a horizontal section of a well.

Figure 2-6. Pulling drill pipe onto the drilling platform.

Source: Joshua Doubek, Wikicommons, CC-BY-SA-3.0.

The drilling and well construction proceeds with repeated steps (the drill string is lowered, rotated, drilled to a certain depth, pulled out, and then the casing is lowered into the hole, set, and cemented). Successively smaller diameters of casing are used as the hole is drilled deeper (see Figure 2-7). Selection and installation of the casing strings is important for several purposes, including isolating hydrocarbon reservoirs from nearby aquifers, isolating over-pressured zones, and transporting hydrocarbons to the surface (Hyne, 2012). Newly installed casing strings are cemented in place before drilling continues (or before the well is completed in the instance of the production casing). The cement protects the casing from corrosion by formation fluids, stabilizes the casing and the wellbore, and prevents fluid movement along the well between the outside of the casing and wellbore (Renpu, 2011). The well can be cemented continuously from the surface down to the production zone of the well. Partially cemented wells are also possible with, for example, cement from the surface to some distance below the deepest fresh water-bearing formation and perhaps cement across other deeper formations. Chapter 6 and Appendix D contain more details on casing and cement.

Figure 2-7. Sections of surface casing lined up and being prepared for installation at a well site in Colorado.

Photo credit: Gregory Oberley (U.S. EPA).

When drilling, casing, and cementing are finished, the well can be completed in the production zone in several ways. The production casing may be cemented all the way through the production zone and perforated prior to hydraulic fracturing in the desired locations. Alternatively, operators may use an open hole completion, in which the casing is set just into the production zone and cemented. The remainder of the wellbore within the production zone is left open with no cement (Hyne, 2012). Once all aspects of well construction are completed, the operator can remove the drilling rig, install the wellhead, and prepare the well for stimulation by hydraulic fracturing and subsequent production.

2.1.1. Hydraulic Fracturing

Hydraulic fracturing is typically a short, intense, repetitive process requiring specialized equipment and (for high volume horizontal wells) large amounts of water, chemicals, and proppant. Machinery and equipment are often brought to the site mounted on trucks and remain that way during use. Tanks, totes, and other storage containers of various sizes holding water and chemicals are also transported and installed on site. Figure 2-8 shows a well pad prepared for hydraulic fracturing with the necessary equipment and structures.

Figure 2-8. Hydraulic fracturing operation in Troy, PA.

Site with all equipment on site in preparation for injection. Source: NYSDEC (2011).

2.1.1.2. Injection Process

Prior to injection, hydraulic fracturing fluids are mixed using specialized feeding and mixing equipment. The mixing is generally performed mechanically on a truck-mounted blender and is electronically monitored and controlled by the operator in a separate van (see Chapter 5). Numerous hoses and pipes are used to transfer hydraulic fracturing fluid components from storage units to the mixing equipment and ultimately to the wellhead.

A wellhead assembly is temporarily installed on the wellhead during the fracture treatment to allow high pressures and volumes of proppant-laden fluid to be injected into the well. Pressures required for fracturing can vary widely depending on depth, formation pressure, and rock type. Fracturing pressures have been reported ranging from 4,000 psi to 12,000 psi (Ciezobka and Salehi, 2013; Abou-Sayed et al., 2011; Thompson, 2010). The pressure during fracturing is measured using pressure gauges, which can be installed at the surface and/or downhole (Ross and King, 2007). Figure 2-9 shows two wellheads side-by-side being prepared for fracturing.

Figure 2-9. Two wellheads side-by-side being prepared for hydraulic fracturing at a well site in Pennsylvania.

Photo credit: Mark Seltzer (U.S. EPA).

The entire length of the well in the production zone is not fractured all at once; instead, shorter lengths or segments of the well in the production zone are isolated and fractured in "stages" (Lee et al., 2011). Each stage of a fracturing job can consist of phased injection of different fluids consisting of varying components (i.e., chemicals and additives). These different fluids (1) remove excess drilling fluid or cement from the formation (often using acid) (GWPC and ALL Consulting, 2009), (2) initiate fractures ("pad fluid" without proppant), (3) carry the proppant (Hyne, 2012), and (4) flush the wellbore to ensure that all proppant-laden fluids reach the fractures. Each phase

requires moving up to millions of gallons of fluids around the site through various hoses and lines, blending the fluids, and injecting them at high pressures down the well.

The total number of stages depends on the formation properties and the orientation and length of the well. As technology has improved, the lengths of laterals in horizontal wells and the numbers of stages per well have tended to increase (NETL, 2013; Pearson et al., 2013). The number of stages per well can vary, with several sources suggesting that between 10 and 20 is typical (GNB, 2015; Lowe et al., 2013). 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). For more details on hydraulic fracturing stages, see Chapter 5, Section 5.2.

The induced fractures are designed to achieve the optimum drainage of hydrocarbons from the reservoir formations. Engineers can design fracture systems using modeling software that requires a significant amount of data on formation permeability, porosity, in situ stress, mineralogy, and geologic barrier locations, among other factors (Holditch, 2007). Microseismic monitoring during fracturing can be used to characterize the horizontal and vertical extent of the fractures created and assist with the design of future fracturing jobs (Cipolla et al., 2011). Post-fracture monitoring of pressure or tracers can also help characterize the results of a fracturing job. More details of injection, fracturing, and related monitoring are provided in Chapter 6 and Appendix D.

2.1.1.3. Fracturing Fluids

The fracturing fluids injected into the well serve a variety of purposes and require chemical additives to perform properly (see Chapter 5, Section 5.3). Depending on the geologic setting, reservoir geochemistry, production type, proppant size, and other factors, operators typically choose to use one of several common types of fracturing fluid systems (Arthur et al., 2014; Spellman, 2012; Gupta and Valkó, 2007). Water-based fracturing fluids are the most common, but other fluid types can be used such as: 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). The most common water-based fluid systems are slickwater formulations, which are typically used in very low permeability reservoirs, and gelled fracturing fluids, which can be used in reservoirs with higher permeability (Barati and Liang, 2014).[1,2] More details of hydraulic fracturing fluid systems are discussed in Section 5.3. Importantly, chemical usage in the industry is continually changing as processes are tested and refined by companies. Shifts in fluid formulations are driven by economics, technological developments, and concerns about environmental and health impacts.

[1] Slickwater is a type of fracturing fluid that consists mainly of water with a very low portion of additives like polymers that serve as friction reducers to reduce friction loss when pumping the fracturing fluid downhole (Barati and Liang, 2014).

[2] Gelled fluids are fracturing fluids that are usually water-based with added gels to increase the fluid viscosity to aid in the transport of proppants (Spellman, 2012; Gupta and Valkó, 2007).

The largest constituent of a typical hydraulic fracturing fluid is water (see Figure 2-10). The water sources used for hydraulic fracturing base fluid include ground water, surface water, treated wastewater, and reused flowback or produced water from other wells (URS Corporation, 2011; Blauch, 2010; Kargbo et al., 2010).[1] The water may be brought to the production well site via trucks or piping, or it may be locally sourced (for example, pumped from a local river or obtained from a water well tapping local ground water). Selection of water sources depends upon availability, cost, quality of the water, and the logistics of delivering it to the site. Chapter 4 provides additional details on water acquisition and the amount of water used for hydraulic fracturing.

Figure 2-10. 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, by volume, second to the base fluid in the hydraulic fracturing fluid system. Silicate minerals, most notably quartz sand, are the most commonly used proppants. Increasingly, silicate proppants are being coated with resins that help prevent development and flowback of particles or fragments of particles. Ceramic materials, such as those based on calcined (heated) bauxite or calcined kaolin (mullite) are also used as proppants due to their high strength and resistance to crushing and deformation (Beckwith, 2011).

[1] Base fluid is the fluid into which additives and proppants are mixed to formulate a hydraulic fracturing fluid.

Additives comprise relatively small percentages of hydraulic fracturing fluid systems, generally constituting ≤2.0% of the fluid (GWPC and ALL Consulting, 2009). The EPA analyzed additive data in the EPA FracFocus project database 1.0 and estimated that hydraulic fracturing additives in 2011 and 2012 totaled 0.43% of the total amount of fluid injected for hydraulic fracturing (U.S. EPA, 2015a). Note that this small percentage can total tens of thousands of gallons of chemical additives for a typical high-volume hydraulic fracturing job (see Chapter 5, Section 5.4 for details on additive volumes). A given additive may consist of a single chemical ingredient, or it may have multiple ingredients. The mix of chemicals used in any particular fracturing job is influenced by the properties of the target formation, the amount and type of proppant that needs to be carried, operator preference, and to some degree, by local or regional availability of chemicals and potential interactions between chemicals (King, 2012). Chapter 5 includes details on the number, types, and estimated quantities of chemicals that can be used in hydraulic fracturing.

2.1.2. Fluid Recovery, Management, and Disposal

When the injection pressure is reduced at the end of the fracturing process, the direction of fluid flow reverses, with some of the injected hydraulic fracturing fluid flowing into the well and to the surface along with some naturally-occurring fluids from the production zone (NYSDEC, 2011). The fluid is initially a portion of the injected fluid, which decreases over the first few weeks or months until produced water originating from the fractured oil- or gas-bearing rock formation predominates. This recovery of produced water continues over the life of the well (Barbot et al., 2013). Chapter 7 presents descriptions and discussions of the composition and quantities of fluids recovered at the well, referred to as flowback and produced water.

The hydraulic fracturing flowback and produced water (sometimes referred to as hydraulic fracturing wastewater), as well as any other liquid waste from the well pad itself (e.g., rainwater runoff), is typically stored on-site in impoundments (see Figure 2-11) or tanks. This wastewater can be moved offsite via truck or pipelines. The majority of these hydraulic fracturing wastewaters nationally are managed through disposal into deep Class II injection wells regulated under the Underground Injection Control (UIC) program under the Safe Drinking Water Act (see Chapter 8). Other management strategies include treatment followed by discharge to surface water bodies, or reuse for subsequent fracturing operations either with or without treatment (U.S. EPA, 2012f; U.S. GAO, 2012). Decisions regarding wastewater management are driven by factors such as cost (including costs of storage and transportation), availability of facilities for treatment, reuse, or disposal, and regulations (Rassenfoss, 2011). Wastewater management is yet another aspect of fracturing-related oil and gas production that is changing significantly. Chapter 8 contains details of the treatment, reuse and recycling, and disposal of wastewater.

Figure 2-11. Impoundment on the site of a hydraulic fracturing operation in central Arkansas.

Photo credit: Caroline E. Ridley (U.S. EPA).

2.1.3. Oil and Gas Production

After hydraulic fracturing, equipment is removed and partial site reclamation may take place if drilling of additional wells or laterals is not planned (NYSDEC, 2011). Operators may dewater, fill in, and regrade pits that are no longer needed. Parts of the pad may be reseeded, and the well pad may be reduced in size (e.g., from 3 to 5 acres (1 to 2 hectares) during the drilling and fracturing process to 1 to 3 acres (0.4 to 1 hectares) during production) (NYSDEC, 2011).

Wells may be shut-in immediately after completion if there is no infrastructure to receive the product or if prices are unfavorable. Prior to bringing a well into production, the operator typically runs a production test to determine the maximum flow rate the well can sustain and to optimize equipment settings (Hyne, 2012; Schlumberger, 2006). Such tests may be repeated throughout the life of the well. During production, monitoring (e.g., mechanical integrity testing, corrosion monitoring), including any compliance with state monitoring requirements, may be conducted to enable operators to be sure that the well is operating as intended.

In the case of gas wells, the produced gas typically flows through a flowline to a separator that separates the gas from water or any liquid hydrocarbons (NYSDEC, 2011). The finished gas is sent to a compressor station where it is compressed to pipeline pressure and sent to a pipeline for sale. Production at oil wells proceeds similarly, although oil/water or oil/water/gas separation occurs

most typically on the well pad, no compressor is needed, and the oil can be hauled (by truck or train) or piped from the well pad.

During the life of the well it may be necessary to perform workovers to maintain or repair portions or components of the well and replace old equipment. Such workovers involve ceasing production and removing the wellhead, and may include cleaning out sand or deposits from the well, repairing casing, replacing worn well components such as tubing or packers, or installing or replacing lift equipment to pump hydrocarbons to the surface (Hyne, 2012). In some cases, wells may be recompleted after the initial construction, with re-fracturing if production has decreased (Vincent, 2011). Recompletion also may include additional perforations in the well at a different interval to produce from a different formation than originally done, lengthening the wellbore, or drilling new laterals from an existing wellbore.

As of 2012, Shires and Lev-On (2012) suggested that the rate of re-fracturing in natural gas wells was about 1.6%. 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, 2012d). In the EPA's Inventory of U.S. Greenhouse Gas Emissions and Sinks (U.S. EPA, 2015g), the number of gas wells that were re-fractured in a given year as a percent of the total existing population of hydraulically fractured producing gas wells in a given year ranges from 0.3% to 1% across the 1990-2013 period.

2.1.1.4. Production Rates and Duration

The production life of a well depends on a number of factors, such as the amount of hydrocarbons in place, the reservoir pressure, production rate, and the economics of well operations. It may be as short as three or four years in deep-water, high-permeability formations and as long as 40 to 60 years in onshore tight gas reservoirs (Ross and King, 2007). In hydraulically fractured wells in unconventional reservoirs, production is often characterized by a rapid drop followed by a slower decline compared to conventional hydrocarbon production wells (Patzek et al., 2013). However, most modern, high-volume fractured wells are less than a decade old. Consequently, there is a limited historical basis to determine the full extent of the production decline (Patzek et al., 2013) and to ultimately determine how much they will produce.

2.1.4. Site and Well Closure

Once a well reaches the end of its useful life, it is plugged, and the well site is closed. If a wellbore is not properly plugged, fluids from higher pressure zones may eventually migrate through the wellbore to the surface or to other zones such as fresh water aquifers (NPC, 2011b). Plugging is usually performed according to state regulations governing the locations and materials for plugs (Calvert and Smith, 1994). Operators typically use cement plugs placed across fresh water formations and oil or gas formations (NPC, 2011b). Some surface structures can be left in place, and the local topography and land cover are restored to predevelopment conditions to the extent possible, per state regulations. The wellhead and any surface equipment are removed. Impoundments are dewatered, filled in, and graded. The well casing is typically cut off below the surface and a steel plate or cap is emplaced to seal the top of the casing and wellbore (API, 2010a), although there may also be an aboveground marker used in some locations. Some states require notification of the landowner or a government agency of the location of the well.

2.2. How Widespread is Hydraulic Fracturing?

Hydraulic fracturing activity in the United States and worldwide is substantial. One industry cumulative estimate stated that by the time of writing in 2010, close to 2.5 million fracture treatments had been performed globally (Montgomery and Smith, 2010). In 2002, the Interstate Oil and Gas Compact Commission (IOGCC) stated that close to 1 million wells had been hydraulically fractured in the United States since the 1940s (IOGCC, 2002). A recent U.S. Geological Survey (USGS) publication analyzed 1 million hydraulically fractured wells and 1.8 million hydraulic fracturing treatment records from the United States from 1947 to 2010 (USGS, 2015). Although some form of hydraulic fracturing has been used for more than 60 years, the technological advancements that combined hydraulic fracturing and directional drilling in the early 2000s resulted in the new era of modern hydraulic fracturing, which uses higher volumes of fracturing fluids than were typically used in prior decades. Modern hydraulic fracturing is typically associated with horizontal wells producing from unconventional shale reservoirs, but hydraulic fracturing continues to be done in vertical wells in conventional reservoirs also. This ongoing mix of traditional and modern hydraulic fracturing activities makes estimates of the total number of hydraulic fracturing wells challenging.

The following series of images illustrates hydraulic fracturing activities and the scale of those activities in the United States. Figure 2-12 (taken in Springville Township, in northeastern Pennsylvania) and Figure 2-13 (taken near Williston, in northwestern North Dakota) show individual well pads in the context of the local landscape. Landsat images in Figure 2-14 and Figure 2-15 provide satellite views of areas in northwest Louisiana and southeast Wyoming, respectively, where hydraulic fracturing activities currently occur as identified by the well pads in the images. These images serve to illustrate activity at a wider scale, though they are not representative of all hydraulic fracturing activities in the eastern or western United States. The light red circles around some of the well pads identify them as hydraulic fracturing wells that were reported by well operators to the FracFocus registry (as summarized in the EPA FracFocus project database 1.0) (U.S. EPA, 2015b). (The FracFocus well locations reflect information in the EPA FracFocus project database for well operations reporting hydraulic fracturing activities between January 2011 and February 2013. The Landsat images are from a later period, July and August of 2014, so additional well pads in the images now may be represented in the FracFocus registry.)

Figure 2-12. Aerial photograph of a well pad and service road in Springville Township, Pennsylvania.

Image © J Henry Fair / Flights provided by LightHawk.

Figure 2-13. Aerial photograph of hydraulic fracturing activities near Williston, North Dakota.

Image © J Henry Fair / Flights provided by LightHawk.

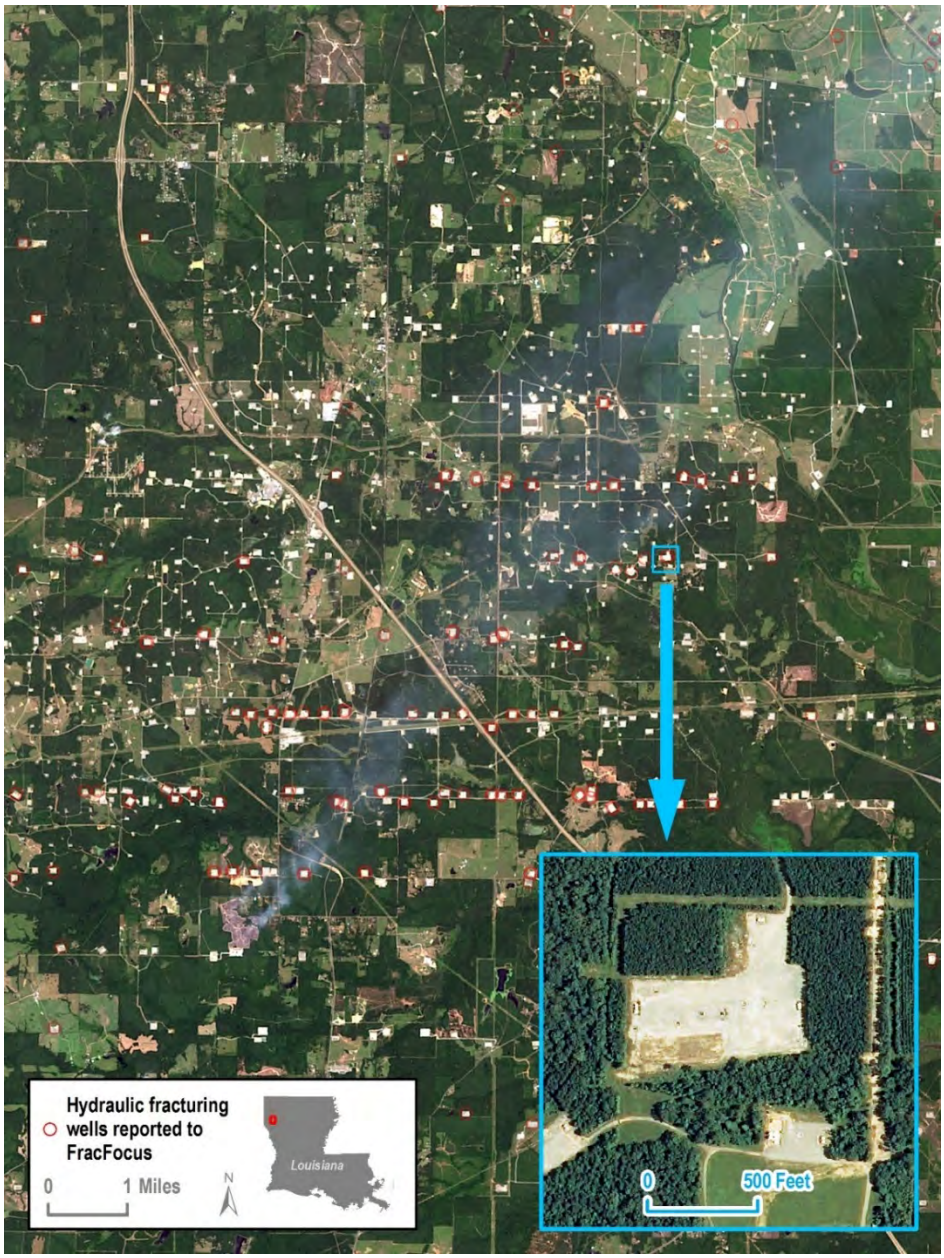


Figure 2-14. Landsat photo showing hydraulic fracturing well sites near Frierson, Louisiana.

Source: Imagery from USGS Earth Resources Observation and Science, Landsat 8 Operational Land Imager (scene LC80250382014232LGN00) captured August 20, 2014 and accessed on May 1, 2015 from USGS's EarthExplorer (http://earthexplorer.usgs.gov/).
Inset imagery from USDA National Agriculture Imagery Program (entity M 3209351_NE 15_1_20130703_20131107) captured July 3, 2013 and accessed May 1, 2015 from USGS's EarthExplorer (http://earthexplorer.usgs.gov/).
FracFocus well locations are from the EPA FracFocus project database 1.0 (U.S. EPA, 2015b).

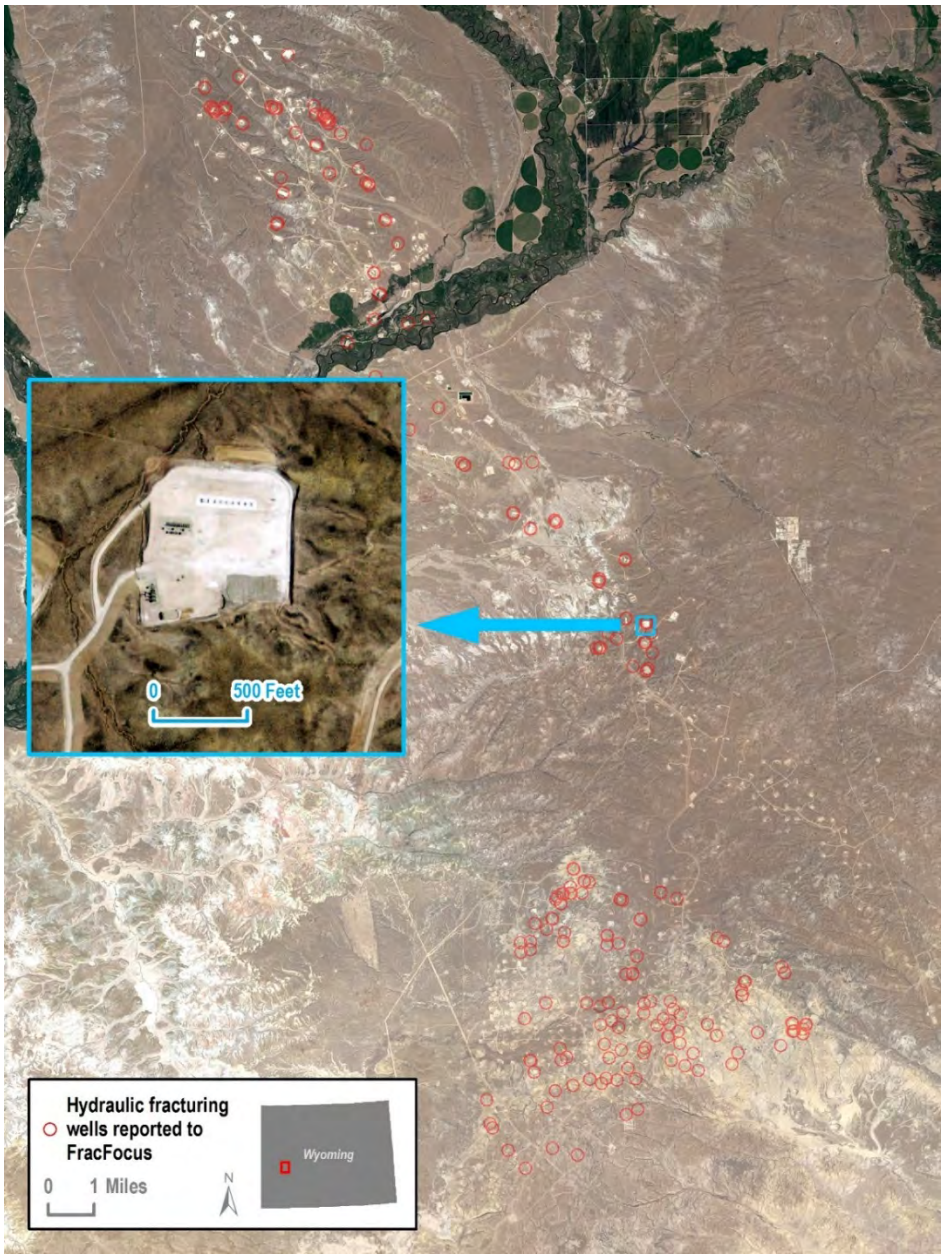


Figure 2-15. Landsat photo showing hydraulic fracturing well sites near Pinedale, Wyoming.

Source: Imagery from USGS Earth Resources Observation and Science, Landsat 8 Operational Land Imager (scene LC80370302014188LGN00) captured July 7, 2014 and accessed May 1, 2015 from USGS's EarthExplorer (http://earthexplorer.usgs.gov/).
Inset imagery from USDA National Agriculture Imagery Program (entity M 4210927_NW 12_1_20120623_20121004) captured June 23, 2012 and accessed May 1, 2015 from USGS's EarthExplorer (http://earthexplorer.usgs.gov/).
FracFocus well locations are from the EPA FracFocus project database 1.0 (U.S. EPA, 2015b).

The maps in Figure 2-16 show recent changes nationally in the geography of oil and gas production through the increased use of horizontal drilling, which occurs together with hydraulic fracturing.

Some traditional oil- and gas-producing parts of the country, such as Texas, have seen an expansion of historically strong production activity as a result of the deployment of horizontal drilling and modern hydraulic fracturing. Pennsylvania, a century ago one of the leading oil- and gas-producing states, has seen a resurgence in oil and gas activity. Other states currently experiencing a steep increase in production activity, such as North Dakota, Arkansas, and Montana, have historically produced less oil and gas and are therefore undergoing new development.

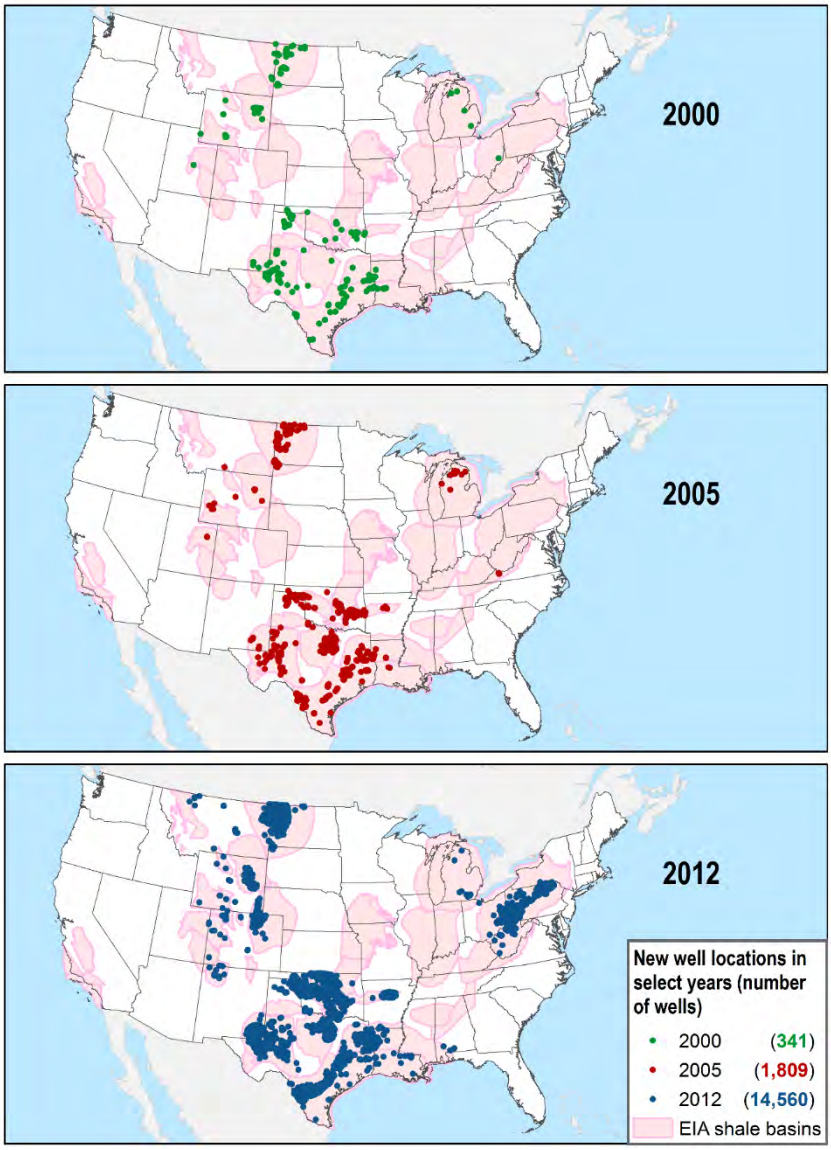


Figure 2-16. Location of horizontal wells that began producing oil or natural gas in 2000, 2005, and 2012, based on data from DrillingInfo (2014a).

2.2.1. Number of Wells Fractured per Year

We estimate that from roughly 2011 to 2014, approximately 25,000 to 30,000 new oil and gas wells were hydraulically fractured each year. Additional, pre-existing wells (wells more than one year old that may or may not have been hydraulically fractured in the past) were also likely fractured each year. Since the early 2000s, the percentage of all hydraulically fractured wells that are either horizontal or deviated has steadily grown. Our estimates are based on data detailed below from several public and private sector organizations that track drilling and various aspects of hydraulic fracturing activity. There is no complete database or registry of wells that are hydraulically fractured in the United States. Another source of uncertainty is the rate at which relatively new hydraulic fracturing wells are re-fractured or the rate at which operators use older, existing wells for hydraulic fracturing. Future trends in the number of wells hydraulically fractured per year will be affected by the cost of well operation and the price of oil and gas. Scenarios of increasing, flat, and decreasing hydraulic fracturing activity all appear to be possible (Weijermars, 2014).

The number of wells reported to the FracFocus registry provides a low estimate of the number of hydraulically fractured wells.[1] As of early April 2015, the FracFocus registry reported receiving information on a cumulative total of approximately 95,000 fracturing jobs, or roughly 22,400 per year over the 51-month period from January 2011 through March 2015 (GWPC, 2015). In a more detailed review of FracFocus data from 2011 and 2012, the EPA found there were approximately 14,000 and 22,500 fracturing jobs reported to the FracFocus website in those years, respectively, across 20 states (U.S. EPA, 2015a). These 2011 and 2012 numbers are likely underestimates of wells hydraulically fractured annually, in part because FracFocus reporting was voluntary for most states for at least a portion of 2011 to 2012 (though the increase from 2011 to 2012 in part reflects more states requiring reporting to the registry). Hydraulic fracturing practices may alternately (or in addition to FracFocus) be tracked by states. Compared to state records of hydraulic fracturing from North Dakota, Pennsylvania, and West Virginia in 2011 and 2012, we found that the count of wells based on records submitted to FracFocus was an underestimate of the number of fracturing jobs in those states by an average of approximately 30% (see Text Box 4-1).

An additional estimate of the number of hydraulically fractured wells can be obtained from DrillingInfo, a commercial database compiling data from individual state oil and gas agencies (DrillingInfo, 2014a). The data indicate an increase in the number of new hydraulically fractured wells drilled each year, from approximately 12,800 in 2000 to slightly more than 21,600 in 2005, to nearly 23,000 in 2012. The number of new horizontal wells (which are likely all hydraulically fractured) show a significant increase, from 344 (about 1% of all new production wells) in 2000, to 1,810 in 2005, to 14,560 (nearly 41% of all new production wells) in 2012 (see Figure 2-16).

[1] The FracFocus registry was developed by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission. Oil and gas well operators can use the FracFocus registry to disclose information about hydraulic fracturing well locations, and water and chemical use during hydraulic fracturing operations. Submission of information to FracFocus was initially voluntary (starting in January 2011), but now about half of the 20 states represented in FracFocus have enacted reporting requirements for well operators that either mandate reporting to FracFocus or allow it as one reporting option. FracFocus data are discussed in more detail in Chapter 4 (regarding water volumes) and Chapter 5 (regarding chemical use). For more information see www.fracfocus.org and U.S. EPA (2015a).

Because DrillingInfo data do not directly report whether a well has been hydraulically fractured, we relied on properties of the well and the oil or gas producing formation to infer which wells were hydraulically fractured and when. First, we assumed that *all* horizontal wells were hydraulically fractured in the year they started producing. Second, we 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.[1]

We used well-specific data provided by oil and gas well operators to the EPA to supplement our estimates of hydraulic fracturing using DrillingInfo data (U.S. EPA, 2015o). Matching wells in each dataset using API well numbers, we found that 80% of 171 newly drilled wells known to be fractured in 2009 and 2010 according to their well files were correctly identified as fractured using well and formation properties in DrillingInfo.[2] We did not correctly identify all of the vertical or deviated wells that were known to be fractured. (We were unable to identify wells for which hydraulic fracturing was inferred using the properties in DrillingInfo but were not fractured.) This comparison suggests that the estimates of hydraulically fractured wells from DrillingInfo are likely underestimates.

Another source of estimates is from a U.S. Geological Survey publication that reviewed data from the commercial IHS database of U.S. oil and gas production and well data (USGS, 2015). The study period was from 1947 through 2010. The authors estimated a total of approximately 277,000 hydraulically fractured wells between 2000 and 2010 (compared to close to 212,000 during the same time period estimated based on DrillingInfo data). This is roughly 25,000 wells per year over that time period. Approximately three-quarters of these wells were vertical. Reflecting advances in directional drilling technology over the decade ending in 2010, the percentage of total wells fractured that were horizontal or deviated wells grew from less than 10% to over 60%.

Well counts tracked by Baker Hughes provide another estimate of new wells fractured annually. Since 2012, this oilfield service company has published a quarterly count of new wells spudded; it includes only new inland U.S. wells "identified to be significant consumers of oilfield services and supplies."[3] A reported total of 36,824 oil and gas wells were spudded in the United States in 2012, with new wells per quarter fluctuating between about 8,500 and 9,500 (Baker Hughes, 2014b). While 100% of new wells are probably not hydraulically fractured (see below for estimates of hydraulic fracturing rates in new wells), a count of new wells also does not include hydraulic fracturing taking place in older, existing wells.

[1] The assignment of formation type (shale, coalbed, low-permeability, or conventional) for each well was based on a crosswalk of information on basin/play provided in DrillingInfo (2014a) with expert knowledge of those basins/plays at EIA (2012a). If formation type could not be determined, it was considered conventional by default. This is similar methodology to that used by the EPA for its greenhouse gas inventory (U.S. EPA, 2013c).

[2] An API well number is a unique identifying number given to each oil and gas well drilled in the United States. The system was developed by the American Petroleum Institute.

[3] To spud a well is to start the well drilling process by removing rock, dirt, and other sedimentary material with the drill bit.

Data collected under the EPA's Greenhouse Gas Reporting Program (GHGRP) provide information on completions and workovers with hydraulic fracturing (i.e., re-fracturing) of gas wells. Data reported to GHGRP for years 2011 to 2013 suggest that 9-14% of the gas wells reported to be hydraulically fractured in each year were pre-existing wells undergoing re-fracturing (U.S. EPA, 2014e).[1] The GHGRP requirements do not include reporting of re-fracturing in oil wells, and other data sources for information specifically on re-fracturing of existing oil wells compared to initial fracturing of oil wells were not identified. For comparison, an EPA survey of an estimated 23,200 oil and gas production wells that were hydraulically fractured by nine oil and gas service companies in 2009 and 2010 suggests that 42% of the wells were pre-existing (i.e., more than one year old) when they were hydraulically fractured (U.S. EPA, 2015o). Differences in data (including data from different years and data from gas wells only (GHGRP) versus oil and gas wells, for instance), definitions, and assumptions used to estimate the percentage of pre-existing wells hydraulically fractured in a year could account for the different results.

In summary, determination of the national scope of hydraulic fracturing activities in the United States is complicated by a lack of a centralized source of information and the fact that well and drilling databases each track different information. There is also uncertainty about whether information sources are representative of the nation, whether they include data for all production types, whether they represent only modern (high volume) hydraulic fracturing, and whether they include activities in both conventional and unconventional reservoirs. Taking these limitations into account, however, it is reasonable to assume 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.

2.2.2. Hydraulic Fracturing Rates

Estimates of hydraulic fracturing rates, or the proportion of all oil and gas production wells that are associated with hydraulic fracturing, also indicate widespread use of the practice. Based on an assessment described above of data from DrillingInfo (2014a), hydraulic fracturing rates have increased over time. From 2005 to 2012, rates of hydraulic fracturing increased from 57% to 64% of all new production wells (including oil wells, gas wells, and wells producing both oil and gas).

In 2009, industry consultants stated that hydraulic fracturing was used on nearly 79% of all wells and more than 95% of "unconventional" wells (IHS, 2009). A 2010 article in an industry publication noted "some believe that approximately 60% of all wells drilled today are fractured" (Montgomery and Smith, 2010). Of 11 important oil and gas producing states that responded to an IOGCC survey (Arkansas, Colorado, Louisiana, New Mexico, North Dakota, Ohio, Oklahoma, Pennsylvania, Texas, Utah, and West Virginia), ten estimated that 78% to 99% of new oil and gas wells in their states were hydraulically fractured in 2012; Louisiana was the one exception, reporting a fracturing rate of 3.9% in 2012 (IOGCC, 2015). Although estimates of fracturing rates are variable, largely ranging from near 60% to over 90% (as described above), they are often higher for gas wells than they are for oil wells. A 2010 to 2011 industry survey of 20 companies involved in natural gas production

[1] The GHGRP reporting category that covers re-fracturing is "workovers with hydraulic fracturing."

found that 94% of the wells that they operated were fractured; among those, roughly half were vertical and half were horizontal (Shires and Lev-On, 2012).

2.3. Trends and Outlook for the Future

Fossil fuels are the largest source of all energy generated in the United States. They currently comprise approximately 80% of the energy produced (EIA, 2014f). However, the mix of fossil fuels has shifted in recent years. Coal, the leading fossil fuel produced by the U.S. since the 1980s, has experienced a significant decrease in production. In 2007, coal accounted for approximately 33% of U.S. energy production, and by 2013 it decreased to approximately 24% (EIA, 2014f). On the other hand, natural gas production has risen to unprecedented levels, and oil production has resurged to levels not seen since the 1980s (see Figure 2-17). Oil went from accounting for 15% of U.S. energy production to 19% between 2007 and 2013, and natural gas (both dry and liquid) went from 31% to 35% (EIA, 2014f).

Below, we discuss recent and projected shifts in oil and natural gas production that can primarily be attributed to hydraulic fracturing and directional drilling technologies.

2.3.1. Natural Gas (Including Coalbed Methane)

Natural gas production in the United States peaked in the early 1970s, reached those levels again in the mid-1990s, and between the mid- to late-2000s has increased to even higher levels (see Figure 2-17). The recent increase in total gas production has been driven almost entirely by shale gas (see Figure 2-18).

As natural gas prices fell between 2008 and 2012 (EIA, 2014e), drilling of new natural gas wells declined markedly (EIA, 2014g) (see Figure 2-19). Nevertheless, natural gas production is expected to increase over the coming decades (see Figure 2-18). EIA (2013b) predicts that shale gas production will more than double between 2011 and 2040 and that the portion of total natural gas production represented by shale gas will increase from one-third to one-half. The EIA projects steady growth in the development of tight gas as well (about a 25% increase in production over the 30-year period) and delayed growth in the development of coalbed methane resources, for which production is not expected to increase again until sufficiently high natural gas prices are realized around 2035. Overall, the EIA projects that the share of U.S. natural gas production from shales, tight formations, and coalbeds will increase from 65% in 2011 to nearly 80% in 2040.

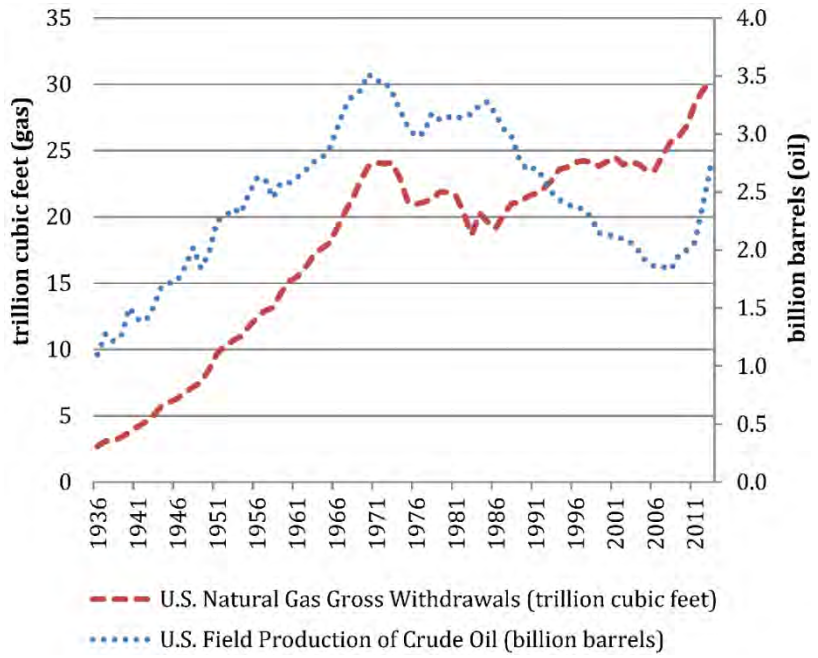


Figure 2-17. Trends in U.S. oil and gas production.

Source: EIA (2013d) and EIA (2014d).

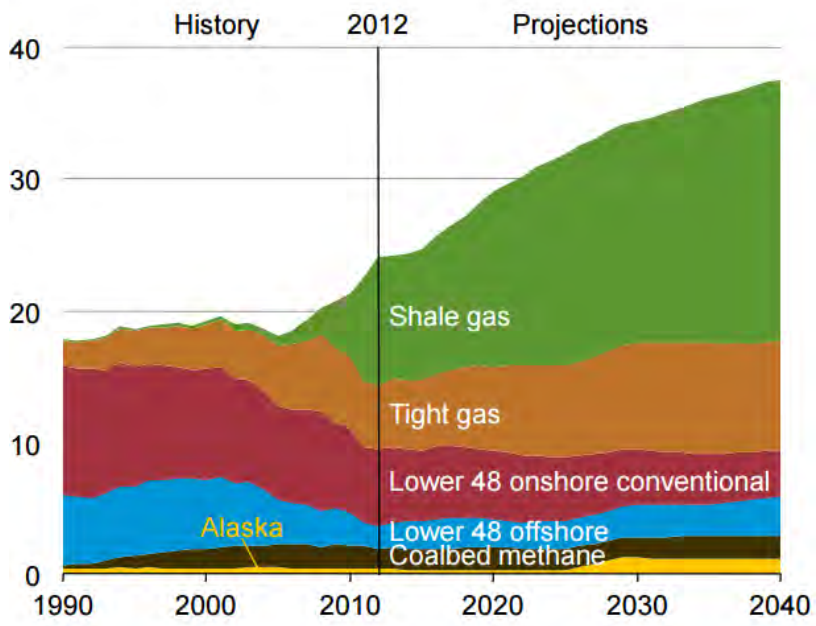


Figure 2-18. Historic and projected natural gas production by source (trillion cubic feet).

Source: EIA (2014a).

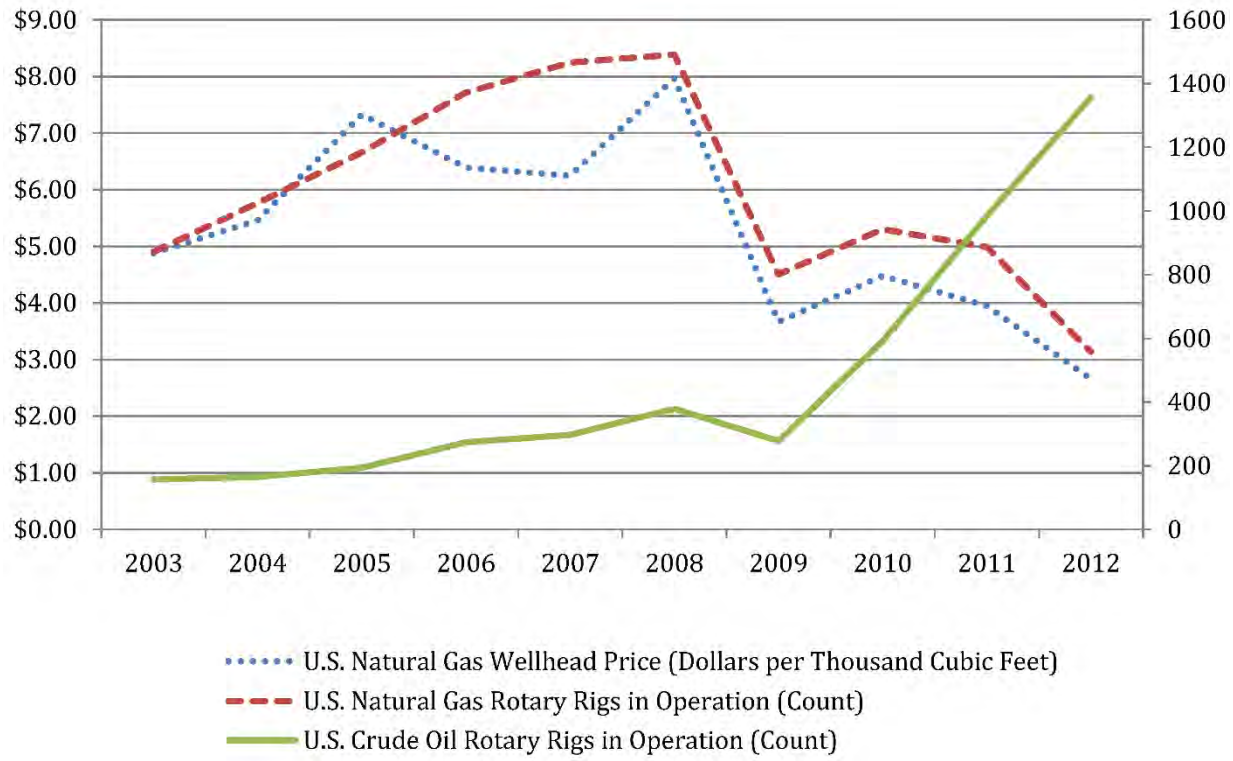


Figure 2-19. Natural gas prices and oil and gas drilling activity, 2008–2012.

Source: EIA (2014e), EIA (2014g), and EIA (2013b).

Shale gas production varies by play (see Figure 2-20a). Until 2010, the Texas Barnett Shale was the play with the most production. Although production from the Barnett Shale is still significant, production has increased sharply in other plays. By 2012, production from the Haynesville play (on the Louisiana/Texas border) surpassed that in the Barnett play, and by 2013 the Marcellus Shale (in the Appalachian Basin underlying Pennsylvania, West Virginia, and other states) was the play with the most production. Because technically recoverable resources are an order of magnitude higher in the Marcellus than in any other U.S. shale gas play, it is likely that the Marcellus Shale will be very active in shale gas production for the foreseeable future (EIA, 2011a).[1]

In the 1970s, most tight gas production in the United States was in the San Juan Basin centered in New Mexico. As modern hydraulic fracturing came into common usage in the mid-2000s, the lead in tight gas production shifted to Texas (especially East Texas) and the Rocky Mountain states (Vidas and Hugman, 2008).

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

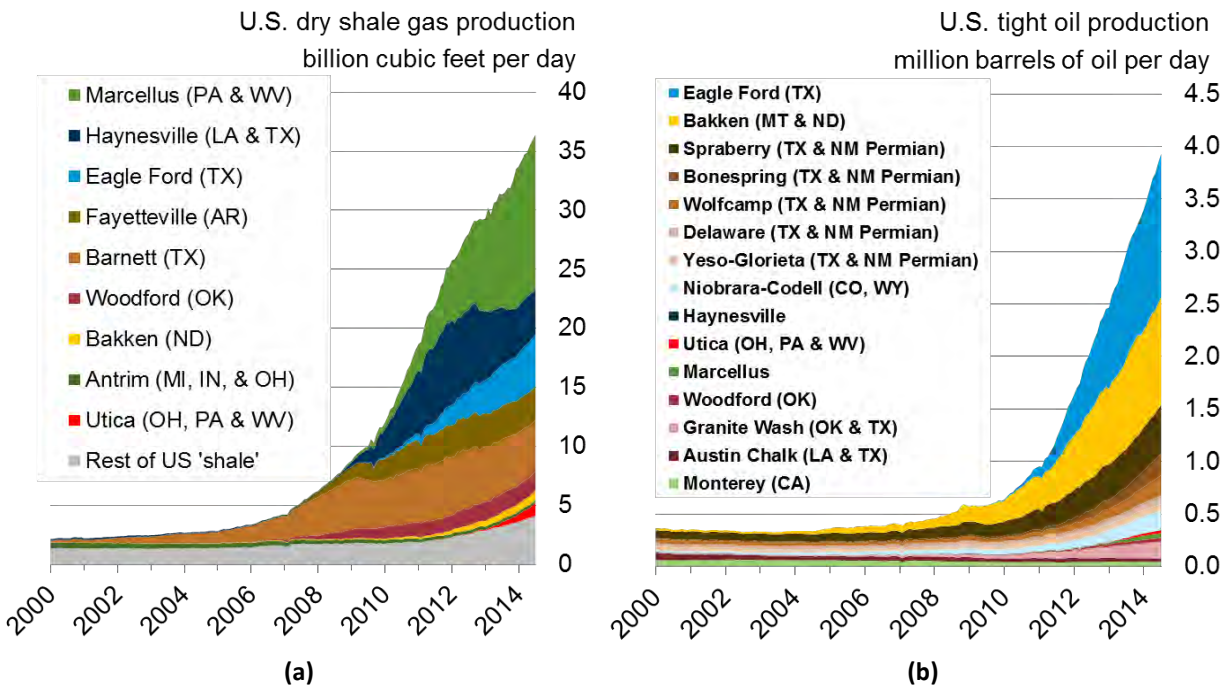


Figure 2-20. (a) Production from U.S. shale gas plays, 2000–2014, in billion cubic feet per day; (b) Production from U.S. tight oil plays, 2000-2014.

Tight oil includes oil from shale and other tight formations, plus lease condensate from natural gas production. Source: EIA (2012c).

Modern coalbed methane production techniques were pioneered in the Black Warrior Basin in Alabama and in the San Juan Basin (Vidas and Hugman, 2008). With the use of hydraulic fracturing, most coalbed methane production in the United States now comes from the San Juan Basin and from Rocky Mountain Basins (e.g., the Uinta-Piceance Basin in Colorado and Utah and the Powder River Basin centered in Wyoming) (Vidas and Hugman, 2008).

2.3.2. Oil

The EIA data indicate that as drilling activity for natural gas declined between 2008 and 2012, drilling for oil increased by a similar order of magnitude (see Figure 2-19). Figure 2-21 shows past and projected future trends in U.S. oil production and importation (EIA, 2013a). Note that this graph shows production and importation in millions of barrels (bbl) *per day*. The current surge in tight oil production is expected to continue until the latter part of the current decade and then taper, while conventional oil production is projected to remain fairly level. However, downward trends in the price of oil since mid-2014 are not reflected in these projections.

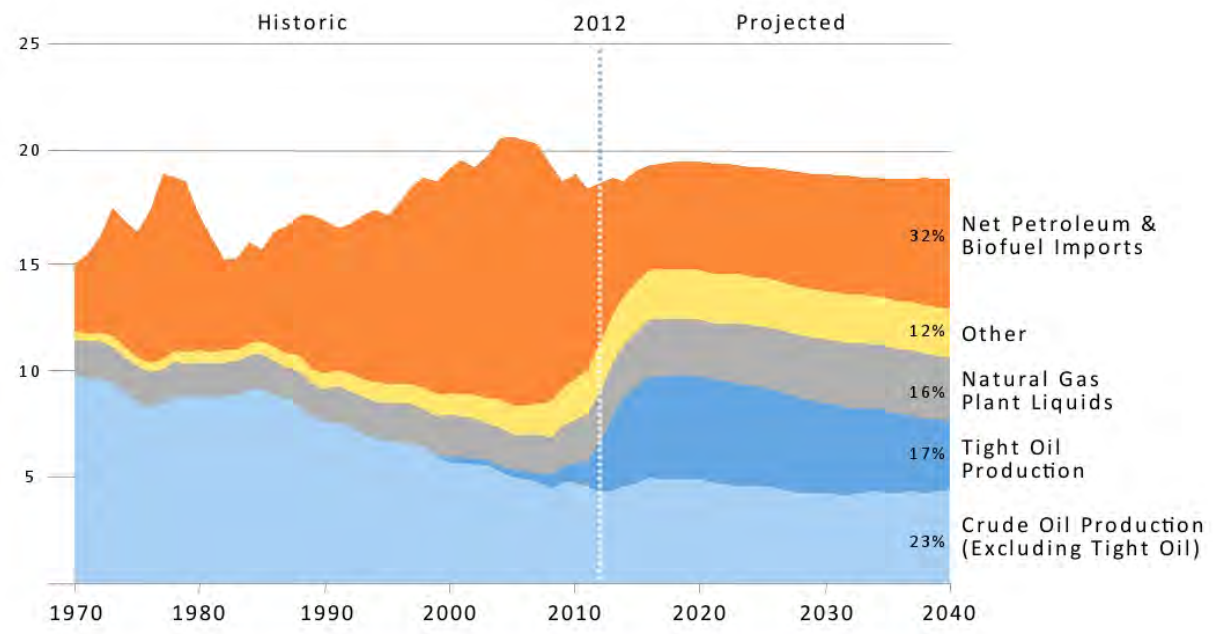


Figure 2-21. U.S. petroleum and other liquid fuels supply by source, past and projected future trends (million barrels per day).

Source: EIA (2013a).

Like shale gas production, tight oil production varies by play (Figure 2-20b). The Bakken Shale play, centered in western North Dakota, is important for shale oil production with production increasing from 123 million bbl (20 billion L) in 2011 to 213 million bbl (34 billion L) in 2012. Proved reserves in the Bakken have increased from almost 2 billion to over 3 billion bbl (316 billion L to 503 billion L). The Eagle Ford play in Texas is another major area of shale oil activity, with production increasing from 71 million bbl (11 billion L) in 2011 to 210 million bbl (33 billion L) in 2012, and proved reserves increasing from 1.25 billion to 3.4 billion bbl (199 billion to 536 billion L) (EIA, 2014b). Oil production from the Eagle Ford surpassed that from the Bakken in 2013 (EIA, 2014h). Among other shale oil plays that might become important in future domestic U.S. oil production, the Niobrara (centered in Colorado) and Austin Chalk (in Texas, Louisiana, and Mississippi) are believed to have quantities of recoverable resources on the same order of magnitude as the Bakken and Eagle Ford plays (EIA, 2012b).

2.4. Conclusion

Since about 2005, the combination of hydraulic fracturing and horizontal drilling pioneered in the Barnett Shale have become widespread in the oil and gas industry. Hydraulic fracturing is now a standard industry practice and has significantly contributed to a surge in U.S. production of both oil and gas. Modern hydraulic fracturing has resulted in additional types of geological formations being tapped, and sometimes these formations are located in regions of the country new to intensive oil

and gas exploration and production. In other areas, the improved techniques have made possible a resurgence of production.

An estimated 25,000 to 30,000 new wells drilled in the United States were hydraulically fractured as a production-enhancing technique in each year from 2011 to 2014. Additional pre-existing wells were also fractured. Since the early 2000s, the percentage of all hydraulically fractured wells that are either horizontal or deviated has steadily grown. Reserves of oil and gas that are now accessible with modern hydraulic fracturing are considerable, and if technical improvements outpace depletion of oil and gas resources, the quantity of resources that are deemed economically and technically recoverable may continue to grow. Given current trends, it appears likely that hydraulic fracturing will continue to play an important role in the oil and gas industry, and the United States' energy portfolio, in the decades ahead.

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Chapter 3

Drinking Water Resources in the United States

3. Drinking Water Resources in the United States

Consideration of how and where hydraulic fracturing activities potentially impact drinking water resources requires an understanding of both the activities and the potentially impacted resources. In Chapter 2, we provided background on hydraulic fracturing and in this chapter, we provide an overview of drinking water resources in the United States. We describe the use of these resources, including patterns in current use and trends for future use (Section 3.1). We then characterize the spatial distribution of hydraulically fractured wells and current surface and ground water supplies throughout the United States (Section 3.2) to evaluate where potential impacts of hydraulic fracturing on drinking water resources may occur.

3.1. Current and Future Drinking Water Resources

In this assessment, drinking water resources are defined broadly as any body of ground water or surface water that now serves, or in the future could serve, as a source of drinking water for public or private use. Drinking water resources provide not only water that individuals actually drink but also water used for many additional purposes such as cooking and bathing. Our definition of drinking water resources includes both fresh and non-fresh bodies of water.

The average American uses about 90 gal (341 L) of drinking water per day for indoor and outdoor purposes (e.g., drinking, food preparation, washing clothes and dishes, flushing toilets, and watering lawns or gardens (Maupin et al., 2014; AWWA, 1999). Drinking water is supplied to households by either public water systems (PWSs) or private water systems (private ground water wells and surface water intakes).[1] In 2011, approximately 270 million people (86% of the population) in the United States relied on water supplied to their homes by one of the more than 51,000 community water systems (Maupin et al., 2014; U.S. EPA, 2013b).[2] These systems provided households with nearly 24 billion gal (91 billion L) of water per day (Maupin et al., 2014).[3] In areas without service by PWSs, approximately 43 million people (14% of the population) relied on private sources for drinking water, and private water systems account for about 3.6 billion gal (14 billion L) of daily water withdrawals (Maupin et al., 2014).

Drinking water resources can be surface waters such as rivers, streams, lakes, or reservoirs, as well as ground water aquifers. In 2011, approximately 70% of the population receiving drinking water from PWSs relied on surface water, and 30% relied on ground water (U.S. EPA, 2013b). However,

[1] Public water systems (PWSs) provide water for human consumption from surface or ground water 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, 2012e). Private (non-public) water systems serve fewer than 15 connections and fewer than 25 individuals (U.S. EPA, 1991).

[2] The EPA categorizes public water systems 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. Approximately 101,000 non-community water systems provide water to non-residential facilities (e.g., schools, small businesses, churches, and campgrounds (U.S. EPA, 2013b).

[3] The U.S. Geological Survey (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 (Maupin et al., 2014; USGS, 2014b).

the relative importance of surface and ground water sources for supplying drinking water varies geographically (see Figure 3-1). Most larger PWSs rely on surface water and are located in urban areas (U.S. EPA, 2011b), whereas most smaller PWSs rely on ground water and are located in rural areas (U.S. EPA, 2014j, 2013b). In fact, more than 95% of households in rural areas obtain their drinking water from ground water aquifers (U.S. EPA, 2011b).

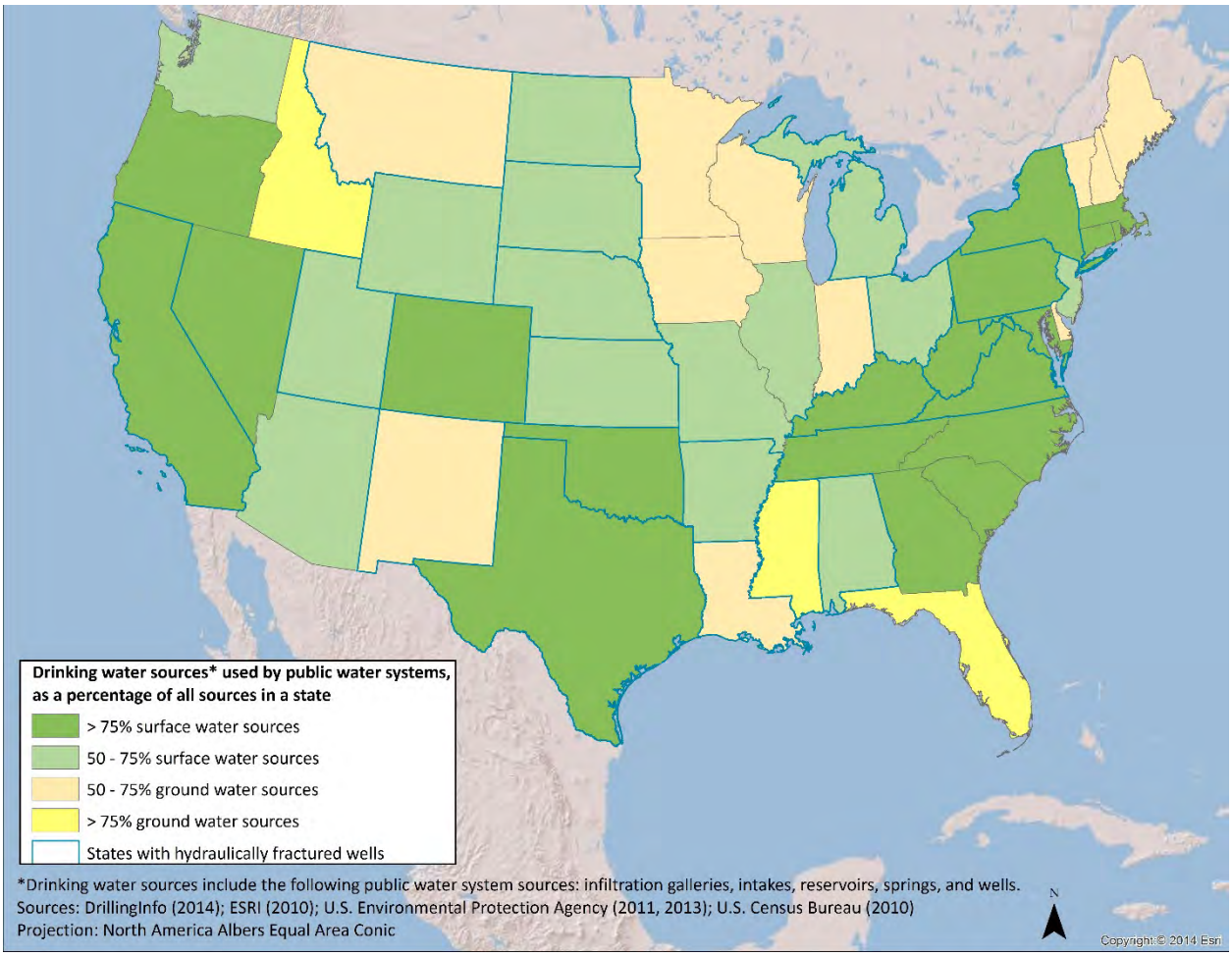

Figure 3-1. Geographic variability in drinking water sources for public water systems.

The relative importance of surface and ground water as drinking water sources varies by state. The public water system sources used in this analysis include infiltration galleries, intakes, reservoirs, springs, and wells. States with hydraulically fractured wells were identified from DrillingInfo data.

The future availability of drinking water resources that are considered fresh in the United States will be affected by changes in climate and water use (Georgakakos et al., 2014; U.S. Global Change

Research Program, 2009).[1] 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, 2015r). Declines in surface water resources have already led to increased withdrawals and cumulative net depletions of ground water in some areas (Castle et al., 2014; Georgakakos et al., 2014; Konikow, 2013a; Famiglietti et al., 2011). Other sources of water that might not be considered fresh, such as wastewater from sewage treatment plants, brackish (containing 3,000–10,000 mg/L TDS) and saline (containing more than 10,000 mg/L TDS) surface and ground water, as well as seawater (containing about 35,000 mg/L TDS) 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 resources or to recharge aquifers that supply drinking water to PWSs (NRC, 2012; Sheng, 2005).

An increasing number of states are developing new water supplies to augment existing water through reuse of reclaimed water, recycling of storm water, and desalination (U.S. GAO, 2014). Most desalination programs currently use brackish water, although plans are underway to expand the use of seawater for desalination in some states. 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 resources beyond those currently being considered for use as drinking water. Therefore, these potential future sources are also considered drinking water resources in this assessment.

3.2. The Proximity of Drinking Water Resources to Hydraulic Fracturing Activity

The colocation of hydraulic fracturing activities with surface and ground water increases the potential for impacts to current and future drinking water resources (Vengosh et al., 2014; Entrekin et al., 2011). In this section, we analyze the aboveground proximity of hydraulically fractured well sites, drinking water resources (including the location of surface water bodies and ground water wells that supply public water systems), and populated areas.[2]

To determine the spatial relationship between hydraulically fractured wells and populated areas, we analyzed the locations of the approximately 273,000 oil and gas wells that were hydraulically fractured in 25 states between 2000 and 2013 (see Chapter 2) with respect to where people live (i.e., census blocks).[3] Nationwide, approximately 9.4 million people lived within one mile of a

[1] Fresh water qualitatively refers to water with relatively low TDS that is most readily available for drinking water currently.
[2] The vertical proximity of ground water resources to geologic formations and hydraulic fracturing operations is addressed in Chapter 6.
[3] In the analyses in this chapter, we only include the oil and gas production wells that we identified were hydraulically fractured using criteria outlined in Chapter 2 and that began producing between 2000 and 2013. The well data found in DrillingInfo may not represent the full year for 2013 since the frequency with which DrillingInfo updates the database varies by state. The final update performed by DrillingInfo for 2013 ranges by state from June 2013 to December 2013.

hydraulically fractured well for some period of time between 2000 and 2013 (DrillingInfo, 2014a; U.S. Census Bureau, 2010); more than 5.7 million people lived within half a mile of a hydraulically fractured well.

We then analyzed trends in the proximity of hydraulically fractured wells to highly populated areas. For this analysis, we considered metropolitan areas (areas with more than 50,000 people) and micropolitan areas (areas with 10,000 to 49,999 people) (U.S. Census Bureau, 2013c).[1] Approximately 81,300 (30%) of new wells hydraulically fractured between 2000 and 2013 were located within a metropolitan or micropolitan area (see Figure 3-2) (DrillingInfo, 2014a; U.S. Census Bureau, 2013c; U.S. EPA, 2013b; ESRI, 2010). From 2000 to 2008, the number of new wells hydraulically fractured per year within metropolitan and micropolitan areas increased 300%; the proportion of wells hydraulically fractured per year in metropolitan and micropolitan areas almost doubled over the same eight-year period (see Figure 3-3).[2] From 2008 to 2012, however, the number of wells hydraulically fractured per year in metropolitan and micropolitan areas decreased by about half in comparison to the peak of approximately 10,000 wells in 2008 (see Figure 3-3), whereas hydraulic fracturing in areas outside of metropolitan and micropolitan areas increased or remained relatively constant (DrillingInfo, 2014a; U.S. Census Bureau, 2013b).

[1] Metropolitan and micropolitan combined statistical areas are geographic entities delineated by the Office of Management and Budget. Specifically, a metropolitan combined statistical area is a core urban area of 50,000 or more people while a micropolitan combined statistical area is an urban core of at least 10,000, but less than 50,000, people (U.S. Census Bureau, 2013c). These terms are referred to as metropolitan and micropolitan areas in this assessment.
[2] For comparison, the DrillingInfo data indicate an increase in the number of wells estimated to be hydraulically fractured each year, regardless of location, from approximately 12,800 in 2000 to slightly more than 21,600 in 2005 to nearly 23,000 in 2012, the last year for which complete data are available.

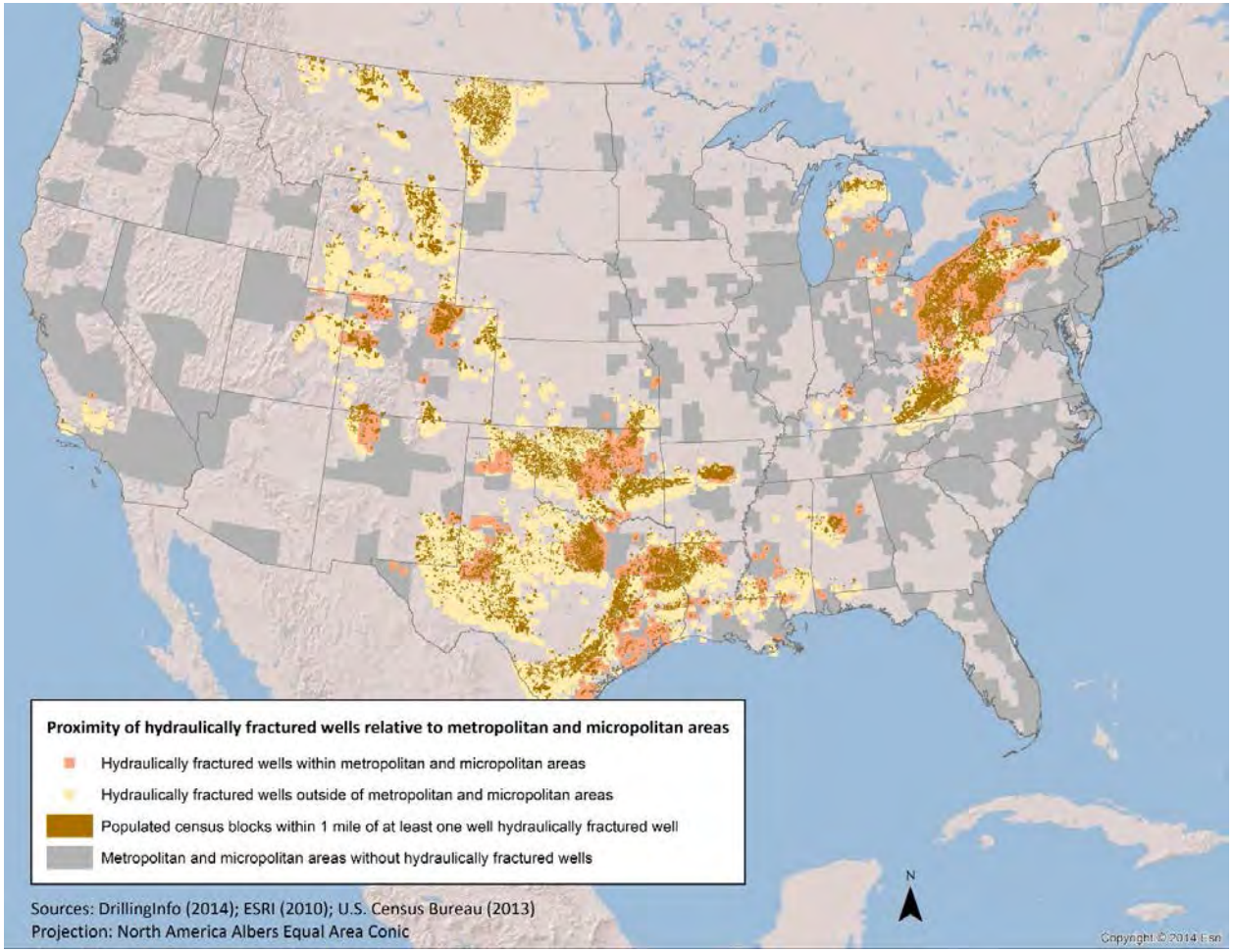

Figure 3-2. Proximity of hydraulically fractured wells relative to populated areas.

The estimates of hydraulically fractured wells from 2000 to 2013 developed from the DrillingInfo data were based on several assumptions described in Chapter 2.

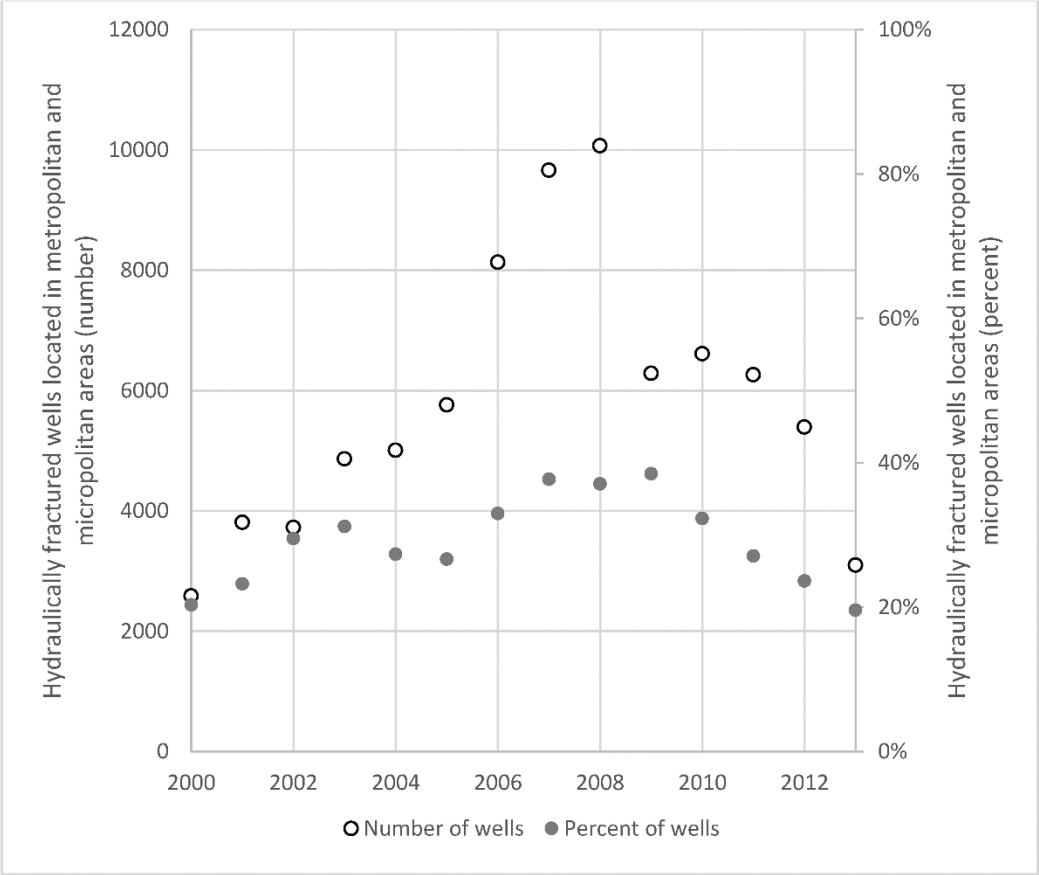

Figure 3-3. Temporal trends (2000–2013) in the number and percent of hydraulically fractured wells located within populated areas.

The estimates of hydraulically fractured wells from 2000 to 2013 developed from the DrillingInfo data were based on several assumptions described in Chapter 2. The graph shows the number of hydraulically fractured wells by the year they started producing. Well data may not be complete for 2013 since final updates to the database for 2013 ranged from June 2013 to December 2013, depending on the state. Original data from DrillingInfo (2014a) and U.S. Census Bureau (2013c).

We next considered the proximity of hydraulically fractured wells to water sources for PWSs. We present proximity from both the vantage point of hydraulically fractured wells (e.g., on average, how far away is the nearest PWS source?) and from the vantage point of PWSs (e.g., if there is at least one fractured well within 1 mile of a PWS, are there usually more?).

Based on the 2000–2013 DrillingInfo data, the distance from hydraulically fractured wells to the nearest source supplying a PWS ranged from 0.01 to 41 miles, with an average distance of 6.2 miles (9.9 km) and a median distance of 4.8 miles (7.6 km) (DrillingInfo, 2014a; U.S. EPA, 2014j). These PWS sources included both surface water sources (e.g., infiltration galleries, intakes, reservoirs, and springs) and ground water wells. An estimated 21,900 of hydraulically fractured oil and gas wells (8%) were within 1 mile of at least one PWS source (see Figure 3-4). The maximum number was 40 PWS sources within 1 mile of a single hydraulically fractured well.

Between 2000 and 2013, approximately 6,800 PWS sources had a hydraulically fractured well within a 1 mile radius. Most of these PWS sources were located in Colorado, Louisiana, Michigan, North Dakota, Ohio, Oklahoma, Pennsylvania, Texas, and Wyoming (see Figure 3-5). These PWS sources had an average of seven fractured wells and a maximum of 144 fractured wells within that one mile proximity. They also 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, 2014j; U.S. Census Bureau, 2013a; U.S. EPA, 2013b).[1]

We also analyzed the location of hydraulically fractured wells relative to populations where a high proportion (≥30%, or twice the national average) obtain drinking water from private systems (private ground water wells and surface water intakes).[2] Between 2000 and 2013, approximately 3.6 million people obtained drinking water from private systems in counties with at least one hydraulically fractured well (DrillingInfo, 2014a; USGS, 2014b), and approximately 740,000 people obtained drinking water from private supplies in counties with more than 400 fractured wells (DrillingInfo, 2014a; USGS, 2014b) (see Figure 3-6).[3] These counties were located in Colorado, Kentucky, Michigan, Montana, New Mexico, New York, Oklahoma, Pennsylvania, Texas, and Wyoming (see Figure 3-6).

[1] 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 fractured well. If non-community water systems are included, the estimated number of customers increases by 533,000 people (U.S. EPA, 2012e).
[2] There is no national data set of private water systems. The USGS estimates the proportion of the population reliant on private water systems, referred to as the "self-supplied population," by county, based on estimates of the population without connections to a public water system (Maupin et al., 2014). We used the USGS estimates for this analysis.
[3] Approximately 14% of the U.S. population is supplied by private water systems (Maupin et al., 2014). In this analysis, we only considered counties in which more than double the national average—that is, at least 30% of the county's population—was supplied by private water systems.

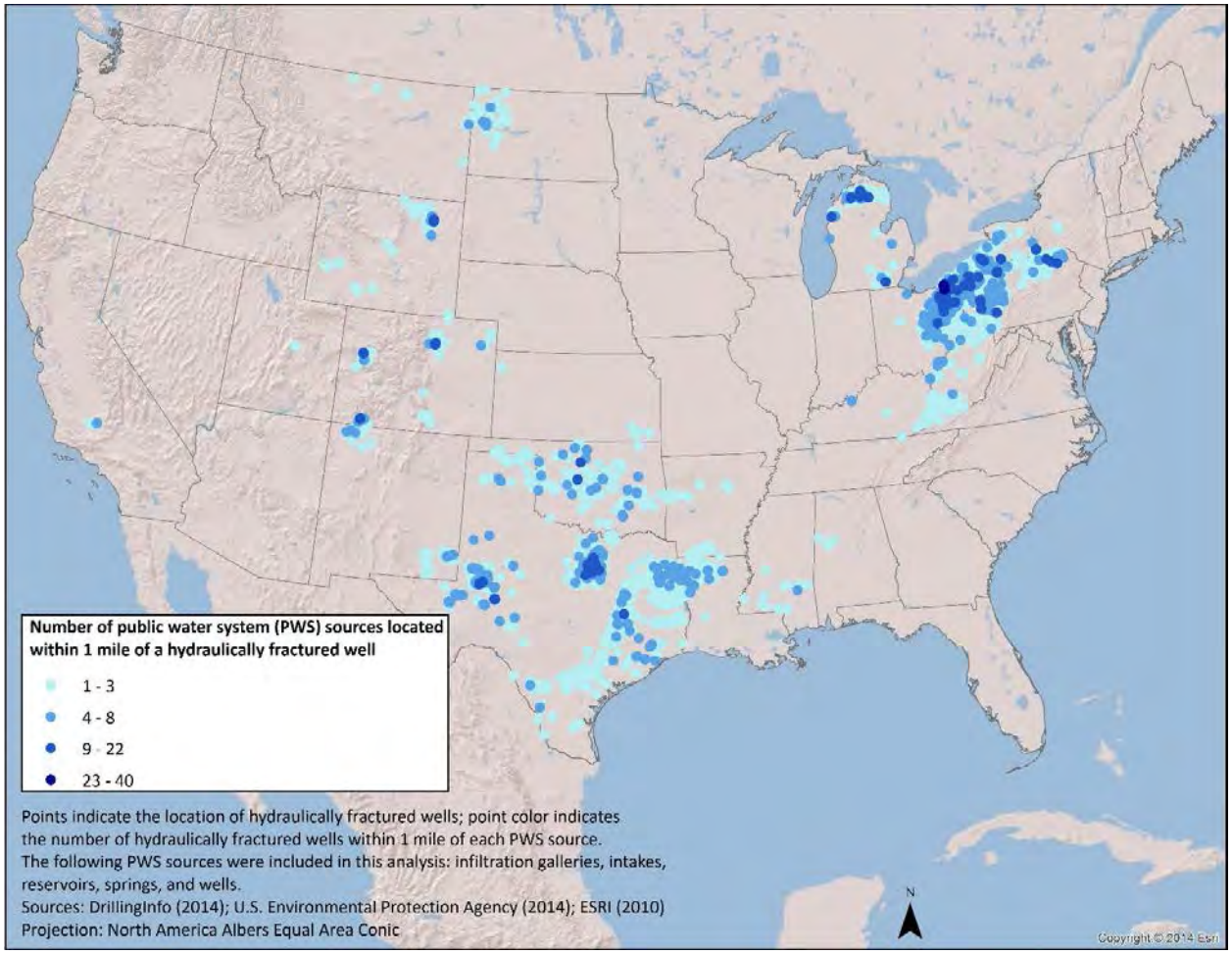

Figure 3-4. Location and number of public water system (PWS) sources located within 1 mile of a hydraulically fractured well.

Points indicate the location of hydraulically fractured wells; point color indicates the number of hydraulically fractured wells within 1 mile of each PWS source. The following PWS sources were included in this analysis: infiltration galleries, intakes, reservoirs, springs, and wells. The estimates of wells hydraulically fractured from 2000 to 2013 developed from the DrillingInfo data were based on several assumptions described in Chapter 2.

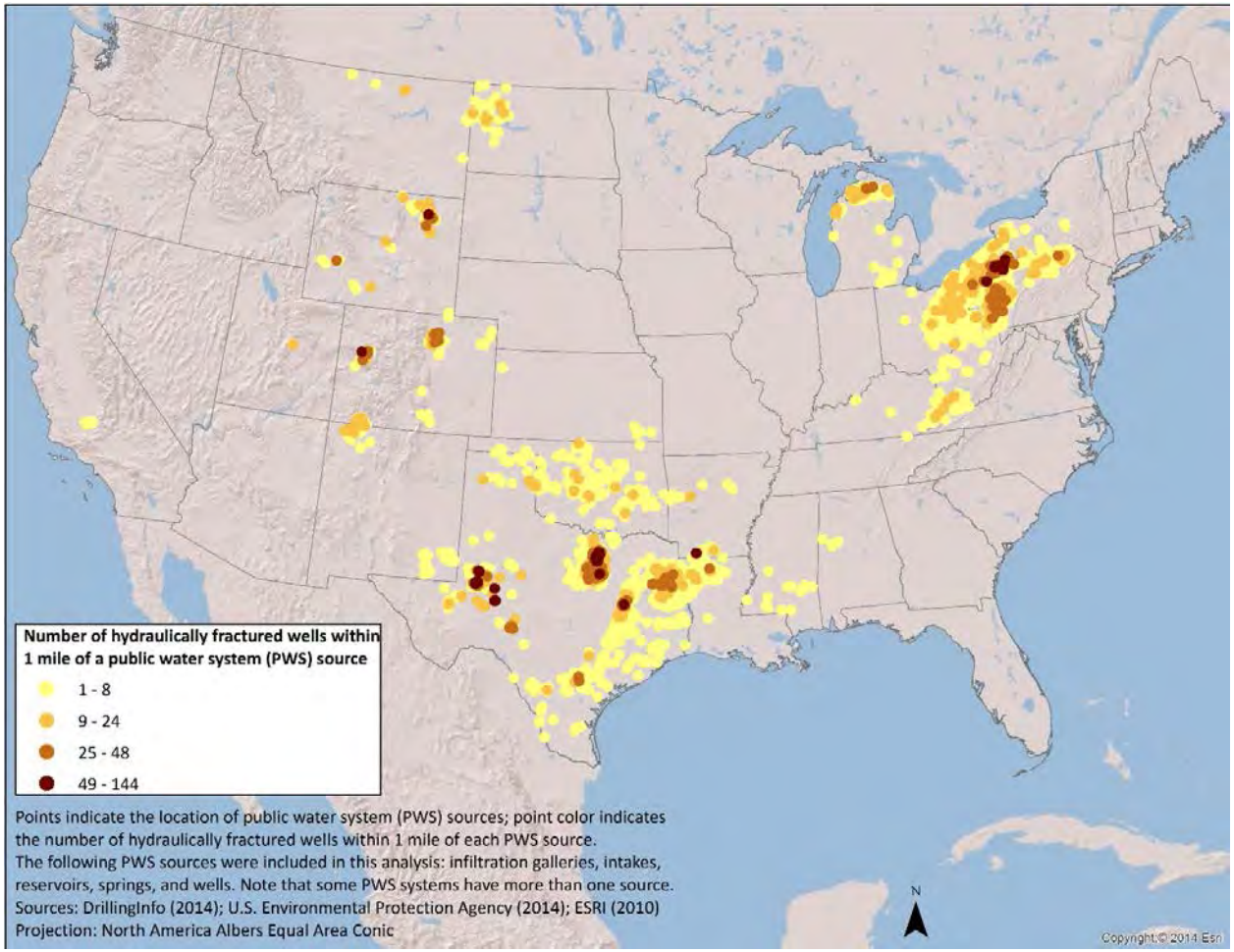

Figure 3-5. The location of public water system sources within 1 mile of hydraulically fractured wells.

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 several assumptions described in Chapter 2.

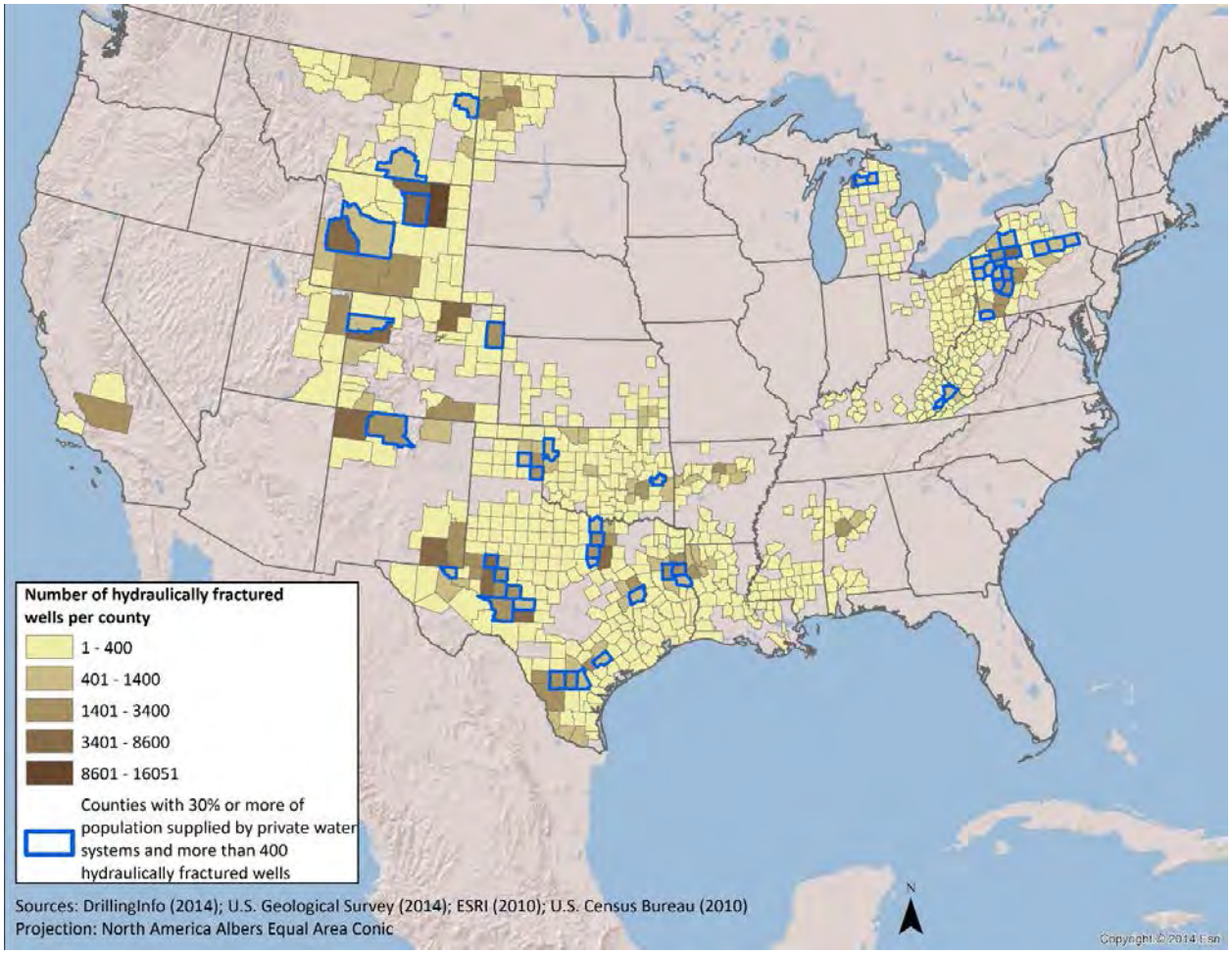

Figure 3-6. Co-occurrence of hydraulic fracturing activity and populations supplied by private water systems.

Color indicates the number of hydraulically fractured wells per county. The estimates of wells hydraulically fractured from 2000 to 2013 developed from the DrillingInfo data were based on several assumptions described in Chapter 2. Counties with more than 400 hydraulically fractured wells and in which at least 30% of the population is supplied by private water systems are outlined in blue.

3.3. Conclusion

The evaluation of potential hydraulic fracturing impacts on drinking water resources in the United States depends on an understanding of how the country's current and future drinking water needs are and will be met. The U.S. population requires sufficient drinking water resources—that is, bodies of fresh or non-fresh surface or ground water that now serve, or in the future could serve, as a source of water for drinking water for public or private use—to meet everyday needs. Currently, most people in the United States rely on water supplied to their homes via public water systems, and most of this water comes from fresh surface water bodies. Shortages in fresh water availability in the United States, especially in the western United States, have already led some states to augment their water supplies with other water sources (e.g., brackish and saline surface and ground water, seawater, and reclaimed wastewater), suggesting that additional water bodies may provide drinking water as the quantity and quality of existing sources change.

The colocation of hydraulic fracturing activities with drinking water resources increases the potential for these activities to affect the quality and quantity of current and future drinking water resources. While close proximity of hydraulically fractured wells to drinking water resources does not necessarily indicate that an impact has or will occur, information about the relative location of wells and water supplies is an initial step in understanding where potential impacts might occur.

Millions of people live in areas where their drinking water resources are located near hydraulically fractured wells. While most hydraulic fracturing activity from 2000 to 2013 did not occur in close proximity to public water supplies, a sizeable number of hydraulically fractured wells (21,900) were located within 1 mile of at least one PWS source (e.g., infiltration galleries, intakes, reservoirs, springs and ground water wells). Approximately 6,800 sources of drinking water for public water systems, serving more than 8.6 million people year-round, were located within 1 mile of at least one hydraulically fractured well. An additional 3.6 million people obtain drinking water from private systems in counties with at least one hydraulically fractured well and in which at least 30% of the population is reliant on private water systems.

Text Box 3-1. Major Findings

Current and future drinking water resources

- Most of the U.S. population (270 million in 2011, or 86%) relies on water supplied to their homes through a public water system, 70% of which comes from surface water and 30% of which comes from ground water.
- An estimated 14% of the U.S. population relies on private water systems for drinking water.
- An increasing number of states are developing new drinking water supplies via reuse of reclaimed water, recycling of storm water, and desalination. These new supplies can augment existing water sources.
- Most of the U.S. population (270 million in 2011, or 86%) relies on water supplied to their homes through a public water system, 70% of which comes from surface water and 30% of which comes from ground water.
- An estimated 14% of the U.S. population relies on private water systems for drinking water.
- An increasing number of states are developing new drinking water supplies via reuse of reclaimed water, recycling of storm water, and desalination. These new supplies can augment existing water sources.

Proximity of drinking water resources to hydraulic fracturing activity

- Nationwide, while most hydraulic fracturing activity from 2000 to 2013 did not occur in close proximity to public water supplies, a sizeable number of hydraulically fractured wells (21,900) were located within 1 mile of at least one PWS source.
- The distance between wells that were hydraulically fractured between 2000 and 2013 and the nearest source supplying a PWS ranged from 0.01 to 41 miles, with an average distance of 6.2 miles (9.9 km).
- An estimated 6,800 public water system sources were located within 1 mile of a hydraulically fractured oil and gas well between 2000 and 2013. These PWS sources supplied water to 3,924 public water systems and served more than 8.6 million people year-round in 2013.
- Approximately 9.4 million people lived within 1 mile of at least one hydraulically fractured oil and gas well between 2000 and 2013.
- Approximately 3.6 million people obtain drinking water from private systems in counties with at least one hydraulically fractured well and in which at least 30% of the population (i.e., double the national average) is reliant on private water systems.

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Chapter 4

Water Acquisition

4. Water Acquisition

4.1. Introduction

Water is a crucial component of nearly all hydraulic fracturing operations, making up approximately 90% or more of fluid injected into a well (U.S. EPA, 2015a; GWPC and ALL Consulting, 2009). Given that at least 25,000 to 30,000 wells may be fractured each year (Chapter 2), and that each well requires thousands to millions of gallons of water (Section 4.3), the potential exists for effects on the quantity of drinking water resources. Large volume water withdrawals also could alter the quality of drinking water resources by decreasing dilution of pollutants by surface waters, or in the case of ground water, allowing the infiltration of lower-quality water from the land surface or adjacent formations.

In this chapter, we consider potential effects 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. We define drinking water resources broadly, to include not just currently designated drinking waters, but waters that could in the future be used as drinking water sources (see Chapter 1). Although most available data and literature pertain to water use, we discuss water consumption where possible.[1]

We provide an overview of the types of hydraulic fracturing water used (Section 4.2); the amount of water used per well (Section 4.3); and cumulative water use and consumption estimates (Section 4.4).[2] We then discuss these three factors for 15 states where hydraulic fracturing presently occurs and consider the potential for hydraulic fracturing water withdrawals to affect water quantity and quality in localities within those states (Section 4.5). We primarily discuss results at the state and county level because data are most available at these scales. Moreover, states and localities often differ in industry activity, formation type, and water availability, all of which affect potential impacts.[3] Lastly, we provide a synthesis that summarizes major findings, factors affecting the frequency or severity of impacts, uncertainties, and conclusions (Section 4.6).

[1] 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 Underground Injection Control (UIC) Class II injection wells.

[2] In this chapter, cumulative annual water use or water consumption refers to the amount of water used or consumed by all hydraulic fracturing wells in a given area per year.

[3] 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.

4.2. Types of Water Used

Water used for hydraulic fracturing generally comes from surface water (i.e., rivers, streams, lakes, and reservoirs), ground water aquifers, or reused hydraulic fracturing wastewater.[1,2,3] These sources can 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 or ground water resources is largely determined by the amount of water needed and 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 is typically available to supply most of the water needed in the eastern United States, whereas mixed supplies of surface and ground water are used in the more semi-arid to arid western states. In western states that lack available surface water resources, ground water supplies the majority of water needed for fracturing unless alternative sources, such as reused wastewater, are available and utilized. 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 ground water due to concerns over aquifer depletion (Section 4.5).

The reuse of wastewater from past hydraulic fracturing operations can reduce the need for fresh surface or ground water and offset total new water withdrawals for hydraulic fracturing.[4,5] Based on available data, the median reuse of wastewater as a percentage of injected volume is 5% nationally, but this percentage varies by location (Table 4-1).[6,1]

[1] 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.
[2] 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.
[3] We use "wastewater" as a general term to include both flowback and produced water that may be reused in hydraulic fracturing; we do not distinguish between flowback and produced water except when specifically reported in the literature.
[4] 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.
[5] 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.
[6] 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.

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 injected fluid volume may be collected, with values varying across geologic formations (see Chapter 7, Table 7-1). Longer duration measurements are rare, but between 10% and 30% of injected fluid volume has been collected in the Marcellus Shale in Pennsylvania over 9 years of production, while over 100% has been collected in the Barnett Shale in north-central Texas over six years of production (see Chapter 7, Table 7-2). Assuming that 10% of injected fluid volume is collected in the first 30 days and the reuse rate is 100%, 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.

Besides hydraulic fracturing wastewater, other wastewaters may be reclaimed for use in hydraulic fracturing. These may 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.

Table 4-1. Percentage of injected water volume that comes from reused hydraulic fracturing wastewater in various states, basins, and plays.

States listed by order of appearance in the chapter. See Section 4.5 for additional discussion of reuse practices by state and locality and variation over time where data are available.

State, basin, or play	Available estimate	Year of estimate (NA = not available)

[1] 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 injection wells). This distinction is sometimes overlooked, which sometimes leads to a misrepresentation of the extent to which wastewater is reused to offset total fresh water used for hydraulic fracturing.

State, basin, or play	Available estimate	Year of estimate (NA = not available)
Texas—Barnett Shale	5%[a]	2011
Texas—Eagle Ford Shale	0%[a]	2011
Texas—TX-LA-MS Salt Basin[b]	5%[a]	2011
Texas—Permian Basin (far west portion)	0%[a]	2011
Texas—Permian Basin (Midland portion)	2%[a]	2011
Texas—Anadarko Basin	20%[a]	2011
Colorado—Garfield County, Uinta-Piceance Basin	100%[c]	NA
Colorado—Wattenberg Field, Denver-Julesburg Basin	0%[d]	NA
Pennsylvania—Marcellus Shale, Susquehanna River Basin	18%[e]	2012
West Virginia—Marcellus Shale, Statewide	15%[f]	2012
California—Monterey Shale, Statewide	4%[g]	2014
Overall Mean[h]	15%	
Overall Median[i]	5%	

[a] Estimated percentage of recycling/reused water in 2011 (Nicot et al., 2012).
[b] Nicot et al. (2012) refer to this region of Texas as the East Texas Basin.
[c] Based on industry practices reported in U.S. EPA (2015c).
[d] 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).
[e] Volume of flowback injected as a percentage of total water injected, 2012 (Hansen et al., 2013). This is the most recent estimate available. For 2008 to 2011, reuse as a percentage of injected volume averaged 13%, with a median of 8%, according to U.S. EPA (2015c).
[f] Reused fracturing water as a percentage of total water used for hydraulic fracturing, 2012, calculated from data provided by the West Virginia DEP (2014).
[g] Reported data on planned hydraulic fracturing operations as described in 249 well stimulation notices submitted during the first half of January 2014 to CCST (2014). Of these notices, 4% indicated planned use of produced water (sometimes blended with fresh water) for fracturing, while 96% indicated planned use of only fresh water.
[h] The overall mean is not weighted by the number of wells in a given state, basin, or play.
[i] The overall median is not weighted by the number of wells in a given state, basin, or play.

4.2.2. Quality

Water quality is an important consideration when sourcing water for hydraulic fracturing. Fresh water is often preferred 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 FracFocus 1.0 (hereafter the EPA FracFocus report) (U.S. EPA, 2015a), as well as by regional analyses from Texas (Nicot et al., 2012) and the Marcellus (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 by water quality. As a hydraulically fractured well ages, the wastewater quality begins to resemble the water quality of the geologic formation and may be characterized by high 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 wellbore or by interfering with certain chemical 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 may require treatment to meet the level of water quality desired in the hydraulic fracturing fluid formulation. Minimal treatment or blending of wastewater and fresh water is sometimes done to dilute high TDS or other constituents. Fresh water typically makes up the largest proportion of the base fluid when blended with water sources of lesser quality (U.S. EPA, 2015a).[4] However, direct reuse of wastewater with minimal or no treatment is sometimes possible with higher-quality wastewater (U.S. EPA, 2015c) (Section 4.5.2). No data are currently available to characterize the relative frequency of reuse done with treatment, minimal treatment, or no treatment.

4.2.3. Provisioning

Water for hydraulic fracturing is typically either self-supplied by the industry or purchased from public water systems.[5] Self-supplied water for fracturing generally refers to permitted direct

[1] FracFocus is a national hydraulic fracturing registry for oil and gas well operators to disclose information about hydraulic fracturing well locations, and water and chemical use during hydraulic fracturing operations developed by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission (U.S. EPA, 2015a). The registry was originally established in 2011 for voluntary reporting. However, 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, 2015a).
[2] Of all disclosures to FracFocus 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, 2015a).
[3] Service companies did not provide data on the percentage of fresh water versus non-fresh water used for hydraulic fracturing (U.S. EPA, 2015a).
[4] In FracFocus disclosures indicating that fresh water was used in any combination with "recycled," "produced," or "brine," the median concentration of fresh water across all states ranged from 69% to 93% (U.S. EPA, 2015a).
[5] 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 or ground water 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.

withdrawals from surface or ground water or the reuse of wastewater. Nationally, self-supplied water is more common, although there is much regional variation (U.S. EPA, 2015a; CCST, 2014; Mitchell et al., 2013a; Nicot et al., 2012). Public water systems encompass a variety of water suppliers (U.S. EPA, 2015c). 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), national patterns and associated variability (Section 4.3.2), as well as the factors affecting water use per well including well length, geology, and fracturing fluid formulation (Section 4.3.3). More detailed state- and 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 water used and consumed in the upstream portion of the life cycle occurs during hydraulic fracturing (Jiang et al., 2014; Clark et al., 2013; Laurenzi and Jersey, 2013).[1] Water use per well estimates in this chapter focus on hydraulic fracturing in the upstream portion of the oil and gas life cycle.[2]

4.3.2. National Patterns of Water Use Per Well for Fracturing

Hydraulic fracturing for oil and gas requires a large volume of water to create sufficient pressures. According to the EPA's project database of disclosures to FracFocus 1.0 (hereafter the EPA FracFocus project database), the median volume of water used per well, based on

[1] 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, 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.

[2] 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 evaporation (209.0 gal (791.2 L)/MWh).

37,796 disclosures nationally, was 1.5 million gal (5.7 million L) (U.S. EPA, 2015b).[1] There was substantial variability around this median, however, with 10th and 90th percentiles of 74,000 and 6 million gal (280,000 and 23 million L) per well, respectively.[2] Even in specific basins and plays, water use per well varied widely. Water injected also can vary within a single field; Laurenzi and Jersey (2013) reported volumes for the Wattenberg Field of the Niobrara play ranging from 1 to 6 million gal (3.8 to 23 million L) per well (10th to 90th percentile).

4.3.3 Factors Affecting Water Use Per Well

Water use varies depending on many factors, including well length, geology, and the composition of the fracturing fluid.

Well length: Well length is a principal driver of the amount of water used per well. Increases in well length affect total water volumes injected primarily by allowing a larger fracture volume to be stimulated (Economides et al., 2013). Fracture volume is the volume of the fractures in the geologic formation that fill with hydraulic fracturing fluid. The total volume of injected fluid equals fracture volume plus the volume of the wellbore itself, plus any fluid lost due to "leakoff" or other unintended losses.[3] Thus, as wells get longer, fracture, well, and total volumes all increase. This is particularly evident in longer horizontal wells versus vertical wells. For example, median water use in horizontal gas wells was over 35 times higher than in vertical gas wells (2.9 million gal vs. 82,000 gal (11 million L vs. 310,000 L), respectively) between the years 2000 and 2010 (USGS, 2015).

Geology: Geologic characteristics also influence the amount of water used per well. There are three major formation types: shales, tight sands, and coalbeds (see Chapter 2). Reported differences in water use for shales versus tight sands are rare. However, Nicot et al. (2012) reported that total water use in tight sand formations is less than half of that of shale in Texas, although results were not reported per well.

In contrast to hydrocarbons from shales and tight sands, 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, 2015l). Thus, dewatering is often necessary to stimulate production of CBM. In addition, geologic pressures are lower (leading to higher permeability) and well lengths are shorter, all of which result in lower water use per well. Water use per well in CBM operations can be lower by an order of magnitude or more compared to operations in shales or tight sands. For example, Murray (2013) reported water use across formations in Oklahoma, and found that water use in the CBM-dominated Hartshorn Formation was much lower than in the shale gas-dominated Woodford Formation.

[1] Water use data from the EPA's FracFocus project database were obtained from disclosures made to FracFocus 1.0. 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, 2015b). For the purposes of this chapter, we discuss water use per disclosure in terms of water use per well.
[2] 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.
[3] 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. See Chapter 6 for more information about leakoff.

Fracturing Fluid Type: The majority of wells use fracturing fluids that consist mostly of water (U.S. EPA, 2015a; 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, 2015a). 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 (643 disclosures, 84% of non-aqueous formulations) or carbon dioxide (83 disclosures, 11% of non-aqueous formulations). Both of these formulations still contained substantial amounts of water, as water made up roughly 60% (median value) of fluid in them (U.S. EPA, 2015a). Other formulations were rarely reported. Non-aqueous formulations are discussed further in Chapter 5.

4.4. Cumulative Water Use and Consumption

In this section we provide an overview of cumulative water use and consumption for hydraulic fracturing at the national, state, and county scales. We then compare these values to total water use and consumption. We discuss both use and consumption because hydraulic fracturing is both a user and consumer of water. Water use refers to water withdrawn for a specific purpose, part or all of which may be returned to the local hydrologic cycle. Water consumption refers to water that is removed from the local hydrologic cycle following its use, and is therefore unavailable to other users (Maupin et al., 2014). Hydraulic fracturing water consumption can occur through such means as evaporation from storage ponds, the retention of water in the subsurface through imbibition, or disposal in UIC Class II injection wells. In the latter two cases, the water consumed is generally completely removed from the hydrologic cycle. In this section, water consumption estimates are derived from 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

Cumulatively, hydraulic fracturing uses and consumes billions of gallons of water each year in the United States, but at the national or state scale, it is a relatively small user (and consumer) of water compared to total water use and consumption. According to the EPA's FracFocus project database, hydraulic fracturing used 36 billion gal (136 billion L) of water in 2011, and 52 billion gal (197 billion L) in 2012; therefore, hydraulic fracturing used an annual average of 44 billion gal (167 billion L) of water in 2011 and 2012 across all 20 states in the project database (U.S. EPA, 2015a, b). Cumulative 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 project database is multiplied by 25,000 to 30,000 wells fractured annually (see Chapter 2), cumulative national water use for hydraulic fracturing is estimated to range from 37.5 to 45.0 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 50-72 billion gal (190-273 billion L) (U.S. EPA, 2015c). 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 cumulative water use for hydraulic fracturing are small relative to total water use and consumption at the national scale. For example, in the combined 20 states where operators reported water use to FracFocus in 2011 and 2012 (U.S. EPA, 2015b), annual hydraulic fracturing water use and consumption averaged over those two years was less than 1% of total annual water use and consumption in 2010 (see Appendix Table B-1).[2,3]

At the state scale, hydraulic fracturing also generally uses billions of gallons of water cumulatively, but accounts for a low percentage of total water use or consumption. Of all states, operators in Texas used the most water cumulatively (47% of cumulative water use reported in the EPA FracFocus project database) (U.S. EPA, 2015b) (see Appendix Table B-1). This was due to the large number of wells in that state. Over 94% of reported cumulative water use occurred in just seven of the 20 states in the EPA FracFocus project database: Texas, Pennsylvania, Arkansas, Colorado, Oklahoma, Louisiana, and North Dakota (U.S. EPA, 2015b). Hydraulic fracturing is a small percentage when compared to total water use (<1%) and consumption (<3%) in each individual state (see Appendix Table B-1). Other studies have shown similar results, with hydraulic fracturing water use and consumption ranging from less than 1% of total use in West Virginia (West Virginia DEP, 2013), Colorado (Colorado Division of Water Resources; Colorado Water Conservation Board; Colorado Oil and Gas Conservation Commission, 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

Cumulative water use and consumption for hydraulic fracturing is also relatively small in most, but not all, counties in the United States (see Table 4-2, Figure 4-1, and Figure 4-2a,b). Reported

[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 EPA FracFocus project database likely leads to a more robust estimate when used to calculate national cumulative 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 (U.S. EPA, 2015b).

[2] The USGS compiles water use estimates approximately every five years in the National Water Census including the 1995 Census in Solley et al. (1998); 2005 Census in Kenny et al. (2009); and 2010 Census in Maupin et al. (2014). The 2010 version is the most updated version available. The Census includes uses such as public supply, irrigation, livestock, aquaculture, thermoelectric power, industrial, and mining at the national, state, and county scale. The 2010 Census included hydraulic fracturing water use in the mining category; there was no designated category for hydraulic fracturing alone.

[3] Percentages were calculated by averaging annual water use for hydraulic fracturing in 2011 and 2012 for a given state or county (U.S. EPA, 2015b), 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 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). See footnotes for Appendix Table B-1 and Table 4-2 for description of the consumption estimate calculations.

fracturing water use in FracFocus in 2011 and 2012 was less than 1% compared to 2010 USGS total water use in 299 of the 401 reporting counties (U.S. EPA, 2015b) (see Figure 4-2a and 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 (see Table 4-2 and Figure 4-2a). 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) (see Table 4-2 and Figure 4-2b). Note, estimates based on the EPA's FracFocus 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, 2015a). We conclude that this likely does not substantially alter the overall patterns observed in Figure 4-2a,b (see Text Box 4-1 for further details).

These percentages 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 certain county does not necessarily mean it originated in that county. While the cost of trucking water can be substantial (Slutz et al., 2012), and the industry tends to acquire water from nearby sources when possible (see Section 4.2.1), 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 (or 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.

[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 4-2. Annual average 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). Annual average hydraulic fracturing water use data in 2011 and 2012 from the EPA's FracFocus project database (U.S. EPA, 2015b). 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]	Annual average 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

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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]
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
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 as reported to FracFocus (U.S. EPA, 2015b).
[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, 2015b), 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 (USGS, 2014h). 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 UIC Class II injection wells—see Chapter 8).

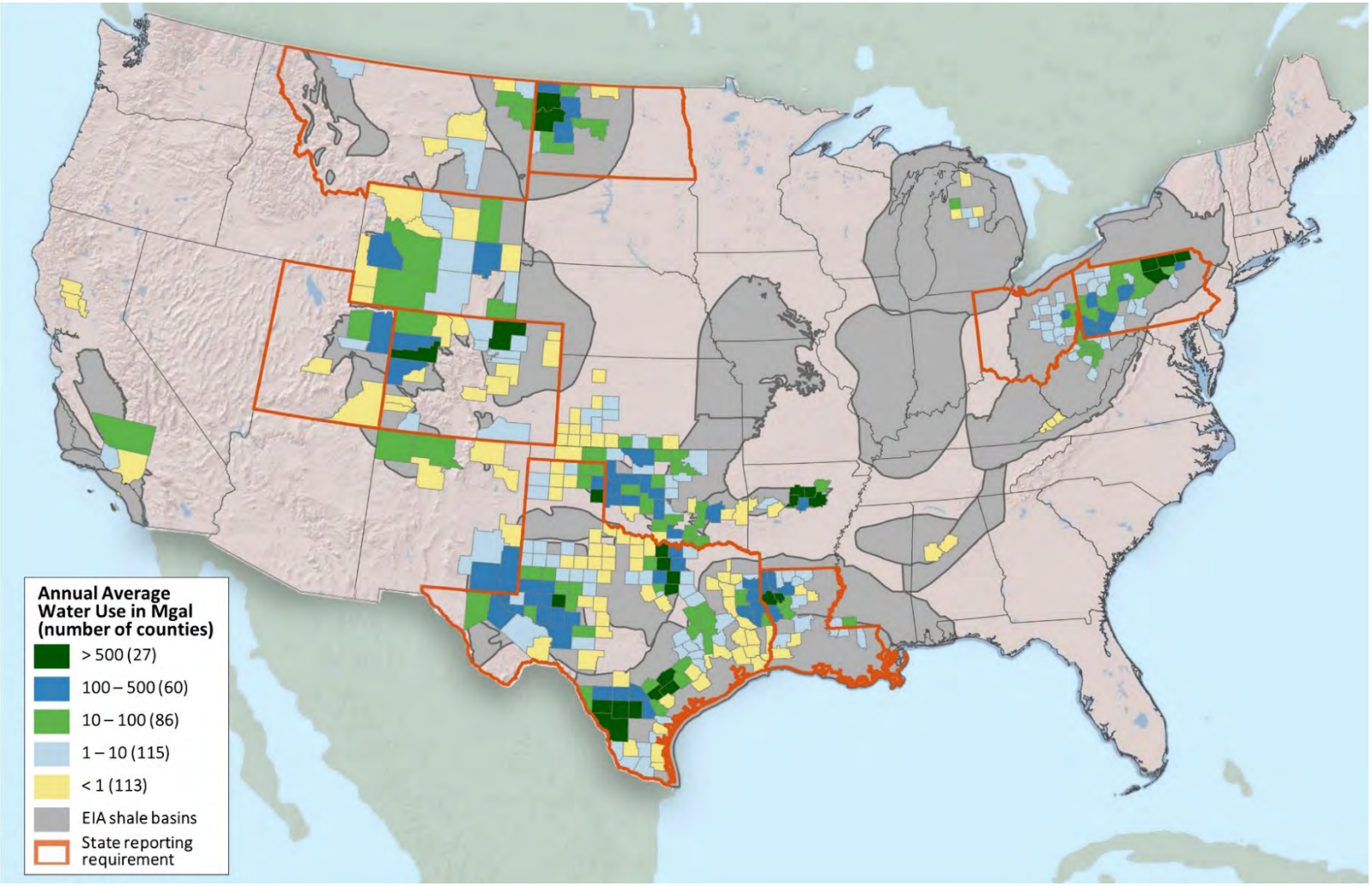
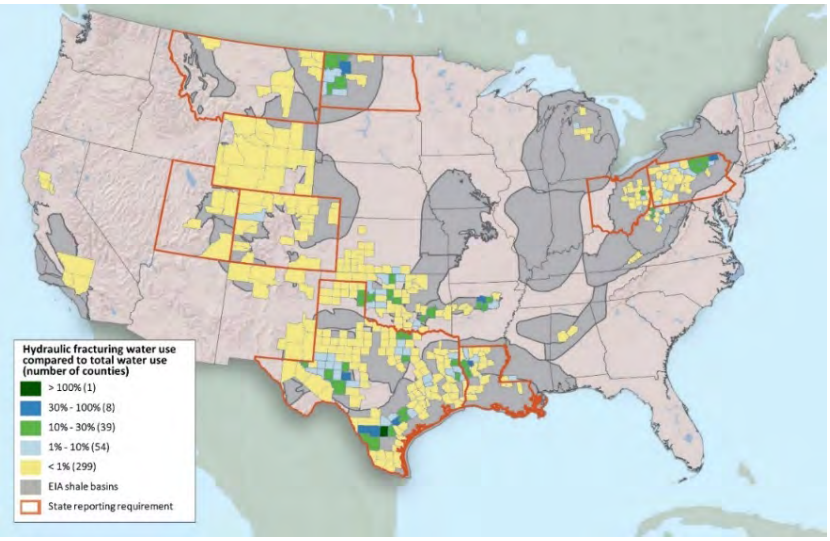
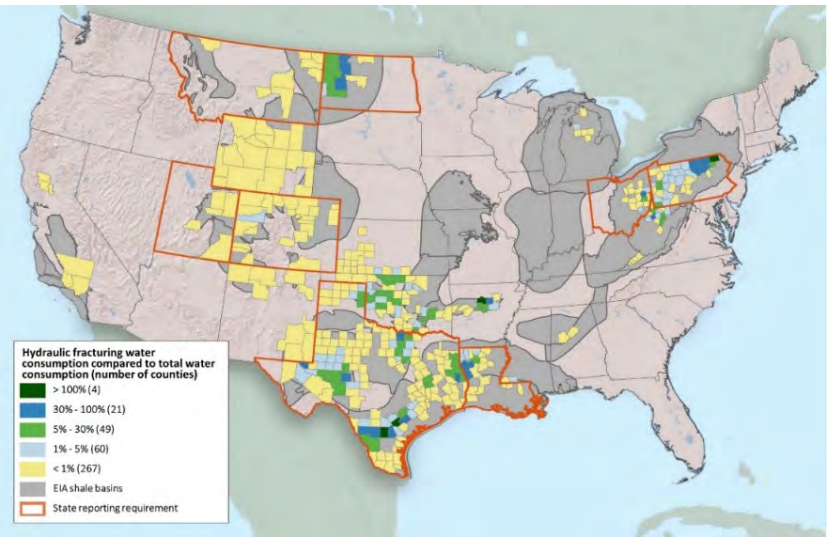


Figure 4-1. Annual average hydraulic fracturing water use in 2011 and 2012 by county (U.S. EPA, 2015b).

Source: (U.S. EPA, 2015b). Water use in millions of gallons (Mgal). Counties shown with respect to major U.S. Energy Information Administration (EIA) shale basins (EIA, 2015b). Orange borders identify states that required some degree of reporting to FracFocus 1.0 in 2011 and 2012.



(a)



(b)

Figure 4-2. (a) Annual average hydraulic fracturing water use in 2011 and 2012 compared to total annual water use in 2010, by county, expressed as a percentage; (b) Annual average hydraulic fracturing water consumption in 2011 and 2012 compared to total annual water consumption in 2010, by county, expressed as a percentage.

Annual average hydraulic fracturing water use data in 2011 and 2012 from the EPA's FracFocus project database (U.S. EPA, 2015b). Total annual water use data in 2010 from the USGS (Maupin et al., 2014). See Table 4-2 for descriptions of calculations for estimating consumption. Counties shown with respect to major U.S. EIA shale basins (EIA, 2015b). Orange borders identify states that required some degree of reporting to FracFocus 1.0 in 2011 and 2012. Note: Values over 100% denote counties where the annual average 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 Project Database to Estimate Water Use for Hydraulic Fracturing.

FracFocus is a national hydraulic fracturing registry managed by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission (GWPC, 2015). The registry was established in 2011 for voluntary reporting. However, 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 (U.S. EPA, 2015a). Estimates based on the EPA's FracFocus project database likely 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, 2015a).

Cumulative water use for fracturing is a function of the water use per well and the total number of wells fractured. For water use per well, we found seven literature values for comparison with values from the EPA's FracFocus 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%) (see Appendix Table B-3). In general, water use per well estimates from the EPA's FracFocus project database appear to provide a reasonable approximation for most areas for which we have data, with the exception of the Denver Basin of Colorado.

For number of wells, we compared data in the EPA's FracFocus project database to numbers available in state databases from North Dakota, Pennsylvania, and West Virginia (see Appendix Table B-4). These were the state databases from which we could distinguish hydraulically fractured wells from total oil and gas wells. On average, we found that the EPA FracFocus project database included 67% of the wells listed in state databases for 2011 and 2012 (see 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 project database values of 77% for water use per well and 67% for well counts yields 52%. Thus, the EPA FracFocus 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 a small sample sizes (7 literature values and 3 state databases) and should be interpreted with caution. Nevertheless, these numbers at the very least suggest that estimates based on the EPA's FracFocus project database may 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 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% of 2010 total water use in the majority of U.S. counties (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 project database likely do not substantially alter the overall pattern shown in Figure 4-2. 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 Water Use Impacts by State

High fracturing water use or consumption alone does not necessarily result in impacts to drinking water resources. Rather, impacts most often result from the combination of water use and water availability at a given withdrawal point. Where water availability is high compared to water

withdrawn for hydraulic fracturing, this water use can be accomodated. However, where water availability is low compared to use, hydraulic fracturing withdrawals are more likely to impact drinking water resources. Water management, such as the type of water used or the timing or location of withdrawals, can modify this relationship. All of these factors can vary considerably by location.

Besides potential water quantity effects, water withdrawals for hydraulic fracturing have the potential to alter the quality of drinking water resources. This possibility is not unique to the oil and gas industry, as any large-volume water withdrawal has the potential to affect water quality. Although there is little research that specifically connects water withdrawals for hydraulic fracturing to potential water quality impacts, multiple studies have described the impact of drought or industrial withdrawals on water quality (Georgakakos et al., 2014; Whitehead et al., 2009; Murdoch et al., 2000; Schindler, 1997). For instance, in the absence of controls, surface water withdrawals can lower water levels and alter stream flows, potentially decreasing a stream's capacity to dilute contaminants (Mitchell et al., 2013a; Entrekin et al., 2011; NYSDEC, 2011; van Vliet and Zwolsman, 2008; IPCC, 2007; Environment Canada, 2004; Murdoch et al., 2000). Furthermore, ground water withdrawals exceeding natural recharge rates may lower the water level in aquifers, potentially mobilizing contaminants or allowing the infiltration of lower-quality water from the land surface or adjacent formations (USGS, 2003; Jackson et al., 2001).

In the following section, we assess the potential for water quantity and quality impacts by location, organized by state. We focus our discussion on the 15 states that account for almost all disclosures reported in the EPA FracFocus project database (U.S. EPA, 2015b): 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); Oklahoma and Kansas (Section 4.5.5); Arkansas and Louisiana (Section 4.5.6); and Utah, New Mexico, and California (Section 4.5.7).[1] Each section describes the extent of hydraulic fracturing activity in that state or group of states; the type of water used in terms of source, quality, and provisioning; and the water use per well. We then discuss cumulative estimates and the potential for impacts to drinking water resources in the context of water availability.

We have ordered the states by the number of hydraulically fractured wells reported, and combined states with similar geographies or activity. Most of the available data did not allow us to assess the potential for impacts at a finer resolution than the county scale. Any potential adverse impacts are most likely to be observed locally at a particular withdrawal point. Therefore, our analysis most often suggests where the potential for impacts exists, but does not indicate where impacts will occur at the local scale. Where possible, we utilize local-scale case studies in southern Texas, western Colorado, and eastern Pennsylvania to provide details at a much finer resolution, and offer insight into whether any impacts from water acquisition for hydraulic fracturing were realized in these areas.

[1] We do not highlight the remaining five states included in the EPA FracFocus project database because of low reported activity: Virginia (90 disclosures), Alabama (55), Alaska (37), Michigan (15), and Mississippi (4).

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 project database (U.S. EPA, 2015b) (see Figure 4-3 and 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 (see Figure 4-4); together, these five basins contain 99% of Texas' reported wells (see Appendix Table B-5).

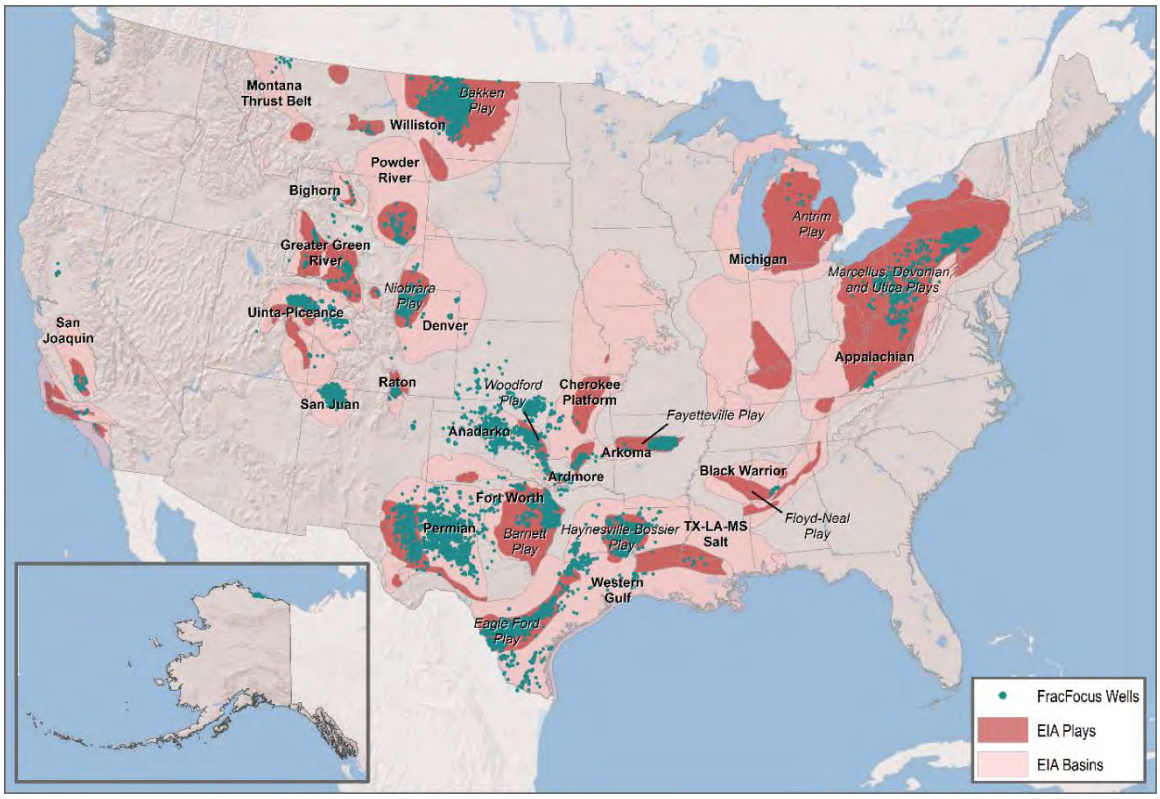


Figure 4-3. Locations of wells in the EPA FracFocus project database, with respect to U.S. EIA shale plays and basins (EIA, 2015; US. EPA, 2015b).

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

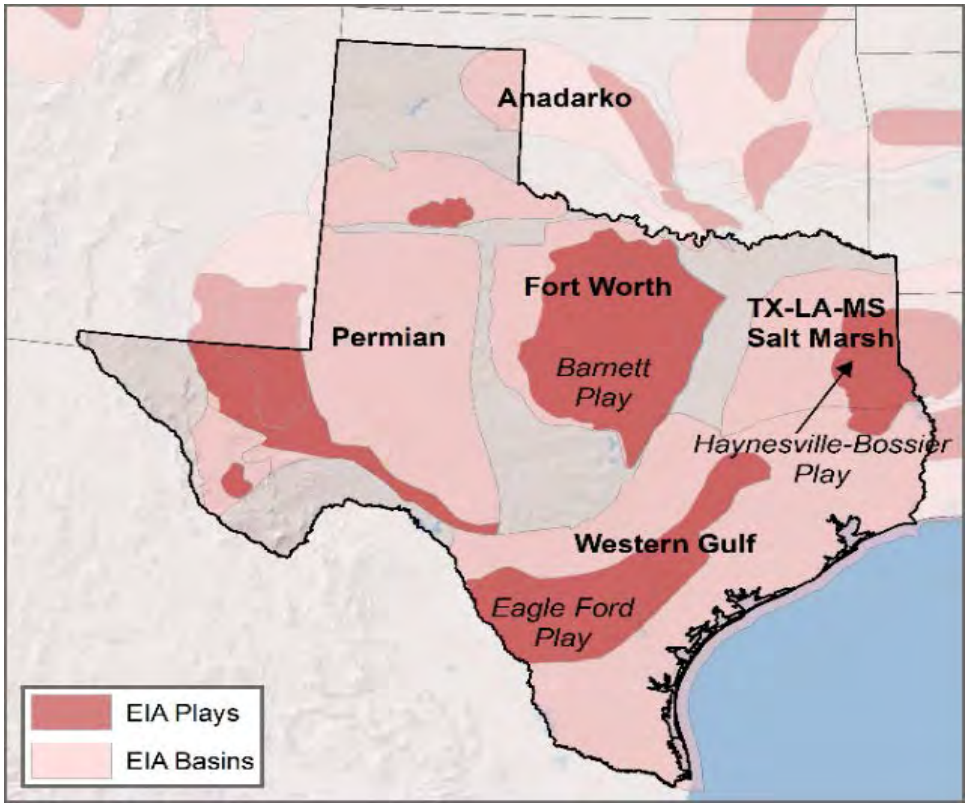


Figure 4-4. Major U.S. EIA shale plays and basins for Texas (EIA, 2015).

Source: (EIA, 2015b)

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, ground water is the dominant source throughout most of the state (Nicot et al., 2014; Nicot et al., 2012) (see Table 4-3). The exception is the Barnett Shale, where both surface and ground water 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 and the Midland portion of the Permian Basin (see Table 4-4). Reuse of wastewater as a percentage of total water injected is generally very 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) (see Table 4-1).

[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, 2015a). However, 19% of Texas disclosures included information related to water sources (U.S. EPA, 2015a).

Table 4-3. Estimated proportions of hydraulic fracturing source water from surface and ground water.

States listed by order of appearance in the chapter.

Location	Surface water	Ground water
Texas—Barnett Shale	50%[a]	50%[a]
Texas—Eagle Ford Shale	10%[b]	90%[b]
Texas—TX-LA-MS Salt Basin[c]	30%[b]	70%[b]
Texas—Permian Basin	0%[b]	100%[b]
Texas—Anadarko Basin	20%[b]	80%[b]
Pennsylvania—Marcellus Shale, Susquehanna River Basin	78%[d]	22%[d]
West Virginia—Statewide, Marcellus Shale	91%[e]	9%[e]
Oklahoma—Statewide	63%[f]	37%[f]
Louisiana—Haynesville Shale	87%[g]	13%[g]

[a] Nicot et al. (2014).

[b] Nicot et al. (2012).

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

[d] Estimated proportions are for 2011 (U.S. EPA, 2015c).

[e] 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 or ground water. Therefore, we excluded purchased water in calculating the relative proportions of surface and ground water shown in Table 4-3 (West Virginia DEP, 2014).

[f] Proportion of surface and ground water 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).

[g] Data from October 1, 2009, to February 23, 2012, for 1,959 Haynesville Shale natural gas wells (LA Ground Water Resources Commission, 2012).

Table 4-4. Brackish water use as a percentage of total hydraulic fracturing water use in Texas' main hydraulic fracturing areas, 2011.

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

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

[a] 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%.

[b] 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 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 (see Appendix 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 horizontal well increased from a median of 1.25 million gal (4.73 million L) in 2001 to 4.7 million gal (17.8 million L) in 2012, as the number of wells and horizontal lengths increased (Nicot et al., 2014). Similar increases in lateral length and water use per well were reported for the Texas-Haynesville, East Texas, Anadarko, and most of the Permian Basin (Nicot et al., 2012; Nicot and Scanlon, 2012).[1]

[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).

Cumulative water use/consumption: Cumulative 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 nationwide where fracturing water use in 2011 and 2012 was 30% or more compared to total water use in those counties in 2010 (see Table 4-2, Figure 4-2a, and Appendix Table B-2).[1,2]

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). The majority of counties are expected to have relatively low cumulative water use for fracturing in the future, but cumulative 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 (see Appendix Table B-7). Thus, potential hydraulic fracturing water acquisition impacts in Texas may be most likely to occur over the next 15–25 years as water demand for fracturing is highest.

Potential for impacts: Of all locations surveyed in this chapter, the potential for water quantity and quality impacts due to hydraulic fracturing water use appears to be highest in western and southern 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 (see Text Box 4-2 and Figure 4-5). The Texas Water Development Board 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). Moreover, the state has experienced moderate to extreme drought conditions for much of the last decade (National Drought Mitigation Center, 2015). The 2012 Texas State Water Plan emphasizes that "in serious drought conditions, Texas does not and will not have enough water to meet the needs of its people, its businesses, and its agricultural enterprises" (TWDB, 2012).

[1] 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 (see Table 4-2).
[2] 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 cumulative 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 19.3% 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.

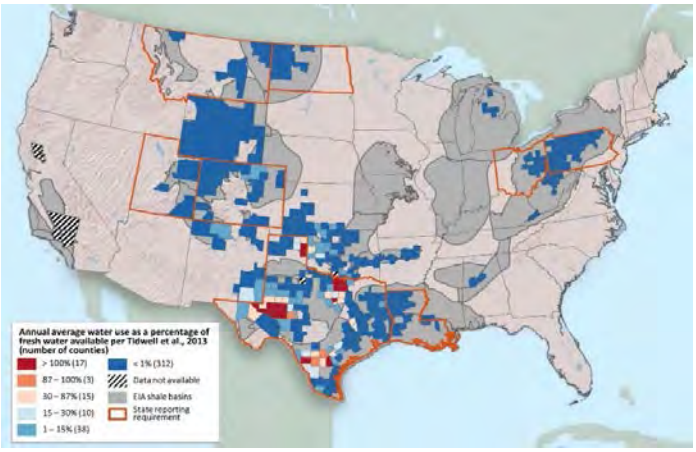
Researchers at Sandia National Laboratories assessed county-level water availability across the continental United States (Tidwell et al., 2013). Assessments of water availability in the United States are generally lacking at the county scale, and this analysis—although undertaken for siting new thermoelectric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

The authors generated annual availability estimates for five categories of water: unappropriated surface water, unappropriated ground water, 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.

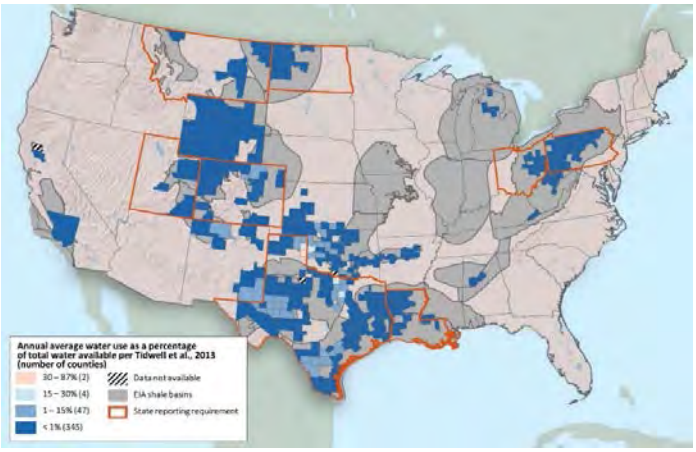
Combining their estimates of unappropriated surface and ground water and appropriated water potentially available for purchase, we derived a fresh water availability estimate for each county (except for those in California) and then compared this value to reported water use for hydraulic fracturing (U.S. EPA, 2015b). We also added the estimates of brackish and wastewater 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.

Overall, hydraulic fracturing water use represented less than 1% of fresh water availability in over 300 of the 395 counties analyzed (see Figure 4-5a). 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 (see Figure 4-4). 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) (see Figure 4-5b). 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 confirms this (see Text Box 4-3).

Text Box 4.2 (continued): Hydraulic Fracturing Water Use as a Percentage of Water Availability Estimates.



a



b

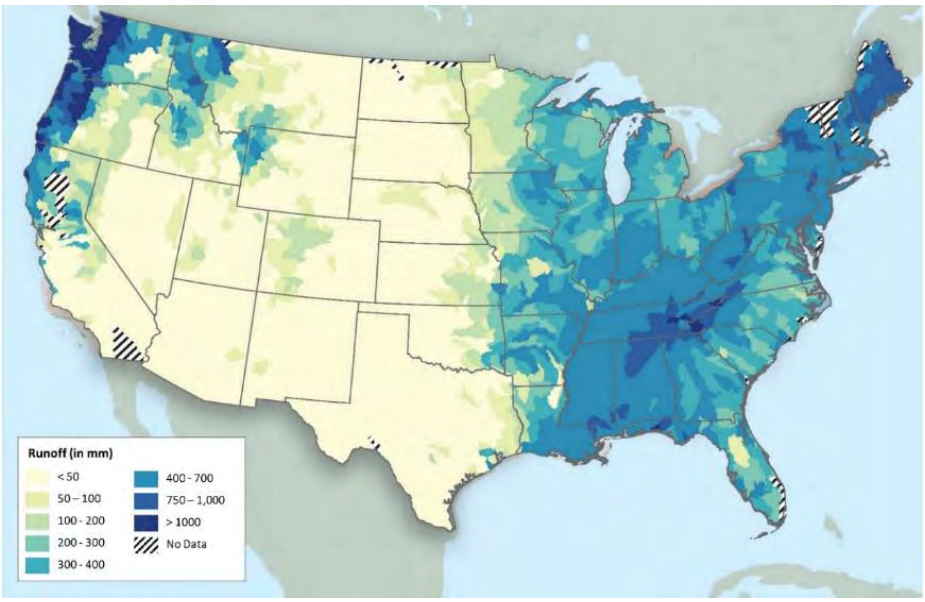
Figure 4-5. Annual average hydraulic fracturing water use in 2011 and 2012 compared to (a) fresh water available and (b) total water (fresh, brackish, and wastewater) available, by county, expressed as a percentage.

Counties shown with respect to major U.S. EIA shale basins (EIA, 2015b). Orange borders identify states that required some degree of reporting to FracFocus 1.0 in 2011 and 2012. Data from U.S. EPA (2015b) 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 (a). The total water available for California is the sum of brackish water plus wastewater only (b).

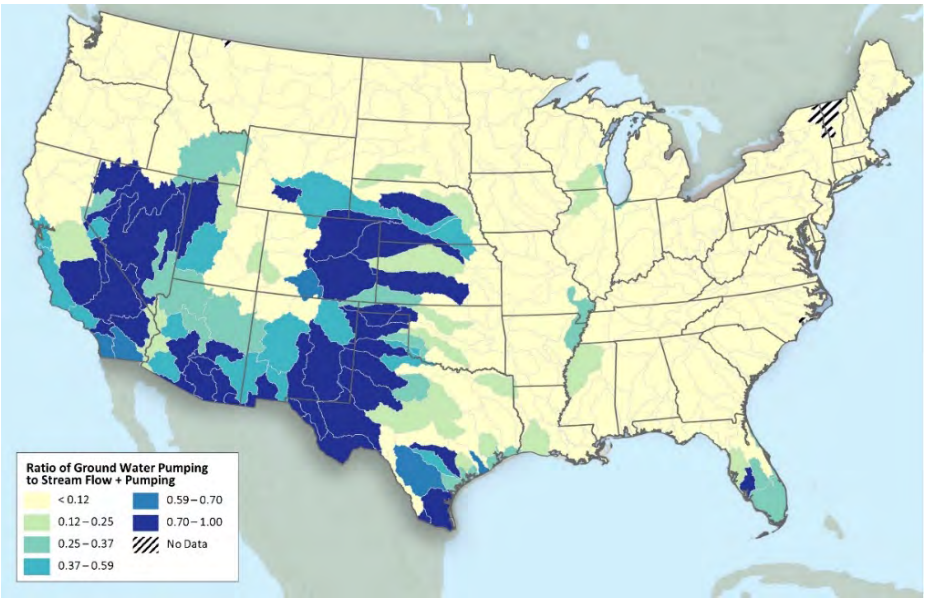
Surface water availability is generally low in western and southern Texas (Figure 4-6a), and both fracturing operations and residents rely heavily on ground water (Figure 4-6b). Similar to trends nationally, ground water aquifers in Texas have experienced substantial declines caused by withdrawals (Konikow, 2013b; TWDB, 2012; George et al., 2011). Ground water in the Pecos Valley, Gulf Coast, and Ogallala aquifers in southern and western Texas is estimated to have declined by roughly 5, 11, and 43 cubic miles (21, 45.5, and 182 cubic kilometers), respectively, between 1900 and 2008 (Konikow, 2013b).[1] The Texas Water Development Board expects ground water supply in the major aquifers to decline by 30% between 2010 and 2060, mostly due to declines in the Ogallala aquifer (TWDB, 2012).[2] Irrigated agriculture is by far the dominant user of water from the Ogallala aquifer (USGS, 2009), but fracturing operations, along with other uses, now contribute to the aquifer's depletion.

[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. Ground water depletion from the Carrizo-Wilcox aquifer is included in the estimate for the southern portion of the Gulf Coast aquifer (Konikow, 2013b).

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



(a)



(b)

Figure 4-6. (a) Estimated annual surface water runoff from the USGS; (b) Reliance on ground water as indicated by the ratio of ground water pumping to stream flow and pumping.

Estimates for Figure 4-6a 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, 2014g). Higher ratios (darker blues) in Figure 4-6b indicate greater reliance on ground water. Figure redrawn from Tidwell et al. (2012), using data provided by the U.S. Department of Energy's Sandia National Laboratories on December 12, 2014.

Extensive ground water pumping can induce vertical mixing of high-quality ground water with recharge water from the land surface that has been contaminated by nitrate or pesticides, or with lower-quality ground water from underlying geologic formations (USGS, 2009; Konikow and Kendy, 2005). Ground water quality degradation associated with aquifer pumping is well documented in the southern portion of the Ogallala aquifer in the Texas panhandle. The quality of ground water 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; USGS, 2009, 2007). Elevated levels of these constituents result from both natural processes and human activities such as ground water pumping (Chaudhuri and Ale, 2014a; USGS, 2009). Similar patterns of ground water quality degradation (i.e., salinization and contamination) have also been observed in other Texas aquifers.[1]

Ground water 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 ground water pumping are most likely to experience ground water quality degradation associated with withdrawals (USGS, 2009, 2007). Given that Texas is prone to drought conditions, ground water recharge is limited, making the already declining aquifers in southern and western Texas especially vulnerable to further ground water depletion and resulting potential impacts to ground water quality (USGS, 2009; Jackson et al., 2001).

This survey of the available literature and data points to the potential for impacts in southern and western Texas, but generally does not indicate whether impacts will occur at the local scale around specific withdrawal points. An exception is a case study in the Eagle Ford play of southwestern Texas that compared water demand for hydraulic fracturing with water supplies at the scale of the play, county, and one square mile (Scanlon et al., 2014). The authors observed generally adequate water supplies for hydraulic fracturing, except in specific locations, where they found excessive drawdown of local ground water in a small proportion (~6% of the area) of the Eagle Ford play (see Text Box 4-3).

[1] Persistent salinity has also been observed in west Texas, specifically in the southern Ogallala, northwest Edwards-Trinity (plateau), and Pecos Valley aquifers, largely due to prolonged irrigational ground water pumping and ensuing alteration of hydraulic gradients leading to ground water mixing (Chaudhuri and Ale, 2014b). High levels of ground water 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, 2013b; 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).

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., 2014). 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. (2014) compared water demand for hydraulic fracturing currently and over the projected play life (20 years) relative to water supply from ground water recharge, ground water storage (brackish and fresh), and stream flow. Using detailed ground water availability models developed by the Texas Water Development Board, they reported that water demand for hydraulic fracturing in 2013 was 30% of annual ground water 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 ground water storage. The dominant water user in the play is irrigation (62 to 65% of water use, 53 to 55% 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 ground water supplies (Maverick).

Although supply was found to be sufficient even in this semi-arid region, there were important caveats 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 ground water drawdowns of up to 50 feet (12% of the play area), and in others of 100 feet or more (6% of the play area). This was corroborated with well monitoring data that showed a sharp decline in water levels in several ground water monitoring wells after hydraulic fracturing activity increased in 2009. The researchers concluded that any impacts in these locations could be minimized if brackish ground water were used. Projected hydraulic fracturing water use represents less than 1% of total brackish ground water storage in the play area. By contrast, they concluded there is limited potential for reuse of wastewater in this play because of small volumes available (less than or equal to 5% of hydraulic fracturing water requirements).

The potential for water quantity and quality effects appears to be lower in north-central and eastern Texas, 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 ground water and surface water sources (see Appendix Table B-6). Counties encompassing Dallas and Fort Worth rely mostly on publically-supplied surface water (TWDB, 2012) (see Appendix Table B-6).

Although the Trinity, the major aquifer in northeast Texas, is projected to decline only slightly between 2010 and 2060 (TWDB, 2012), Bene et al. (2007) estimate that hydraulic fracturing ground water withdrawals will increase from 3% of total ground water use in 2005 to 7%–13% in 2025, suggesting the potential for localized aquifer drawdown and potential impacts to water quality. Additionally, ground water quality degradation associated with aquifer drawdown has been documented in the Trinity and Woodbine aquifers underlying 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. Impacts are likely to be localized drawdowns of ground water, as shown by a detailed case study of the Eagle Ford play (see Text Box 4-3). Scanlon et al. (2014) suggested that a shift towards brackish water use could minimize potential future impacts to fresh water resources. This finding is consistent with our county-level data (see Text Box 4-2).

4.5.2. Colorado and Wyoming

Colorado had the second highest number of disclosures in the EPA FracFocus project database, (13% of disclosures) (see Figure 4-3 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 (see Figure 4-7). 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 (see Appendix Table B-5). Fewer wells (roughly 4% of disclosures) are present 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 (see Appendix Table B-5).

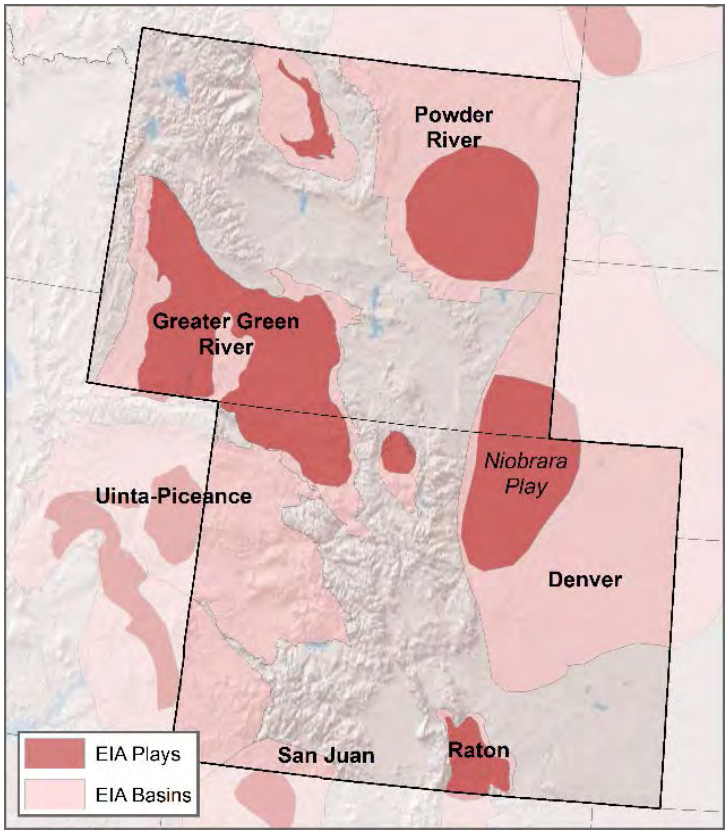


Figure 4-7. Major U.S. EIA shale plays and basins for Colorado and Wyoming (EIA, 2015).

Source: (EIA, 2015b)

Types of water used: Water for hydraulic fracturing in Colorado and Wyoming comes from both ground water and surface water, as well as reused wastewater (Colorado Division of Water Resources; Colorado Water Conservation Board; Colorado Oil and Gas Conservation Commission, 2014; BLM, 2013b). The only publicly available information on water sources for each state is a list of potential sources; it does not appear that either state provides more specific information on water sources for hydraulic fracturing. In the Uinta-Piceance Basin of northwestern Colorado, the EPA (2015c) reports that most of the fresh water used for fracturing comes from surface water, although fresh water sources make up a small proportion of the total water used. In the Denver Basin (Niobrara play) of southeastern Wyoming, qualitative information suggests that ground water supplies much of the water used for fracturing, although no data were available to characterize the ratio of ground water to surface water withdrawals (AMEC, 2014; BLM, 2013b; Tyrrell, 2012).

Non-fresh water sources (e.g., industrial and municipal wastewater, brackish ground water, 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; Colorado Water Conservation Board; Colorado Oil and Gas Conservation Commission, 2014; BLM, 2013b); no data are available to show the extent to which these non-fresh water sources are used at the state or basin level. In northwest Colorado's Garfield County (Uinta-Piceance Basin), the EPA (2015c) reports that fresh water is used solely for drilling and that reused wastewater supplies nearly all the water for hydraulic fracturing (see Table 4-1). This estimate of reused wastewater as a percentage of injected volume is markedly higher than in other locations and 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, 2015c).

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 (see Table 4-1). 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 EPA (2015c) 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 363,000 L) in the Uinta-Piceance, Denver, and Raton Basins, respectively according to the EPA FracFocus project database (see Appendix Table B-5). Low water volumes per well are reported in Wyoming (see Appendix Table B-5). Low volumes reported for the Raton Basin of Colorado and the Powder River Basin of Wyoming are due to the prevalence of CBM extraction in these locations (U.S. EPA, 2015l; USGS, 2014d).

More difficult to explain are the low volumes reported for the Denver Basin in the EPA FracFocus project database. These values are lower than any other non-CBM basin reported in Appendix Table B-5. Goodwin et al. (2014) report much higher water use per well in the Denver Basin, 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 to 14.4 million L) from Goodwin et al. (2014) are almost completely above those from the EPA FracFocus project database for the Denver Basin (see Appendix Table B-5).[1] It is difficult to draw clear conclusions because of differences in scale (i.e., field in Goodwin versus basin in the project database) and operators (i.e., Noble Energy in Goodwin versus all in the project database). However, it seems plausible that the EPA FracFocus project database may be incomplete for estimating the amount of water used per well in the Denver Basin.

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.

Cumulative water use/consumption: Hydraulic fracturing operations in Colorado cumulatively use billions of gallons of water, but this amount is a small percentage compared to total water used or consumed at the county scale. Operators in both Garfield and Weld Counties, located in the Uinta-Piceance and Denver Basins, respectively, use more than 1 billion gal (3.8 billion L) annually. Fracturing water use and consumption in these counties exceed those in all other Colorado counties combined (see Appendix Table B-2), but the water used for hydraulic fracturing in Garfield and Weld counties is 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; Kenny et al., 2009). Overall, hydraulic fracturing accounts for less than 2% compared to 2010 total water use in all Colorado counties represented in the EPA FracFocus project database (see Appendix Table B-2). Water use estimates based on the EPA FracFocus 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 5.5% 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 (see Appendix Table B-1). Fracturing water use and consumption did not exceed 1% of 2010 total water use and consumption, respectively, in any county (see Appendix Table B-2). Unlike Colorado, Wyoming did not require disclosure to FracFocus during the time period analyzed by the EPA (U.S. EPA, 2015a) (see Appendix Table B-5).

The Colorado Division of Water Resources et al. (2014) project that annual water use for hydraulic fracturing in the state will increase by approximately 16% between 2012 and 2015, but demand in

[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 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.

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.

Potential for impacts: The potential for water quantity and quality impacts 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 (see Figure 4-2a,b). This conclusion is also supported by the comparison of hydraulic fracturing water use to water availability at the county scale (see Text Box 4-2 and Figure 4-5a,b). However, counties in Colorado and Wyoming may be too large to detect the potential for impacts, and local scale studies help provide details at a finer resolution. In a multi-scale case study in western Colorado, the EPA (2015c) also did not observe any impacts in the Upper Colorado River Basin. Due to the high reuse rate of wastewater, they did not identify any locations where fracturing currently contributed to locally high water use intensity. They did conclude, however, that future water use effects were possible (see 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 EPA (2015c) 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. Fresh water is used only for drilling, and the water used for fracturing is reported to be 100% reused wastewater (see Table 4-1). Due to the high reuse rate, The EPA (2015c) 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 EPA (2015c) 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 4 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, sub-county effects may be possible given the combination of high hydraulic fracturing activity and low water availability, but lack of available data and literature at this 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 ground water control areas, which were established as management districts in the southeast portion of the state in response to declining ground water levels (AMEC, 2014; Wyoming State Engineer's Office, 2014; Tyrrell, 2012; Bartos and Hallberg, 2011). Ground water withdrawals for hydraulic fracturing may have the potential to contribute to water quality degradation particularly in these areas.

Overall, the potential for impacts appears low at the county scale in Colorado and Wyoming, but sub-county effects may be 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 project database (6.5% of disclosures) (see Appendix Table B-5 and Figure 4-3). 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) (see Figure 4-8); however, much less activity is reported in these two states (see Appendix Table B-5).

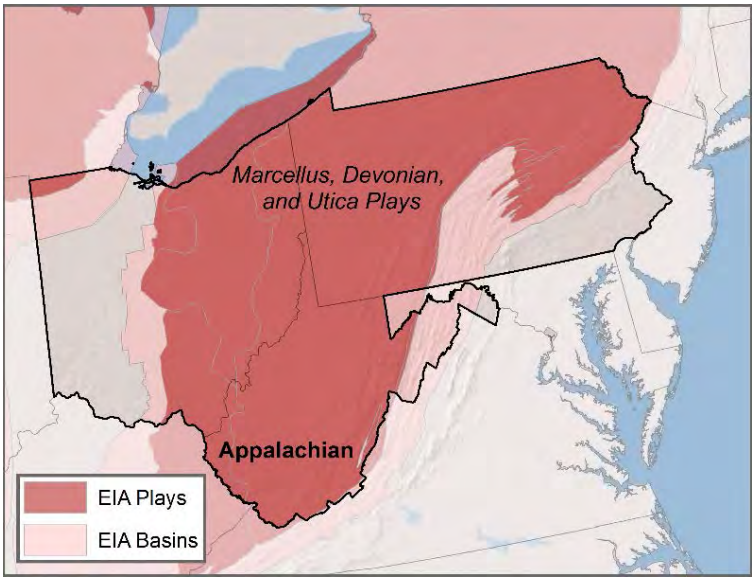


Figure 4-8. Major U.S. EIA shale plays and basins for Pennsylvania, West Virginia, and Ohio (EIA, 2015).

Source: (EIA, 2015b).

Types of water used: Surface water is the primary water source for hydraulic fracturing in Pennsylvania, West Virginia, and Ohio (Mitchell et al., 2013a; SRBC, 2013; West Virginia DEP, 2013; Ohio EPA, 2012b). Available data for Pennsylvania are specific to the Susquehanna River Basin (SRB), where hydraulic fracturing water is sourced mostly from surface water (SRBC, 2013) (see Table 4-3). The industry also uses mostly surface water in West Virginia (West Virginia DEP, 2014, 2013) (see Table 4-3). Although specific data are not available, state reports indicate that most water for hydraulic fracturing in Ohio's Marcellus or Utica Shale formations is sourced from nearby surface water bodies (Ohio EPA, 2012b; STRONGER, 2011b).

Given that surface water is the primary water source, the water used for hydraulic fracturing is most often fresh water in all three states. In both Pennsylvania's SRB and throughout West Virginia, most water for hydraulic fracturing is self-supplied via direct withdrawals from surface water and ground water (U.S. EPA, 2015a; 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 may be used as well, particularly in urban areas of Ohio (STRONGER, 2011b).

Reused hydraulic fracturing wastewater accounted for an estimated 18% and 15% of total water used for fracturing in 2012 in Pennsylvania's SRB and West Virginia, respectively (West Virginia DEP, 2014; Hansen et al., 2013; SRBC, 2013) (see Table 4-1). Available data indicate increased reuse of wastewater over time in this region likely due to the lack of nearby disposal options; from 2010-2012 reused wastewater as a percentage of injected water volume ranged from 10% to 18% and 6% to 15% in Pennsylvania's SRB and West Virginia, respectively (West Virginia DEP, 2014; Hansen et al., 2013). In Ohio's Marcellus and Utica Shales, reuse of wastewater is reportedly uncommon (STRONGER, 2011b), potentially due to the prevalence of disposal wells in Ohio (see Chapter 8).

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 nationally in the EPA FracFocus project database, with 5.0, 4.2, and 3.9 million gal (18.9, 15.9, and 14.8 million L) per well in West Virginia, Pennsylvania, and Ohio, respectively (U.S. EPA, 2015b) (see Appendix Table B-5). Hansen et al. (2013) report similar water use estimates for Pennsylvania and West Virginia (see 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, 2015a), Mitchell et al. (2013a) report an average of 2.3 million gal (8.7 million L) for vertical wells (62 wells) and 4.6 million gal (17.4 million L) for horizontal wells (612 wells) in the Pennsylvania portion of the 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 project database listed above.

Cumulative water use/consumption: In this tri-state region, highest cumulative 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) cumulatively reported 500 million gal (1.9 billion L) or more used annually (see Table 4-2). On average, hydraulic fracturing water use is 3.2% compared to 2010 total county water use for counties with disclosures in the EPA FracFocus project database in these three states (see Table 4-2 and 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 quantity and quality. At the county scale, water supplies appear adequate to accommodate this use (Tidwell et al., 2013) (see Text Box 4-2 and Figure 4-5a,b).

However, impacts could still occur at specific withdrawal points. In a second, multi-scale case study, EPA researchers concluded that individual streams in this region can be vulnerable to typical hydraulic fracturing water withdrawals depending on stream size, as defined by contributing basin area (U.S. EPA, 2015c) (see 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). Passby flows can reduce the frequency of high consumption-to-stream flow events, particularly in the smallest streams (U.S. EPA, 2015c).[1]

[1] A passby flow is a prescribed, low stream flow threshold below which withdrawals are not allowed. The SRBC uses passby flows to protect streams in the Susquehanna River Basin, an area including much of eastern Pennsylvania (U.S. EPA, 2015c).

Text Box 4-5. Case Study: Impact of Water Acquisition for Hydraulic Fracturing on Local Water Availability in the Susquehanna River Basin.

The EPA (2015c) conducted a second case study analogous to that in the UCRB (see 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 (see 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 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 makes up approximately 13% to 18% of injected fluid volume on average, as reported by the EPA (2015c) for 2008 to 2011 and Hansen et al. (2013) for 2012, respectively (see Table 4-1). 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 halt water withdrawals during low flows.

The EPA (2015c) demonstrated that streams can be vulnerable from typical 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 EPA (2015c) showed an increased likelihood of impacts in small watersheds (less than 10 mi^2). Furthermore, they showed that in the absence of passby flows, even larger watersheds (up to 600 mi^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.

Without management of the rate and timing of withdrawals, surface water withdrawals for hydraulic fracturing have the potential to affect both water quantity and quality (Mitchell et al., 2013a). Potential effects are generally applicable, but are especially relevant in this region because surface water is the primary water source for hydraulic fracturing in Pennsylvania, West Virginia, and Ohio. Of greatest concern are small, unregulated streams, particularly under drought conditions or during seasonal low flows (U.S. EPA, 2015c; 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 (U.S. EPA, 2015c; NYSDEC, 2011).[1] Water quality impacts

[1] 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).

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).[1]

Overall, there appears to be adequate surface water for hydraulic fracturing, but there is the potential for impacts to both drinking water quantity and quality, particularly in small streams, if withdrawals are not managed (U.S. EPA, 2015c).

4.5.4. North Dakota and Montana

North Dakota was fourth in the number of disclosures in the EPA FracFocus project database (5.9% of disclosures) (see Appendix Table B-5 and Figure 4-3). We combine Montana with North Dakota because both overlie the Williston Basin (which contains the Bakken play, shown in Figure 4-9), although many fewer wells are reported for Montana (see 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).

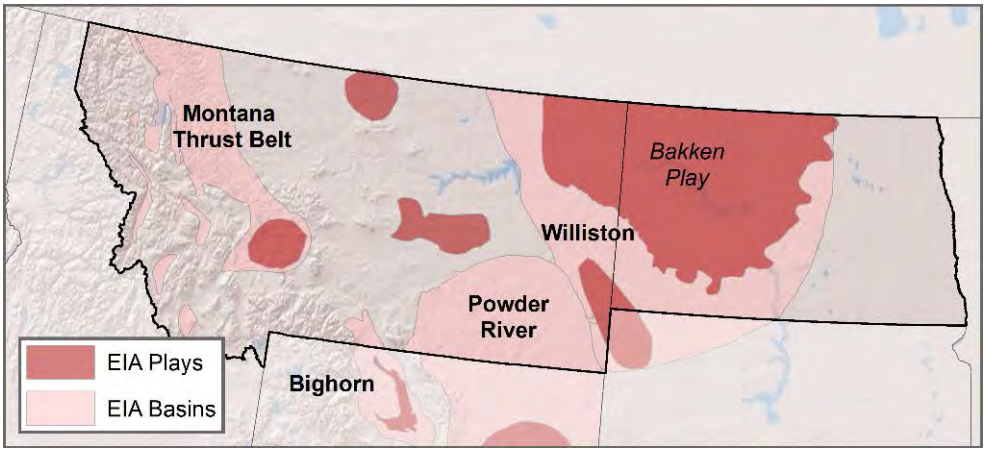


Figure 4-9. Major U.S. EIA shale plays and basins for North Dakota and Montana (EIA, 2015b).

Source: (EIA, 2015b).

[1] 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 react with organic matter in the water being treated (Water Research Foundation, 2014).

Types of water used: Hydraulic fracturing of the Bakken play underlying much of western North Dakota and northeastern Montana 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 (i.e., small 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). Ground water from glacial and bedrock aquifer systems has traditionally supplied much of the water needed for Bakken development, but concerns over limited ground water supplies have led to limits on the number of new ground water 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 described as 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, 2015a).[1] Reuse of Bakken wastewater is limited due to its quality of high TDS, which presents challenges for treatment and reuse. However, the industry is 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 project database (see 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).[2]

A presentation by the North Dakota Department of Mineral Resources (NDDMR) suggests that Bakken wells require an average of 600 gal (2,300 L) per day of "maintenance water" in addition to the initial water for hydraulic fracturing (North Dakota Department of Mineral Resources, 2013).[3] 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. According to the NDDMR, maintenance water can contribute to large additional volumes over a typical well life span (6.6–8.8 million gal (25-33 million L) over 30–40 years). It is unclear whether this phenomenon is restricted to the Bakken play.

[1] However, 25% of North Dakota disclosures included information related to water sources (U.S. EPA, 2015a).
[2] The fact sheet is a stand-alone piece, and it is not accompanied by an underlying report.
[3] The NDDMR's presentation that mentions the issue of maintenance water was later picked up and reported on by *National Geographic* (http://news.nationalgeographic.com/news/energy/2013/11/131111-north-dakota-wells-maintenance-water/) and by Ceres (2014). Peer-reviewed studies on the Bakken also report on maintenance water (e.g., Scanlon et al., 2014), but they refer to the same original sources.

Cumulative water use/consumption: Cumulative water use for fracturing in this region is greatest in the northwestern corner of North Dakota. In counties with 2011 and 2012 disclosures to FracFocus, fracturing water use averaged approximately 123 million gal (466 million L) per county annually in the two-state area, with use in McKenzie and Williams Counties in North Dakota exceeding 500 million gal (1.9 billion L) per year (see Appendix Table B-2). There are 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. Outside of North Dakota's northwest corner, the rest of the state and Montana showed little cumulative water use from hydraulic fracturing (see Table 4-2 and Appendix Table B-2).

Potential for impacts: In this region, there are concerns about over-pumping ground water 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 (see Text Box 4-2 and Figure 4-5a,b.) This area is primarily rural, interspersed with small towns. Residents use a mixture of surface water and ground water for domestic use depending on the county, with most water supplied by local municipalities (see Appendix Table B-6).

The state of North Dakota and the U.S. Army Corps of Engineers concluded that ground water 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 ground water supplies (U.S. Army Corps of Engineers, 2011). By contrast, 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 ground water supplies, the state of North Dakota limits industrial ground water 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 in western North Dakota (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 prolonged 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 ground water quality; rather, the state is concerned with maintaining flows for users through conservation (North Dakota State Water Commission, 2010).

To reduce pressure on ground water, the state is encouraging the industry to seek surface water withdrawals from the Missouri River system, which if used, may be an adequate resource. 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). Industrial surface water withdrawals are presently allowed in Lake Sakakawea on a temporary and controlled basis while the U.S. Army Corps of Engineers conducts a multi-year study to determine whether surplus water is available to meet the demands of regional municipal and industrial users (U.S. Army Corps of Engineers, 2011).

4.5.5. Oklahoma and Kansas

Oklahoma had the fifth most disclosures in the EPA FracFocus project database (5.0% of disclosures) (see Appendix Table B-5, and Figure 4-3). Three major basins— the Anadarko, which includes the Woodford play; the Arkoma, which includes the Fayetteville play; and the Ardmore, which includes the Woodford play—contain 67% of the disclosures in Oklahoma (see Figure 4-9 and Appendix Table B-5). Few wells were reported for Kansas (Kansas disclosures comprise 0.4% of the EPA FracFocus project database), but because of the shared geology of the Cherokee Platform across the two states, we group Kansas with Oklahoma. Oklahoma and Kansas were two of the three states where a large fraction of wells were not associated with a basin defined by the U.S. EIA (U.S. EPA, 2015b) (see Appendix Table B-5).[1]

Types of water used: Water for hydraulic fracturing in Oklahoma and Kansas comes from both surface and ground water (Kansas Water Office, 2014; Taylor, 2012). Data on temporary water use permits in Oklahoma (which make up the majority of water use permits for Oklahoma oil and gas mining) show that, in 2011, approximately 63% and 37% of water for hydraulic fracturing came from surface and ground water, respectively (Taylor, 2012) (see Table 4-3). General water use in Oklahoma follows an east-west divide, with the eastern half dependent on surface sources and the western half relying heavily on ground water (OWRB, 2014). Water obtained for fracturing is assumed to fit this pattern as well. No data are available on the proportion of hydraulic fracturing water that is sourced from surface versus ground water resources in Kansas.

For both Oklahoma and Kansas, no data are available to describe the extent to which reused wastewater is used as a percentage of total injected volume. However, the quality of Oklahoma's Woodford Shale wastewater has been described as low in TDS, and thus reuse could reduce the demand for fresh water (Kuthnert et al., 2012).

[1] Alaska was the other state in the EPA FracFocus project database where the U.S. EIA shale basins did not adequately describe well locations, with all 37 wells in Alaska not associated with a U.S. EIA basin. For all other states, U.S. EIA shale basins captured 86%–100% of the wells in the EPA FracFocus project database (U.S. EPA, 2015b).

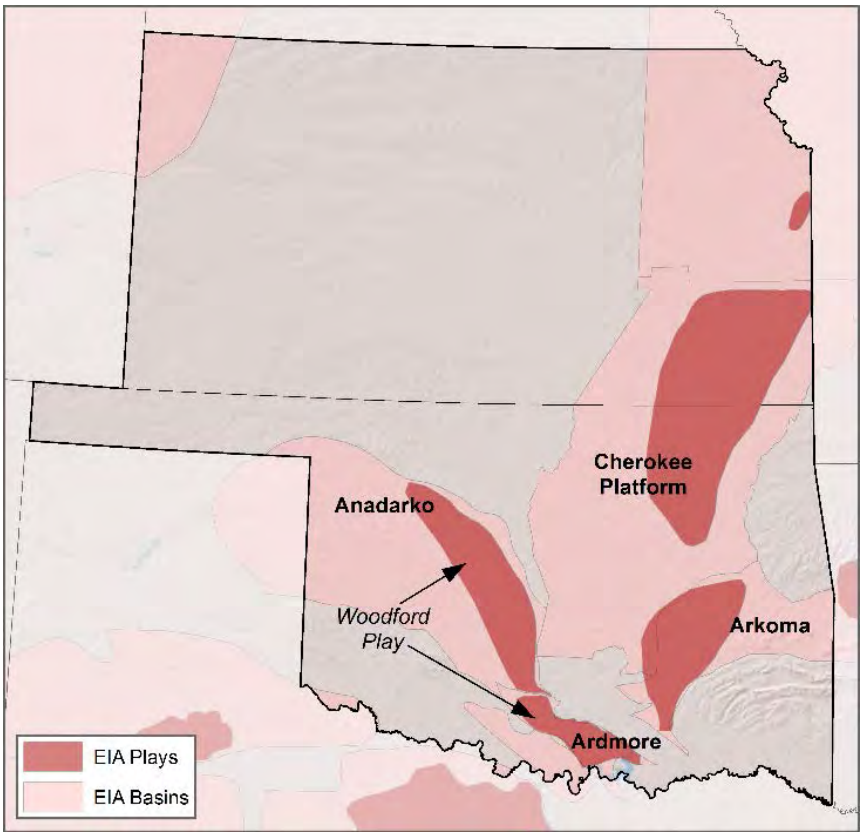


Figure 4-10. Major U.S. EIA shale plays and basins for Oklahoma and Kansas (EIA, 2015).

Source: (EIA, 2015b)

Water Use per Well: State-level estimates of median water use per well in Oklahoma include 2.6 million gal (9.8 million L) and 3 million gal (11 million L) [U.S. EPA (2015b) and, Murray (2013), respectively]. Water use for hydraulic fracturing increased from 2000 to 2011, driven by volumes required for fracturing horizontal wells across the state (Murray, 2013). Within the state there are wide ranges in water use for different formations. According to the EPA FracFocus project database, the Ardmore and Arkoma Basins of Oklahoma, had the highest median water use in the country, with medians of 8.0 and 6.7 million gal (30.3 and 25.4 million L) per well, respectively; whereas the Anadarko Basin had lower median water use per well and higher disclosure counts (3.3 million gal (12.5 million L), 935 disclosures) (see Appendix Table B-5). Wells not associated with a U.S. EIA basin had a median of 1.9 million gal (7.2 million L) per well (592 disclosures) (see Appendix Table B-5). It is not clear why lower water volumes were reportedly used in unassociated wells, but Oklahoma has several CBM deposits in the eastern part of the state where very low water use has been reported (Murray, 2013). Median water use per well in Kansas was 1.5 million gal (5.7 million L), focused mostly in a five-county area in the south-central and southwest portions of the state (see Appendix Table B-5).

Cumulative water use/consumption: Cumulatively, operators reported using an average of 71.9 million gal (272.2 million L) of water annually in Oklahoma counties with disclosures; in

Kansas, this value is only 3.5 million gal (13.2 million L) (see Appendix Table B-2). Average hydraulic fracturing water use in 2011 and 2012 did not exceed 10% of 2010 total water use in any county in Oklahoma or Kansas (see Appendix Table B-2). However, there were six counties in Oklahoma (Alfalfa, Canadian, Coal, Pittsburg, Rogers Mills, and Woods) where fracturing water consumption exceeded 10% of 2010 total county water consumption.

Potential for impacts: The potential for effects on drinking water resources appears to be low in Oklahoma and Kansas, since hydraulic fracturing water use and consumption are generally low as a percentage of total water use and consumption. This finding is generally supported by the comparison of cumulative fracturing water use to water availability at the county scale (see Text Box 4-2 and Figure 4-5a,b). If impacts to water quantity or quality do occur, however, they are more likely to happen in western Oklahoma than in the eastern half of the state or Kansas. Of the six Oklahoma counties where fracturing consumption exceeded 10% of 2010 water consumption, three (Alfalfa, Canadian, and Roger Mills) are in the western half of the state where surface water availability is lowest (Figure 4-6a). Surface water is fully allocated in the Panhandle and West Central regions, encompassing much of the state's northwestern quadrant (OWRB, 2014). As a result, residents generally rely on ground water in western Oklahoma (see Appendix Table B-6), and it is likely that fracturing does as well.

Projecting out to 2060, Oklahoma's Water Plan concludes that aquifer storage depletions are likely in the Panhandle and West Central regions due to over-pumping, particularly for irrigation (OWRB, 2014). Ground water depletions are anticipated to be small relative to storage, but will be the largest in summer months and may lead to higher pumping costs, the need for deeper wells, lower water yields, and detrimental effects on water quality (OWRB, 2014). Drought conditions are likely to exacerbate this problem, and Oklahoma's Water Plan specifically mentions the potential for climate change to affect future water supplies in the state (OWRB, 2014). In the adjacent Texas Panhandle, future irrigation needs may go unmet (TWDB, 2012), and this may be the case in western Oklahoma as well.

Aquifer depletions in western Oklahoma may be associated with ground water quality degradation, particularly under drought conditions. The central portion of the Ogallala aquifer underlying the Oklahoma Panhandle and western Oklahoma contains elevated levels of some constituents (e.g., nitrate) due to over-pumping, although generally it is of better quality than the southern portion of the aquifer (USGS, 2009). Additional ground water withdrawals for hydraulic fracturing in western Oklahoma may add to these water quality issues, particularly in combination with other substantial water uses (e.g., irrigation) (USGS, 2009).

4.5.6. Arkansas and Louisiana

Arkansas and Louisiana were ranked seventh and tenth in the number of disclosures in the EPA FracFocus project database, respectively (see 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 4-11).

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 ground water. However, data are available for Louisiana, where an estimated 87% of water for hydraulic fracturing in the Haynesville Shale is sourced from surface water (LA Ground Water Resources Commission, 2012) (see Table 4-3). In 2008, during the early stages of development, hydraulic fracturing in Louisiana relied heavily on ground water from the Carrizo-Wilcox aquifer, although concerns for the sustainability of ground water resources have more recently 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 only 3% of disclosures reporting a water source noted "fresh" as the exclusive water source (U.S. EPA, 2015a).[1] According to Veil (2011), Arkansas' Fayetteville Shale wastewater is of relatively good quality (i.e., low TDS), potentially facilitating reuse. Data are generally lacking on the extent to which hydraulic fracturing wastewater is reused to offset total fresh water use in Louisiana.

[1] 93% of Arkansas disclosures included information related to water sources (U.S. EPA, 2015a).

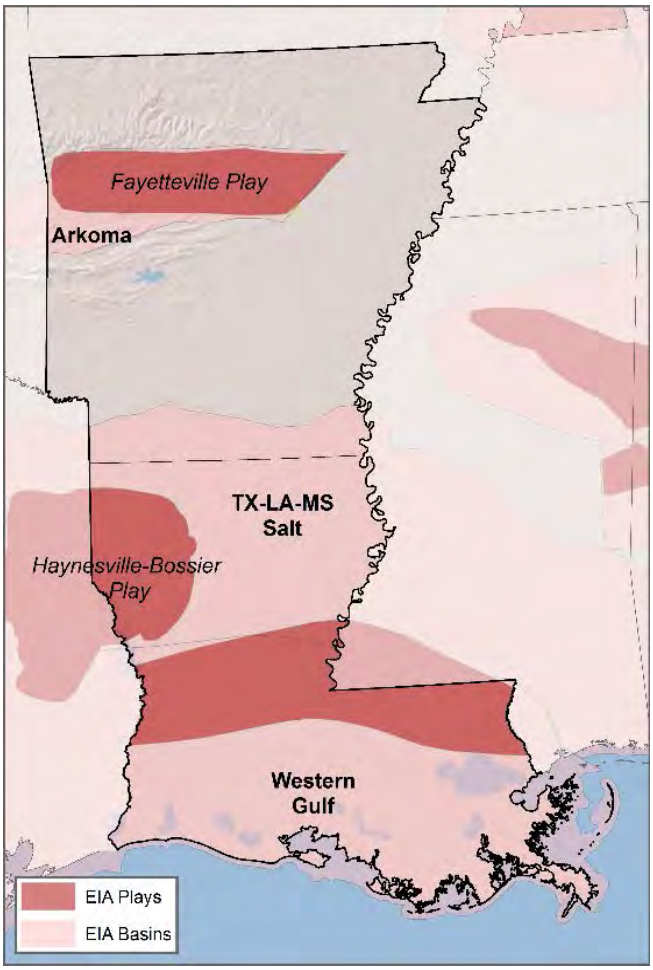


Figure 4-11. Major U.S. EIA shale plays and basins for Arkansas and Louisiana (EIA, 2015b).

Source: (EIA, 2015b).

Water Use per Well: Arkansas and Louisiana have the highest median water use per well in the nation, at 5.3 million and 5.1 million gal (20.1 million and 19.3 million L), respectively based on the EPA FracFocus project database (see Appendix Table B-5).[1]

Cumulative water use/consumption: On average, hydraulic fracturing operations cumulatively use 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) (see Appendix Table B-2). In 2011 and 2012, five counties dominated fracturing water use in Arkansas: Cleburne, Conway, Faulkner, Van Buren, and White Counties (see Appendix Table B-2). Van Buren, which is sparsely populated and thus has relatively low total water use and consumption, is by far the county highest

[1] 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.

in hydraulic fracturing water use and consumption relative to 2010 total water use and consumption (56% and 168%, respectively) (see Table 4-2).

In Louisiana, fracturing water use is concentrated in six parishes in the far northwestern corner of the state, associated with the Haynesville play.[1] 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 (see Appendix Table B-2). Operators in De Soto Parish used the most water (over 1 billion gal (3.8 billion L) annually). 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 (see Table 4-2). 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, 2015a) (see 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, Text Box 4-2, and Figure 4-5). There are, however, concerns about over-pumping of ground water resources in northwestern Louisiana. Prior to 2008, most operators in the Louisiana portion of the Haynesville Shale used ground water, withdrawing from the Carrizo-Wilcox, Upland Terrace, and Red River Alluvial aquifer systems (LA Ground Water Resources Commission, 2012). To mitigate stress on ground water, 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 ground water component (approximately 12% of all fracturing water used) (LA Ground Water Resources Commission, 2012). Of this ground water 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 appears greatly reduced, it is 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. In August 2011, a ground water emergency was declared for southern Caddo Parrish (LA Ground Water Resources Commission, 2012). There are hydraulic fracturing wells in southern Caddo Parrish (U.S. EPA, 2015b), and so it is possible that fracturing withdrawals contributed to the problem of declines in ground water in this instance.

4.5.7. Utah, New Mexico, and California

Together, Utah, New Mexico, and California accounted for approximately 9% of disclosures in the EPA FracFocus project database (3.8%, 3.1% and 1.9% of disclosures, respectively) (see Appendix Table B-5 and Figure 4-3). Almost all reported hydraulic fracturing in Utah and California were in

[1] Louisiana is divided into parishes, which are similar to counties in other states.

the Uinta-Piceance Basin (99%) and San Joaquin Basin (95%), respectively. Activity in New Mexico mostly occurs in the Permian and San Juan Basins, which together comprised 96% of reported disclosures in that state (see Figure 4-12).

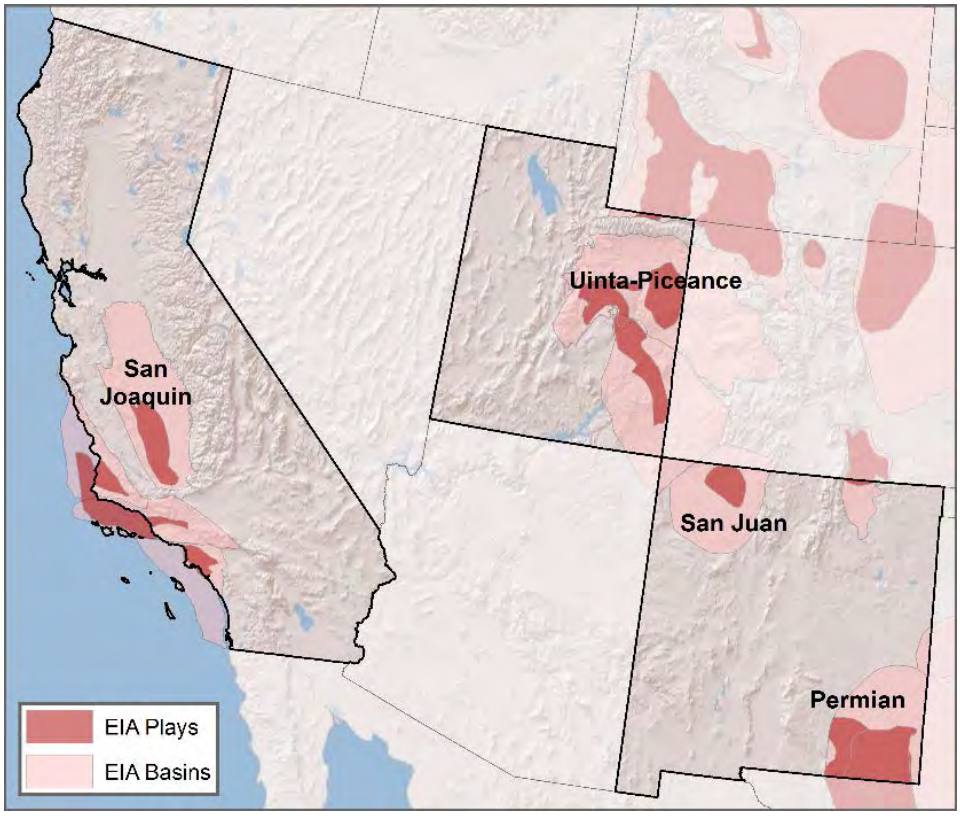


Figure 4-12. Major U.S. EIA shale plays and basins for Utah, New Mexico, and California (EIA, 2015).

Source: (EIA, 2015b).

Types of water used: Of these three states, California has the most information available on the sources of water used for hydraulic fracturing. Most current and proposed fracturing activity is focused in Kern County in the San Joaquin Basin, where well stimulation notices indicate that operators depend mainly on surface water purchased from nearby irrigation districts (CCST, 2014). California irrigation districts receive water allocated by the State Water Project, and deliveries may be restricted or eliminated during drought years (CCST, 2014).[1] In addition to publicly-supplied surface water, operators also may self-supply a smaller proportion of water from on-site ground water wells (CCST, 2014). Operators use primarily fresh water for hydraulic fracturing (96% of well

[1] The California State Water Project is water storage and distribution system maintained by the California Department of Water Resources, which provides water for urban and agricultural water suppliers in Northern California, the San Francisco Bay Area, the San Joaquin Valley, the Central Coast, and Southern California (California Department of Water Resources, 2015).

stimulation notices reported); reused wastewater (sometimes blended with fresh water) is used in small amounts relative to total water use (4% of well stimulation notices reported) (CCST, 2014) (see Table 4-1).

The source, quality, and provisioning of water used for hydraulic fracturing in Utah and New Mexico are not well characterized. The 2010 New Mexico water use report summarizes withdrawals for a variety of water use categories. In 2010, mining water use (which includes water used for oil and gas production) consisted of 26% and 74% of surface and ground water withdrawals, respectively (NM OSE, 2013). Assuming that hydraulic fracturing follows the same pattern as other mining water uses (e.g., for metals, coal, geothermal), water for hydraulic fracturing in New Mexico would be supplied primarily by ground water withdrawals. To our knowledge, no data are available to characterize the source of water for hydraulic fracturing operations in Utah. In addition, no data are available to describe the extent to which reused wastewater is used as a proportion of total water injected for either Utah or New Mexico.

Water use per well: Median water use per well in Utah, New Mexico, and California is lower than in other states in the EPA FracFocus project database: Utah ranks 13th (approximately 302,000 gal (1.14 million L)), New Mexico ranks 14th (approximately 175,000 gal (662,000 L)), and California ranks 15th (approximately 77,000 gal (291,000 L)) out of the 15 states (see Appendix Table B-5). A likely explanation for the low water use per well in Utah and New Mexico is the prevalence of CBM in the Uinta (Utah) and San Juan (New Mexico) Basins. Low water use per well in California is attributed to the prevalence of vertical wells and the use of crosslinked gels. Vertical wells dominate because the complex geology precludes long horizontal drilling and fracturing (CCST, 2014).

For California, the California Council on Science and Technology (CCST) reports average water use per well of 130,000 gal (490,000 L), which agrees with the state average of approximately 131,700 gal (498,500 L) according to the EPA FracFocus project database (CCST, 2014) (see Appendix Table B-5); this is expected because estimates from CCST are also based on data submitted to FracFocus.

Cumulative water use/consumption: Operators in Utah, New Mexico, and California report using low cumulative amounts of water compared to most other states (see Appendix Table B-1). Only four counties (Duchesne and Uintah Counties in Utah, and Eddy and Lea Counties in New Mexico) required more than 50 million gal (189 million L) annually (see Appendix Table B-2). Fracturing water use and consumption did not exceed 1% of 2010 total water use and consumption in any county.

Potential for impacts: The potential for water quantity and quality impacts from hydraulic fracturing water withdrawals in Utah, New Mexico, and California appears to be low at present (see Text Box 4-2 and Figure 4-5a,b). Hydraulic fracturing does not use or consume much water compared to other users or consumers in these states. As in other states, this does not preclude sub-county effects, and this finding of low potential for impacts could change if fracturing activities increase beyond present levels. This is particularly the case because these states generally have low surface water availability (see Figure 4-6a) and high ground water dependence (see Figure 4-6b),

and have experienced frequent periods of drought over the last decade (National Drought Mitigation Center, 2015).

4.6. Chapter Synthesis

In this chapter we examine the potential for water acquisition for hydraulic fracturing to affect drinking water quantity and quality. The potential for impacts largely depends on water use, consumption, and availability. Water management—in terms of the type of water used, the timing or location of water withdrawals, or other factors—also can play a role. Because all of these factors vary considerably from place-to-place, any impacts that occur will be location-specific and occur at the spatial scale of the specific drinking water resource (i.e., the particular stream, watershed, or local ground water aquifer). Therefore, it is important to consider the potential for hydraulic fracturing impacts by location.

We examine the potential for impacts by considering (1) the types of water used for hydraulic fracturing; (2) the amounts of water used per well; (3) cumulative estimates of water used and consumed for hydraulic fracturing; and (4) a state-by-state assessment of the potential for impacts based on water use, consumption, and availability. We often could not assess the potential for impacts at a finer resolution than the county scale due to lack of available local-scale data for most areas. Thus, our assessment suggests areas that are more likely than others to experience impacts, but does not necessarily indicate that these impacts will occur. Three case studies (southern Texas, western Colorado, and eastern Pennsylvania), provide an in-depth examination at finer scales, and we rely on those where possible (see Text Boxes 4-3, 4-4, and 4-5).

4.6.1. Major Findings

Water for hydraulic fracturing typically comes from surface water, ground water, or reused wastewater. Because trucking can be a major expense, operators often use water sources as close to well pads as possible. Operators usually self-supply surface or ground water directly, but also may obtain water secondarily through public water systems or other suppliers. Hydraulic fracturing operations in the eastern United States generally rely on surface water, whereas operations in more semi-arid to arid western states use mixed surface and ground water supplies. In areas that lack available surface water (e.g., western Texas), ground water supplies most of the water needed for fracturing unless alternative sources, such as reused wastewater, are available and utilized.

The vast majority of water used for hydraulic fracturing nationally comes from fresh water sources, although some operators also use lower-quality water (e.g., hydraulic fracturing wastewater, brackish ground water, or small proportions of acid mine drainage and wastewater treatment plant effluent). The use of non-fresh sources can reduce competition for current drinking water resources. Nationally, the proportion of reused wastewater is generally low as a percentage of injected volume; based on available data, the median reuse of wastewater as a percentage of injected volume is 5% nationally, but this percentage varies by location (see Table 4-1).[1] Available

[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).

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. Reuse as a percentage of water injected appears to be low in other areas, likely in part because of the relatively high availability of disposal wells (see Chapter 8).

The median amount of water used per hydraulically fractured well, based on national disclosures to FracFocus, is approximately 1.5 million gal (5.7 million L) of water (U.S. EPA, 2015a, b). This estimate represents a variety of fractured well types, including types that use 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)). There is also wide variation within and among states and basins in the median water volumes reported per disclosure, 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, 2015b). This variation results from several factors, including well length, formation geology, and fracturing fluid formulation (see Section 4.3.3).

Cumulatively, hydraulic fracturing uses billions of gallons of water every year at the national and state scales, and even in some counties. When expressed as a percentage compared to total water use or consumption at these scales, however, hydraulic fracturing water use and consumption is most often a small percentage, generally less than 1%. This percentage may be higher in specific areas. 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, 30% or more in 2.2% of counties, and 50% or more in 1.0% of counties (U.S. EPA, 2015a). Consumption estimates follow the same general pattern, but with slightly higher percentages in each category. In these counties, hydraulic fracturing represents a relatively large user and consumer of water.

High hydraulic fracturing water use or consumption alone does not necessarily result in impacts to drinking water resources. Rather, the potential for impacts depends on both water use or consumption and water availability at a given withdrawal point. Our state-by-state assessment examines the intersection between water use or consumption and availability at the county scale. This approach suggests where the potential for impacts exists, but does not indicate where impacts will occur at the local scale. Where possible, we use local-scale case studies in Texas, Pennsylvania, and Colorado to provide details at finer spatial scales.

In our survey of the published literature, we did not find a case where hydraulic fracturing water use by itself caused a drinking water well or stream to run dry. This could indicate an absence of hydraulic fracturing effects on water availability; alternatively, it could reflect that these events are not typically documented in the types of literature we reviewed. Water availability is rarely impacted by just one use or factor alone. For example, drinking water wells in an area overlapping with the Haynesville Shale in northwest Louisiana ran out of water in 2011, due to higher than normal withdrawals and drought (LA Ground Water Resources Commission, 2012). Hydraulic fracturing water use in the area may have contributed to these conditions, along with other water uses and the lack of precipitation. Other impacts to drinking water quantity or quality (e.g.,

declining aquifer levels, decreased stream flow, increased pollutant concentrations) also may occur before wells and streams actually go dry.

The potential for impacts due to hydraulic fracturing water withdrawals is highest in areas with relatively high fracturing water use and low water availability. Southern and western Texas are two locations where hydraulic fracturing water use combined with low water availability, drought, and reliance on declining ground water sources has the potential to affect the quantity and quality of drinking water resources. Fracturing withdrawals combined with other intensive uses, particularly irrigation, could contribute to ground water quality degradation. Any impacts are likely to be realized locally within these areas. In a detailed case study of southern Texas, Scanlon et al. (2014) observed generally adequate water supplies for hydraulic fracturing, except in specific locations. They found excessive drawdown of local ground water in a small proportion (~6% of the area) of the Eagle Ford play. They suggested water management, particularly a shift towards brackish water use, could minimize potential future impacts to fresh water resources (see Text Box 4-3). County-level data confirm that high brackish water availability in Texas may help offset hydraulic fracturing water demand (see Text Box 4-2).

Comparatively, the potential for hydraulic fracturing water acquisition impacts to drinking water quantity and quality appears to be lower—but not entirely eliminated—in other areas of the United States. Detailed case studies in western Colorado and northeastern Pennsylvania did not show impacts, despite indicating that streams could be vulnerable to water withdrawals from hydraulic fracturing (U.S. EPA, 2015c). High wastewater reuse rates in western Colorado eliminated the need for more fresh water withdrawals. In northeast Pennsylvania, water withdrawals for hydraulic fracturing could result in high water consumption-to-stream flow events, but water management (e.g., passby flows) limited the potential for impacts, especially on small streams (U.S. EPA, 2015c). In western North Dakota, ground water is limited, but the industry may have sufficient supplies of surface water from the Missouri River system. These location-specific examples emphasize the need to focus on regional and local dynamics when considering the potential impacts of hydraulic fracturing water acquisition on drinking water resources.

4.6.2. Factors Affecting Frequency or Severity of Impacts

The potential for hydraulic fracturing water use to affect drinking water resource quantity or quality depends primarily on the amount of water used or consumed versus water availability at a given withdrawal point. Potential impacts to drinking water resources reflect all uses, including hydraulic fracturing demands, compared to available water. Areas with high water use, low water availability, slowly replenishing sources, and/or episodic water shortages (e.g., seasonal or longer-term droughts) are more vulnerable to potential impacts. Areas with high water availability relative to existing uses, high rainfall distributed throughout the year, or high storage capacity, are less likely to be affected.

Water management can alter this dynamic between water use and availability. The type of water used (e.g., fresh, brackish, reused hydraulic fracturing wastewater, other wastewaters) is a major factor that can either increase or decrease the potential for impacts. Replacing a fresh water source with another type of water can reduce the demand for fresh water and decrease potential

competition for drinking water. Brackish ground water use may reduce the demand for fresh water and decrease competition for drinking water currently, but this may change if desalinization for drinking water becomes more prevalent in the future (see Chapter 3).

The timing and location of water withdrawals can also affect the potential for impacts, particularly for surface water withdrawals. Withdrawing water from small streams is more likely to result in a high-consumption-to-stream flow event than removing water from larger streams (U.S. EPA, 2015c). Withdrawals during periods of low stream flow are also more likely to result in impacts than withdrawals during high flow periods. Hydraulic fracturing operations may have the ability to withdraw water during periods of high stream flow, and store it for future use during drier periods.

4.6.3. Uncertainties

There are several uncertainties inherent in our assessment of hydraulic fracturing water use and potential effects on drinking water quantity and quality. The largest uncertainties stem from the lack of literature and data on this subject at local scales, and the question of whether any impacts would be documented in the types of literature we reviewed.

We used a state-by-state approach to identify areas where potential impacts are likely, based on relatively high fracturing water use and low water availability. Typically, only data at the county-scale were available. Because impacts occur at smaller spatial scales (i.e., at water withdrawal sites), our assessment suggests the potential for impacts, but does not indicate whether impacts will occur. In only a few places could we use local case studies to determine if potential impacts were realized; these case studies show that local factors can greatly affect whether drinking water resources are impacted.

In our survey of the published literature, we did not find a case where hydraulic fracturing water use alone caused a drinking water well or stream to run dry. This could indicate an absence of hydraulic fracturing effects on water availability, or it could reflect that these events are not typically documented in the types of literature we reviewed. Water availability is rarely impacted by just one use or factor alone. These issues may have limited our findings.

Other uncertainties arise from data limitations regarding 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 annual average hydraulic fracturing water use in 2011 and 2012 exceeded total mining water use in 2010, and one county where it exceeded all water use (U.S. EPA, 2015b; 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 project database), or both.

The EPA FracFocus project database represents the most extensive database currently available to estimate hydraulic fracturing water use. However, estimates based on the project database form an incomplete picture of hydraulic fracturing water use because most states with data in the project database did not require disclosure to FracFocus during the time period analyzed (U.S. EPA, 2015a) (see Text Box 4-1). We conclude that this likely does not change the overall hydraulic fracturing water use patterns observed across the United States, but could affect our assessment of the potential impacts in specific locations.

Hydraulic fracturing water use data are often provided in terms of water use per 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, and location of each water withdrawal were documented, the quality of the water used and potential effects on availability could be better estimated. For example, surface withdrawal points could be aggregated by watershed to estimate effects on downstream flow. Alternatively, if the location and depth of ground water pumping were documented, these could be aggregated to assess effects on a given aquifer. 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 easy to analyze—limits our assessment of hydraulic fracturing water use.

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 high 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 cumulative 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, population growth).

4.6.4. Conclusions

Water acquisition for hydraulic fracturing has the potential to impact drinking water resources by affecting drinking water quantity and quality (see Text Box 4-6). In our survey of the published literature, we did not find a case where hydraulic fracturing water use by itself caused a drinking water well or stream to run dry. However, the potential for impacts to drinking water quantity and quality exists and is highest in areas with relatively high fracturing water use and low water availability. Southern and western Texas are two locations where the potential appears highest due to the combined effects of high hydraulic fracturing activity, low water availability, drought, and reliance on declining ground water sources. Even in locations where water is generally plentiful, localized impacts can still occur in certain instances. Excessive ground water pumping can cause localized drawdowns; surface water withdrawals can affect stream flow, particularly in smaller streams or during low flow periods. These findings emphasize the need to focus on regional and local dynamics when examining potential impacts of hydraulic fracturing water acquisition on drinking water quantity and quality.

Text Box 4-6. Research Questions Revisited.

What are the types of water used for hydraulic fracturing?

- Water for hydraulic fracturing typically comes from surface, ground water, or reused wastewater. Operators often use water sources as close to well pads as possible as trucking is a major expense. Operators usually self-supply surface or ground water directly, but also may obtain water secondarily through public water systems or other suppliers. Hydraulic fracturing operations in the eastern United States generally rely on surface water, whereas operations in more semi-arid to arid western states use mixed surface and ground water supplies. In areas that lack available surface water (e.g., western Texas), ground water supplies most of the water needed for fracturing unless alternative sources, such as reused wastewater, are available and utilized.

- The vast majority of water used nationally comes from fresh water sources, although some operators also use lower-quality water (e.g., hydraulic fracturing wastewater, brackish ground water, or small proportions of acid mine drainage and wastewater treatment plant effluent). The use of non-fresh sources can reduce competition for current drinking water resources. Nationally, the proportion of reused wastewater is generally low as a percentage of injected volume; based on available data, median reuse of wastewater across all basins and plays is 5% of injected volume (see Table 4-1). 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. Reuse as a percentage of water injected appears to be low in other areas, likely in part because of the relatively high availability of disposal wells (see Chapter 8).

How much water is used per well?

- The median amount of water used per hydraulically fractured well, based on national disclosures to FracFocus, is approximately 1.5 million gal (5.7 million L) of water (U.S. EPA, 2015a, b). This estimate represents a variety of fractured well types. There is also wide variation within and among states and basins in the median water volumes reported per disclosure, 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, 2015b). This variation results from several factors, including well length, formation geology, and fracturing fluid formulation (see Section 4.3.3).

- Trends indicate that water use per well is increasing in certain locations as horizontal well lengths increase. This may not, however, increase water use per unit energy extracted.

How might cumulative water withdrawals for hydraulic fracturing affect drinking water quantity?

- Cumulatively, hydraulic fracturing uses billions of gallons of water every year at the national and state scales, and even in some counties. When expressed as a percentage compared to total water use or consumption at these scales, however, hydraulic fracturing water use and consumption is most often a small percentage, generally less than 1%. This percentage may be higher in specific areas. 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, 30% or more in 2.2% of counties, and 50% or more in 1.0% of counties (U.S. EPA, 2015a). Consumption estimates follow the same general pattern, but with slightly higher percentages in each category. In these counties, hydraulic fracturing represents a relatively large user and consumer of water.
- High hydraulic fracturing water use or consumption alone does not necessarily result in impacts to drinking water resources. Rather, the potential for impacts depends on both water use or consumption and water availability at a given withdrawal point. Our state-by-state assessment examines the intersection between water use or consumption and availability at the county scale. This approach suggests where the potential for impacts exists, but does not indicate where impacts will occur at the local scale. Local-scale case studies help provide details at finer spatial scales.
- In our survey of the published literature, we did not find a case where hydraulic fracturing water use by itself caused a drinking water well or stream to run dry. This could indicate an absence of hydraulic fracturing effects on water availability, or it could reflect that these events are not typically documented in the types of literature we reviewed. Water availability is rarely impacted by just one use or factor alone. For example, drinking water wells in an area overlapping with the Haynesville Shale in northwest Louisiana ran out of water in 2011, due to higher than normal withdrawals and drought (LA Ground Water Resources Commission, 2012). Hydraulic fracturing water use in the area may have contributed to these conditions, along with other water uses and the lack of precipitation. Other impacts to drinking water quantity or quality (e.g., declining aquifer levels, decreased stream flow, increased pollutant concentrations) also may occur before wells and streams actually go dry.
- The potential for impacts due to hydraulic fracturing water withdrawals is highest in areas with relatively high fracturing water use and low water availability. Southern and western Texas are two locations where hydraulic fracturing water use combined with low water availability, drought, and reliance on declining ground water sources has the potential to affect the quantity of drinking water resources. Any impacts are likely to be realized locally within these areas. In a detailed case study of southern Texas, Scanlon et al. (2014) observed generally adequate water supplies for hydraulic fracturing, except in specific locations. They found excessive drawdown of local ground water in a small proportion (~6% of the area) of the Eagle Ford play. They suggested water management, particularly a shift towards brackish water use, could minimize potential future impacts to fresh water resources (see Text Box 4-3). County-level data confirm that high brackish water availability in Texas may help offset hydraulic fracturing water demand (see Text Box 4-2).
- The potential for hydraulic fracturing water acquisition impacts to drinking water quantity and quality appears to be lower—but not entirely eliminated—in other areas of the United States. Detailed case studies in western Colorado and northeastern Pennsylvania did not show impacts, despite indicating that streams could be vulnerable to water withdrawals from hydraulic fracturing (U.S. EPA, 2015c). High wastewater reuse rates in western Colorado eliminated the need for more fresh water withdrawals. In northeast Pennsylvania, water withdrawals for hydraulic fracturing could result in high water consumption-to-stream flow events, but water management (e.g., passby flows) limited the potential for impacts, especially on small streams (U.S. EPA, 2015c). In western North Dakota, ground water is limited, but the industry may have sufficient supplies of surface water from the Missouri River system. These

location-specific examples emphasize the need to focus on regional and local dynamics when considering the potential impacts of hydraulic fracturing water acquisition on drinking water resources.

What are the possible impacts of water withdrawals for hydraulic fracturing on water quality?

- Water withdrawals for hydraulic fracturing, similar to all water withdrawals, have the potential to alter the quality of drinking water resources. Ground water withdrawals exceeding natural recharge rates decrease water storage in aquifers, potentially mobilizing contaminants or allowing the infiltration of lower-quality water from the land surface or adjacent formations. Withdrawals could also decrease ground water discharge to streams, potentially affecting surface water quality. Areas with numerous high-capacity wells and large amounts of sustained ground water pumping are most likely to experience impacts, particularly in drought-prone regions with limited ground water recharge.

- Surface water withdrawals also have the potential to affect water quality. Withdrawals may lower water levels and alter stream flow, potentially decreasing a stream's capacity to dilute contaminants. Case studies by the EPA show that streams can be vulnerable to changes in water quality due to water withdrawals, particularly smaller streams and during periods of low flow (U.S. EPA, 2015c). Management of the rate and timing of surface water withdrawals can help mitigate potential impacts of fracturing withdrawals on water quality.

- Like water quantity effects, any effects of water withdrawals on water quality will likely occur nearest the withdrawal point, again emphasizing the need for location specific assessments.

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Chapter 5

Chemical Mixing

5. Chemical Mixing

5.1. Introduction

This chapter addresses the potential for on-site spills of chemicals used in the chemical mixing process to affect the quality of drinking water resources. Chemical mixing is a complex process that requires the use of specialized equipment and a range of different additives to produce the hydraulic fracturing fluid that is injected into the well. The number, type, and volume of chemicals used vary from well to well based on site- and company-specific factors. Spills may occur at any point in the hydraulic fracturing process. Chemicals may spill from on-site storage and containment units; from interconnected hoses and pipes used to transfer chemicals to and from mixing and pumping units, and tanker trucks; and from the equipment used to mix and pressurize chemical mixtures that are pumped down the well. The potential for a spill to affect the quality of a drinking water resource is governed by three overarching factors: (1) fluid characteristics (e.g., chemical composition and volume), (2) chemical management and spill characteristics, and (3) chemical fate and transport (see Figure 5-1). This chapter is organized around the three factors.

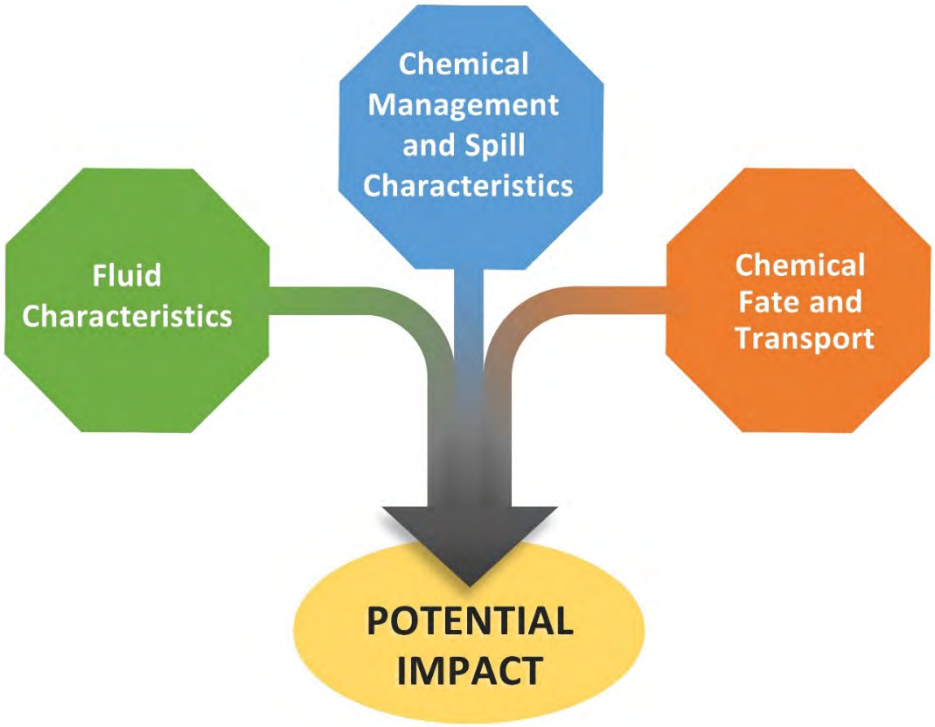

Figure 5-1. Factors governing potential impact to drinking water resources.

Factors include (1) fluid characteristics (e.g., chemical composition and volume), (2) chemical management and spill characteristics, and (3) chemical fate and transport.

Section 5.2 provides an introductory overview of the chemical mixing process. The number and volume of chemicals used and stored on-site are affected by such variables as the type, size, and goals of the operation; formation characteristics; depth of the well; the length of the horizontal leg; and the number of fracturing phases and stages.

Section 5.3 describes the different components of the hydraulic fracturing fluid, generally comprised of the base fluid, proppant, and additives, which may be either individual chemicals or mixtures. The composition of the hydraulic fracturing fluid is engineered to meet specific criteria. The total amount and types of additives vary according to the characteristics of the well, site geology, economics, availability, and the production goals (e.g., Maule et al., 2013). Section 5.4 presents the wide range of different chemicals used and their classes, the most frequently used chemicals nationwide and from state-to-state, and volumes used.[1] Appendix A provides a list of chemicals that the EPA identified as being used in hydraulic fracturing fluids based on eight sources.

Sections 5.5 to 5.7 discuss how chemicals are managed on-site, how spills may occur, and the different approaches for addressing spills. Section 5.5 describes how the potential impact of a spill on drinking water resources depends upon chemical management practices, such as storage, on-site transfer, and equipment maintenance. Section 5.6 discusses spill prevention, containment, and mitigation. A summary analysis of reported spills and their common causes at hydraulic fracturing sites is presented in Section 5.7.

Section 5.8 discusses the fate and transport of spilled chemicals. Spilled chemicals may react and transform into other chemicals, travel from the site of release to a nearby surface water, or leach into the soils and reach ground water. Chemical fate and transport after a release depend on site conditions, environmental conditions, physicochemical properties of the released chemicals, and the volume of the release.

Section 5.9 provides an overview of on-going changes in chemical use in hydraulic fracturing, with an emphasis on efforts by industry to reduce potential impacts from surface spills by using fewer and safer chemicals. A synthesis and a discussion of limitations are presented in Section 5.10.

Factors affecting the frequency and severity of impacts to drinking water resources from surface spills include size and type of operation, employee training and experience, standard operating procedures, quality and maintenance of equipment, type and volume of chemical spilled, environmental conditions, proximity to drinking water resources, spill prevention practices, and spill mitigation measures. 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 also preclude a quantitative analysis of the likelihood or magnitude of chemical spills or impacts. Spills that occur off-site, such as those during transportation of chemicals or storage of chemicals in staging areas, are out of scope. This chapter qualitatively characterizes the potential for impacts to

[1] 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, pesticides, acids, and bases.

drinking water resources given the current understanding of overall operations and specific components of the chemical mixing process.

5.2. Chemical Mixing Process

An understanding of the chemical mixing process is necessary to understand how, why, and when spills that may affect drinking water resources might occur. This description provides a general overview of chemical mixing in the context of the overall hydraulic fracturing process (Carter et al., 2013; Knappe and Fireline, 2012; Spellman, 2012; Arthur et al., 2008).

Figure 5-2 shows a hydraulic fracturing site during the chemical mixing process. The discussion focuses 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 because it is likely to be more complex and because horizontal hydraulic fracturing has become more prevalent over time with advances in hydraulic fracturing technology. A water-based system is described because water is the most commonly used base fluid, appearing in more than 93% of FracFocus disclosures between January 1, 2011 and February 28, 2012 (U.S. EPA, 2015a).

Figure 5-2. Hydraulic fracturing site showing equipment used on-site during the chemical mixing process.

Source: Industry source.

While the number and types of additives may widely vary, the basic chemical mixing process is similar across sites. The on-site layout of hydraulic fracturing equipment is also similar from site to site (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.

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 sequential phases with specific chemicals added at each phase to achieve a specific purpose (Knappe and Fireline, 2012; Fink, 2003). Phases may overlap. The process for water-based hydraulic fracturing is outlined in Figure 5-3 below.

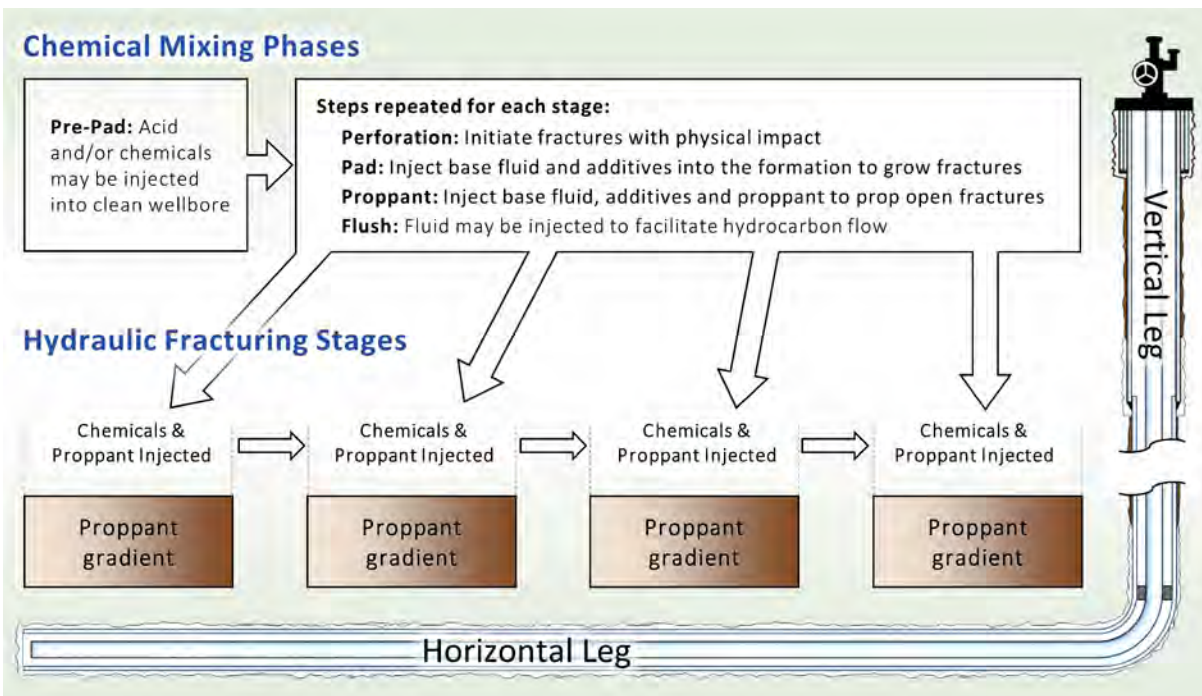

Figure 5-3. Overview of a chemical mixing process of the hydraulic fracturing water cycle.

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 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).

The first phase of the process consists of the cleaning and preparation of the well. The fluid used in this phase is often referred to as the pre-pad fluid or pre-pad volume. Acid is typically the first chemical introduced. Acid, with a concentration of 3%–28% (typically hydrochloric acid, HCl), is used to adjust pH, clean any cement left inside the well from cementing the casing, and dissolve any pieces of rock that may remain in the well and could block the perforations. 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).

In the second phase, a hydraulic fracturing fluid, typically referred to as the pad or pad volume, is mixed, blended, and pumped down the wellbore to create fractures in the formation. The pad is a mixture of base fluid, typically water, and additives. The pad is designed to create, elongate, and enlarge fractures along the natural channels of the formation when injected under high pressure (Gupta and Valkó, 2007). A typical pad consists of, at minimum, a mixture of water and friction reducer. The operator may also add other additives (see U.S. EPA (2015a) and Table 5-1) 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 in the well casing (see Text Box 5-1).

Text Box 5-1. Perforation.

Prior to the injection of the pad, 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 wellbore 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, controlled distance into the formation (Gupta and Valkó, 2007).

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 in with the proppant and base fluid in this phase to increase the viscosity and carry the proppant. Additional chemicals may be added to gelled fluids, initially to maintain viscosity and later to break the gel down into a more readily removable fluid. (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 chemicals 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 horizontal well, as the horizontal section, or leg, of the wellbore is typically fractured in multiple segments referred to as

stages. For each stage, the well is typically perforated and fractured beginning at the end, or toe, of the wellbore and proceeding backwards toward the vertical section. Each fractured stage is isolated before the next stage is fractured. The number of stages corresponds directly to the number of times the chemical mixing process is repeated at the site surface (see Figure 5-3). The number of stages depends upon the length of the leg (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 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). It also appears that the number of stages per well has increased over time. For instance, in the Williston Basin the average number of stages per horizontal well rose from approximately 10 in 2008 to 30 in 2012 (Pearson et al., 2013).

In each of these phases, water is 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, water typically comprises between 90% and 94% of the hydraulic fracturing fluid, proppant comprises 5% to 9%, and additives comprise the remainder, typically 2% or less (Carter et al., 2013; Knappe and Fireline, 2012; SWN, 2011). The exception to this typical fluid composition may be when a concentrated acid is used in the initial cleaning phase of the fracturing process.

5.3. Overview of Hydraulic Fracturing Fluids

Hydraulic fracturing fluids are formulated to perform specific functions: create and extend the fracture, transport proppant, and place the proppant in the fractures (Montgomery, 2013; Spellman, 2012; Gupta and Valkó, 2007). The hydraulic fracturing fluid generally consists of three parts: (1) the base fluid, which is the largest constituent by volume, (2) the additives, which can be a single chemical or a mixture of chemicals, and (3) the proppant. Additives 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 individual chemical compounds (e.g., methanol). 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 chemicals, and the mixing and injection process, varies based on a number of factors as discussed below. The chemical combination determines the amount and what type of equipment is required for storage and, therefore, contributes to the determination of the potential for spills and impacts of those spills.

The particular composition of hydraulic fracturing fluids is selected by a design engineer based on empirical experience, the formation, economics, goals of the fracturing process, availability of the

[1] The number of stages has been reported to be 6 to 9 in the Huron in 2009 (Allison et al., 2009), 25 and up in the Marcellus (NETL, 2013), and up to 40 by STO (2013).

desired chemicals, and preference of the service company or operator (Montgomery, 2013; ALL Consulting, 2012; Klein et al., 2012; Ely, 1989). 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, and concentrations selected. There are broad criteria for hydraulic fracturing fluid selection based on the fracturing temperatures, formation permeability, fracturing pressures, and formation water sensitivity, as shown in Figure 5-4 (Gupta and Valkó, 2007; Elbel and Britt, 2000). One of the most important properties in designing a hydraulic fracturing fluid is the viscosity (Montgomery, 2013).[1]

Figure 5-4 provides a general overview of which fluids can be used in different situations. As an example, crosslinked fluids with 25% nitrogen foam (titanate or zirconate crosslink + 25% N_2) can be used in both gas and oil wells with high temperatures with variation in water sensitivity.

[1] 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).

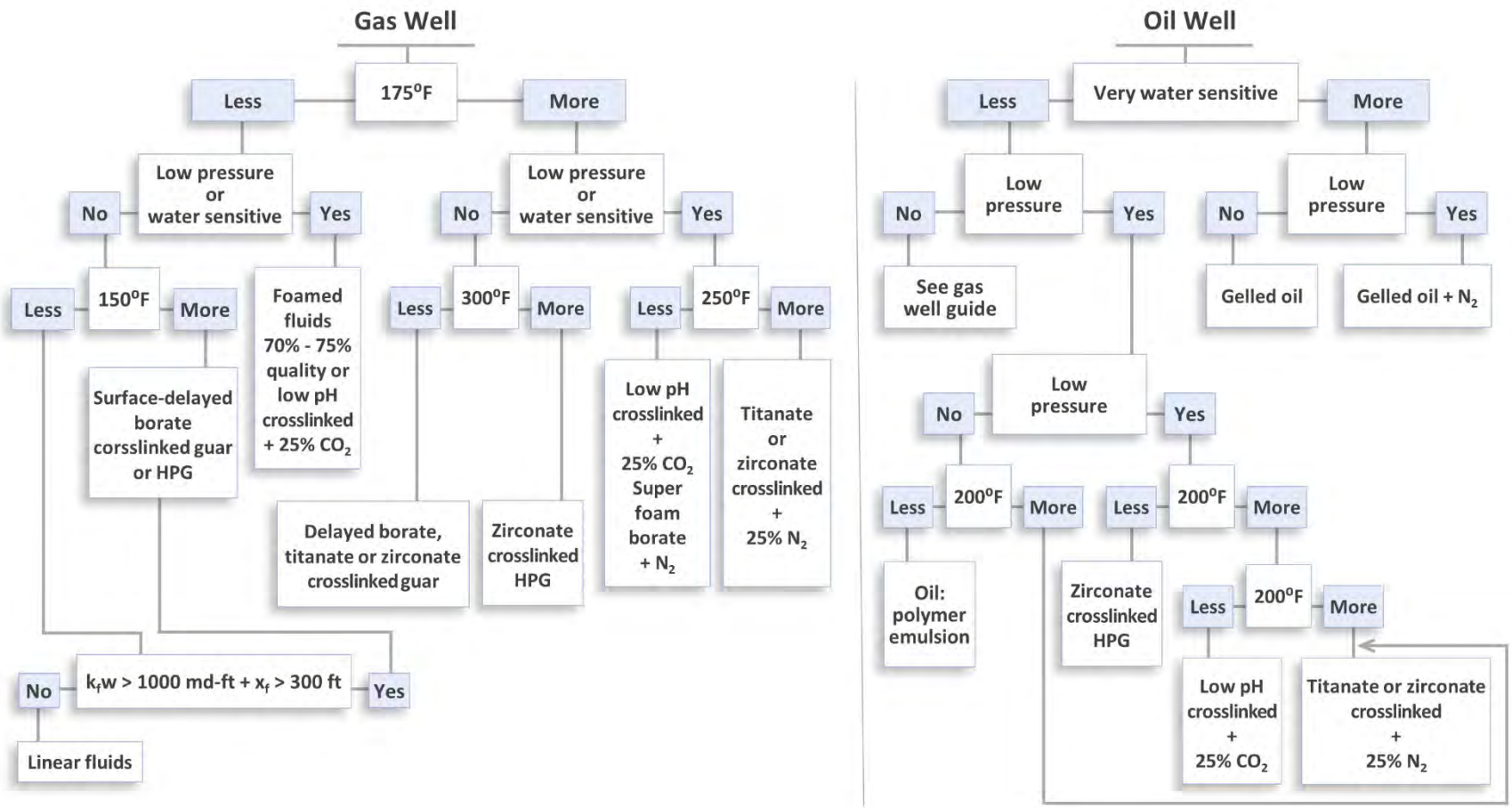

Figure 5-4. Example fracturing fluid decision tree for gas and oil wells.

Adapted from Elbel and Britt (2000).

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 (hereafter EPA FracFocus report; U.S. EPA (2015a)), the EPA's project database of disclosures to FracFocus 1.0 [hereafter EPA FracFocus database; U.S. EPA (2015b)], and other literature sources. Additional information on more additives can be found in U.S. EPA (2015a).

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, b; 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% of FracFocus disclosures for additive[a,b]
Acid	Dissolves cement, minerals, and clays to reduce clogging of the pore space	Hydrochloric acid
Biocide	Controls or eliminates bacteria, which can be present in the base fluid and may have detrimental effects on the fracturing process	Glutaraldehyde; 2,2-dibromo-3-nitrilopropionamide
Breaker	Reduces the viscosity of specialized treatment fluids such as gels and foams	Peroxydisulfuric acid diammonium salt
Clay control	Prevents the swelling and migration of formation clays in reaction 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

Additives	Function	Chemicals reported in ≥20% of FracFocus disclosures for additive[a,b]
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 from solution	Citric acid
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	Hydrochloric acid

[a] Chemicals (excluding water and quartz) listed as reported to FracFocus in more than 20% of disclosures for a given purpose when that purpose was listed as used on a disclosure. 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; 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.

A general description of typical hydraulic fracturing fluid formulations nationwide is difficult because fracturing fluids vary from well to well. Based on the FracFocus report, the median number of chemicals reported for each disclosure was 14, with the 5th to 95th percentile ranging from four to 28. The median number of chemicals per disclosure was 16 for oil wells and 12 for gas wells (U.S. EPA, 2015b). 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).[1]

Water, the most commonly used base fluid for hydraulic fracturing, is inferred to be used as a base fluid in more than 93% of FracFocus disclosures. Alternatives to water-based fluids, such as hydrocarbons and gases, including carbon dioxide or 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 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.

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 recycle the water. The disadvantages are low viscosity, the narrowness of the fractures created, and they may not provide optimal performance in water-sensitive formations (see Section 5.3.2) (Montgomery, 2013; Gupta and Valkó, 2007). 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).

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 requires the addition of biocide to minimize bacterial growth (Spellman, 2012; Gupta and Valkó, 2007). Gels may be linear or crosslinked. Crosslinking 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;

[1] Sources may differ based on whether they are referring to additives or chemicals.

methanol; and other unconventional fluids (Montgomery, 2013; Saba et al., 2012; Gupta and Hlidek, 2009; Gupta and Valkó, 2007; Halliburton, 1988).

Acid fracturing removes the need for a proppant and is generally used in carbonate formations. Fractures are initiated with a viscous fracturing fluid, and the acid (gelled, foamed, or emulsified) is added to irregularly etch the wall of the fracture and prop open the formation for a higher conductivity fracture (Spellman, 2012; Gupta and Valkó, 2007).

Non-aqueous fluids 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 used as an additive or in additive mixtures in hydraulic fracturing fluid formulations.

Energized fluids, foams, and emulsions minimize fluid leakoff, 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, require high pressure, and pose potential health and safety concerns (Montgomery, 2013; Spellman, 2012; Gupta and Valkó, 2007). **Energized fluids** 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 25% to 30% by volume (Montgomery, 2013; Gupta and Valkó, 2007; Mitchell, 1970). **Energized foams** are liquid-gas mixtures, with N_2 or CO_2 gas comprising more than 53% of the fracturing fluid volume, with a typical range of 70% to 80% by volume (Mitchell, 1970). **Emulsions** are liquid-liquid mixtures, typically a hydrocarbon (e.g., condensate or diesel) with water, with the hydrocarbon typically 70% to 80% by volume.[2] 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;

[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.
[2] Diesel is a mixture typically of C8 to C21 hydrocarbons.

Tudor et al., 2009; Gupta and Valkó, 2007; Coulter et al., 2006; Boyer et al., 2005; Fredd et al., 2004; MacDonald et al., 2003).

Alternative fluids have been developed to work in tight formations, shales, and coalbeds, where production is based on desorption of the natural gas, or in formations where the fracturing fluid must displace a fluid that is already in place.

5.3.3. Proppants

Proppants are small particles carried down the well and into fractures by fracturing fluid. They hold the fractures open after hydraulic fracturing fluid has been removed (Brannon and Pearson, 2007). The propped fractures provide a path for the hydrocarbon to flow from the reservoir. Sand is most commonly used, but other proppants include man-made or specially engineered particles, such as resin-coated sand, high-strength ceramic materials, or sintered bauxite (Schlumberger, 2014; Brannon and Pearson, 2007). Proppant types can be used individually or in combinations.

5.4. Frequency and Volume of Hydraulic Fracturing Chemical Use

This section highlights the different chemicals used in hydraulic fracturing and discusses the frequency and volume of use. Based on the U.S. EPA analysis of the FracFocus 1.0 database (see Text Box 5-2), we focus our analysis on individual chemicals rather than mixtures of chemicals used as additives. Chemicals are reported to FracFocus by using the chemical name and the Chemical Abstract Services Registration Number (CASRN), which is a unique number identifier for every chemical substance.[1] The information on specific chemicals, particularly those most commonly used, can be used to assess potential impacts to drinking water resources. The volume of chemicals stored on-site provides information on the potential volume of a chemical spill.

[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."

Text Box 5-2. 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 they use during hydraulic fracturing. The EPA accessed data from FracFocus 1.0 from January 1, 2011 to February 28, 2013, which included more than 39,000 disclosures from 20 states that had been submitted by operators prior to March 1, 2013.

Submission to FracFocus was initially voluntary and varied from state to state. During the timeframe of the EPA's study, six of the 20 states with data in the 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.

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. The EPA's analysis may or may not be nationally representative.

The EPA summarized information on the locations of the wells in the disclosures, water volumes used, and the frequency of use and concentrations (% by mass, reported as maximum ingredient concentration) of the chemicals in the additives and the hydraulic fracturing fluid. Additional information can be found in the EPA FracFocus report (U.S. EPA, 2015a).

The EPA compiled a list of 1,076 chemicals known to be have been used in the hydraulic fracturing process (see a full list, methodology, and the source citations in Appendix A). The chemicals used in hydraulic fracturing fall into different chemical classes and include both organic and inorganic chemicals. 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).
- Salts (e.g., sodium chlorite, dipotassium carbonate).

Text Box 5-3. Confidential Business Information (CBI)

This assessment relies in large part upon information provided to the EPA or to other organizations. The submitters of that information (e.g., businesses that operate wells or perform services to hydraulically fracture the well) may view some of the information as confidential business information (CBI), and accordingly asserted CBI claims to protect such information. Information deemed to be CBI may include information such as 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. FOIA and the 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.

The EPA evaluated data from FracFocus 1.0, a national hydraulic fracturing chemical registry used and relied upon by some states, industry groups and non-governmental organizations. A company submitting a disclosure to FracFocus may choose to not report the identity of a chemical it considers CBI. As part of the EPA's analysis, more than 39,000 FracFocus 1.0 disclosures over the period January 1, 2013 to March 1, 2013 were analyzed and more than 70% of disclosures contained at least one chemical designated as CBI. Of the disclosures containing CBI chemicals, there was an average of five CBI chemicals per disclosure (U.S. EPA, 2015a). The prevalence of CBI claims in FracFocus 1.0 limits completeness of the data set.

Consistent with the hydraulic fracturing study plan, data were submitted by nine service companies to the EPA regarding chemicals used in hydraulic fracturing from 2005 to 2009. Because this submission was to the EPA, the EPA was given 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).

5.4.1. National Frequency of Use of Hydraulic Fracturing Chemicals

The EPA reported that 692 chemicals were reported to FracFocus 1.0 for use in hydraulic fracturing from January 1, 2011, to February 28, 2013, with a total of 35,957 disclosures (U.S. EPA, 2015a).[1]

Table 5-2 presents the 35 chemicals (5% of all chemicals identified in the EPA's study) that were reported in at least 10% of the FracFocus 1.0 disclosures for all states reporting to FracFocus during this time. This table also includes the top four additives that were reported to include the given chemical in FracFocus disclosures from January 1, 2011 to February 28, 2013.

[1] The EPA reported that 692 chemicals were reported to FracFocus 1.0 for use in hydraulic fracturing from January 1, 2011, to February 28, 2013, with a total of 35,957 disclosures. 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 5-2. 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 and the top four reported additives for the chemical.

For chemicals with fewer than four reported additives, the table presents all additives (U.S. EPA, 2015b).

No.	Chemical name[a]	CASRN	Percent of disclosures[b]	Chemical used in these additives (four most common, FracFocus 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	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
14	Ethanol	64-17-5	29%	surfactants, biocides, corrosion inhibitors, fluid foaming agents and energizers

No.	Chemical name[a]	CASRN	Percent of disclosures[b]	Chemical used in these additives (four most common, FracFocus database)[c]
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
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

No.	Chemical name[a]	CASRN	Percent of disclosures[b]	Chemical used in these additives (four most common, FracFocus database)[c]
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).
[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, was 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 at all wells across the nation. Methanol is the most commonly used chemical, reported at 72.1% of wells in FracFocus 1.0, and is associated with 33 types of additives, including corrosion inhibitors, surfactants, non-emulsifiers, and scale control (U.S. EPA, 2015b). Table 5-2 also shows the variability in different chemicals reported to FracFocus 1.0. 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.

In addition to providing information on frequency of use, FracFocus 1.0 data provides the maximum concentration by mass of a given chemical in an additive. For example, for the most frequently used chemical, methanol, the median maximum additive concentration reported in FracFocus disclosures is 30%, by mass, with a range of 0.44% to 100% (5th to 95th percentile). This suggests that methanol is generally used as part of a mixture of chemicals in the hydraulic fracturing fluid, and may be stored in a mixture of chemicals or 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.

5.4.2. Nationwide Oil versus Gas

FracFocus 1.0 data also can elucidate the differences between the chemicals used for oil production and those used for gas production, providing a better understanding of potential spill impacts from each. Table C-1 and C-2 in Appendix C present the chemicals reported in at least 10% of all gas (34 chemicals) and oil (39 chemicals) disclosures nationwide.

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

We conducted a state-by-state analysis of chemical use based on FracFocus 1.0 disclosures (U.S. EPA, 2015b). Some states reported more disclosures than other states, because they have relatively more hydraulic fracturing activity and/or greater numbers of disclosures to FracFocus 1.0. Reporting can bias national numbers towards those states with a disproportionate number of disclosures. For example, the EPA (2015a) reported that Texas had 16,405 of the 34,675 disclosures with parsed ingredients and valid CASRNs and concentrations, making up almost half (47%) of all disclosures for the 20 states reporting to FracFocus 1.0. We attempt to account for the possible effect of having a large number of disclosures in Texas by looking at a compilation of the top 20 chemicals reported to FracFocus for all states.

Table 5-3 presents and ranks chemicals reported most frequently to FracFocus 1.0 for each state (U.S. EPA, 2015b). There are 94 unique chemicals comprising the top 20 chemicals for each state, indicating similarity in chemical usage among states.

Methanol is reported in 19 of the 20 (95%) states. Alaska is the only state in which methanol is not reported (based on the state's 20 disclosures to FracFocus). 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;

[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.

isopropanol; quartz; sodium hydroxide; ethanol; guar gum; hydrochloric acid; and peroxydisulfuric acid, diammonium salt.[1] These 10 chemicals are also the most frequently reported chemicals nationwide.

By performing this analysis by state, we observed that methanol is used across the continental U.S. (not Alaska), and there are 9 other chemicals that are frequently used across the U.S. Beyond those, however, there are a number of different chemicals that are used in one state more commonly than others and many may not be used at all in other states. This suggests that there is regional variability in some chemicals and a common set of the same chemicals that are frequently used.

[1] Quartz was the most commonly reported proppant and also reported as an ingredient in other additives (U.S. EPA, 2015a).

Table 5-3. The percentage of disclosures of the 20 most commonly reported chemical by state, where a chemical is reported in at least three states.

The 20 most frequently reported chemicals were identified for all 20 states that reported to FracFocus 1.0 (U.S. EPA, 2015b). The chemicals were ranked by counting the number of states where that chemical was in the top 20. Chemicals were then ranked so that chemicals used most widely among the most states come first. Methanol is reported in 19 of 20 states, so methanol is ranked first. A chemical was only presented on the list if it were reported in at least three states, resulting in 33 chemicals. The full table of top 20 chemicals (91 chemicals) is presented in Appendix C.

Chemical name	CASRN	Percentage of disclosures per state[a]																			
		AL	AK	AR	CA	CO	KS	LA	MI	MS	MT	NM	ND	OH	OK	PA	TX	UT	VA	WV	WY
Methanol	67-56-1	100%		100%	39%	63%	79%	59%	93%	75%	63%	91%	53%	52%	70%	69%	78%	79%	61%	64%	38%
Distillates, petroleum, hydrotreated light	64742-47-8		45%	56%	55%	74%	90%	84%	100%	100%	60%	63%	47%	84%	70%	60%	66%	75%		82%	51%
Ethylene glycol	107-21-1	100%	100%	22%	60%		63%	34%	71%	75%	49%	45%	36%	57%	47%	34%	59%	85%	28%	59%	
Isopropanol	67-63-0	100%	65%	44%		57%	25%	51%	79%		64%	62%	37%	49%	42%	31%	48%	53%	54%	31%	43%
Quartz	14808-60-7		100%		89%	23%	23%	37%		50%	64%	68%	46%	45%	27%		43%	40%		22%	30%
Sodium hydroxide	1310-73-2		100%	21%	69%	22%	28%	53%		50%	54%	30%	52%		27%	17%	46%	37%			57%
Ethanol	64-17-5			45%		50%	80%	42%		100%		47%	27%	60%	46%	16%	21%		63%	54%	25%
Guar gum	9000-30-0		50%		93%			49%		50%	43%	63%	55%	51%	25%	23%	43%	43%		23%	69%
Hydrochloric acid	7647-01-0	100%		99%		53%	85%	57%			23%	79%		99%	76%	96%	71%	85%	86%	96%	
Peroxydisulfuric acid, diammonium salt	7727-54-0		50%		83%		22%	27%	57%		62%	75%	55%	64%	39%		54%	39%		54%	64%
Propargyl alcohol	107-19-7			61%			71%	30%	36%			68%		49%	41%	58%	39%	36%	28%	58%	
Glutaraldehyde	111-30-8			55%			75%	36%		50%		57%		72%	55%	34%	40%			71%	22%
Naphthalene	91-20-3	100%				30%	42%	29%	86%		49%		43%		25%			38%	9%		
2-Butoxyethanol	111-76-2	100%	100%						79%			37%				21%	24%	53%	89%	26%	

Chemical name	CASRN	Percentage of disclosures per state[a]																			
		AL	AK	AR	CA	CO	KS	LA	MI	MS	MT	NM	ND	OH	OK	PA	TX	UT	VA	WV	WY
Citric acid	77-92-9						46%					40%		66%	36%	29%	24%	79%	80%	41%	
Sodium chloride	7647-14-5					35%		41%		50%			25%				21%		9%	22%	23%
Solvent naphtha, petroleum, heavy aromatics	64742-94-5					33%	43%				70%		49%		31%		17%		9%		35%
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides	68424-85-1			28%			54%			50%				37%	33%	16%				22%	
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	100%				49%			71%		36%					34%			28%		
Potassium hydroxide	1310-58-3							34%		100%	60%		59%	73%			39%				
Acetic acid	64-19-7					21%		28%							24%		31%				31%
Choline chloride	67-48-1					27%						34%		38%				52%	57%		
Polyethylene glycol	25322-68-3	100%							50%		36%		29%			29%					
1,2,4-Trimethylbenzene	95-63-6					27%	40%						25%						9%		
Ammonium chloride	12125-02-9			21%		28%										31%				21%	
Diatomaceous earth, calcined	91053-39-3		100%		71%							38%						35%			
Didecyl dimethyl ammonium chloride	7173-51-5			24%						50%				32%						21%	
Sodium chlorite	7758-19-2							35%		100%			24%								23%
Sodium erythorbate	6381-77-7			33%			30%												13%	32%	
N,N-Dimethylformamide	68-12-2													47%	20%			33%			

Chemical name	CASRN	Percentage of disclosures per state[a]																			
		AL	AK	AR	CA	CO	KS	LA	MI	MS	MT	NM	ND	OH	OK	PA	TX	UT	VA	WV	WY
Nonyl phenol ethoxylate	9016-45-9											30%						36%	32%		
Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture)	127087-87-0					25%	40%												9%		
Sodium persulfate	7775-27-1									100%						16%					26%
Tetramethylammonium chloride	75-57-0										44%		29%								26%

[a] 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.

5.4.4. Volumes of Chemicals Used

Understanding the volume of chemicals used at each hydraulic fracturing site is important for understanding potential impacts of chemicals to drinking water resources, because the chemical volume governs how much will be stored on-site, the types of containers required, and the total amount that could spill. While the on-site operator has precise knowledge of the composition and volume of chemicals stored on-site, this information is generally not 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 (56,000 L) for the two sources, with a mean volume for an individual chemical of 1,900 gal (7,000 L) and 1,225 gal (4,600 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 volumes used in hydraulic fracturing.

Volumes are for wells with and unknown number of stages and at least one perforation zone. Every well and fluid formation is unique. Volumes may be larger for longer horizontal laterals and with a greater number of stages.

		Sjolander et al. (2011)[a]		Occupational Safety and Health Administration (OSHA, 2014a, b)[b]	
Ingredient	**Examples**	**Volume (gal) or mass (lbs)**	**Percent overall[c]**	**Volume (gal)**	**Percent by volume**
Water		4,000,000 gal	94.62	2,700,000	90
Proppant	Sand	~ 1,500,000 lbs[d]	5.17	285,300	9.51
Acid	Hydrochloric acid or muriatic acid	1,338 gal	0.03	3,690	0.123
Friction reducer	Polyacrylamide, mineral oil	2,040 gal	0.05	2,640	0.088
Surfactant	Isopropanol			2,550	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			1,290	0.043

Ingredient	Examples	Sjolander et al. (2011)[a]		Occupational Safety and Health Administration (OSHA, 2014a, b)[b]	
		Volume (gal) or mass (lbs)	Percent overall[c]	Volume (gal)	Percent by volume
pH buffer	Carbonate			330	0.011
Preservative	Ammonium persulfate			300	0.01
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]		
All chemicals		7,458 gal	0.21	14,700	0.49
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 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] The Penn State publication presented 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 FracFocus database. Figure 5-5 plots median estimated chemical volumes, ranked from high to low, with the range of 5th to 95th percentiles.[1] Volumes used are presented for the 74 chemicals that were reported to FracFocus in at least 100 disclosures and for which density data were available.[2] 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).[3]

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

[1] Volumes were estimated using FracFocus disclosures. The total hydraulic fracturing fluid volume reported was used to calculate the total fluid mass by assuming the fluid has a density of 1 g/mL. This is a simplifying assumption based on the fact that more than 93% of disclosures are inferred to use water as a base fluid. Water had a median concentration of 88% by mass in the fracturing fluid. Some disclosures reported using brine, which has a density between 1.0 and 1.1 g/mL. This would introduce at most an error of 10% for the fluid calculation (the difference of a chemical being present at 10 versus 9 gal, 1,000 versus 900 gal). We also assume that the mass of chemicals present in calculating the total fluid mass is negligible. Given that ≤2% of the fluid volume is non-water chemicals, and assuming the density of which is 3 mg/L, the error introduced is approximately 6%. For reference, for the chemicals we are calculating volumes, chlorine dioxide is the densest at 2.757 mg/L. Chemical with densities less than 1 mg/L introduce approximately <1% error.
Next, the mass of each chemical per disclosure was calculated. Each chemical is reported to FracFocus 1.0 as a maximum concentration by mass in the hydraulic fracturing fluid. This introduces error, as we only know that it is equal to or less than this mass fraction. In the U.S. EPA (2015a) EPA's analysis of the FracFocus 1.0 database, an additive is comprised of three chemicals with maximum ingredient concentration of 60% in the additive and a maximum concentration of 0.22% in the hydraulic fracturing fluid. Each of the three chemicals cannot be present at 60%. We have no way to know the actual proportions of each chemical in the additive and thus must calculate chemical mass based on the given information. Therefore, our calculations likely overestimate actual volumes. However, in some cases, the concentration in the additive that is given is less than 100% and only one chemical is listed in the additive. In these cases, it appears that the disclosure is reporting the concentration of that chemical in water. Hydrogen chloride is listed as the sole ingredient in the acid additive, and the maximum concentration is 40% by mass. In this case, the HCl is diluted down to 40%, so the total volume would be underestimated.
After all the chemical masses are calculated, the volume is calculated by dividing chemical mass by density.
Given the limited information available, due to the limits of the FracFocus database and general lack of publicly available data, and despite the errors associated with these calculations, these calculations provide context for the general magnitude of volumes for each of the chemicals used on-site. These calculations are used to calculate median volumes for each chemical. These volume calculations are for the chemicals themselves, not the additives.
Analysis considered 34,495 disclosures and 672,358 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; criteria for water volumes; valid CASRN; and valid concentrations. Disclosures that did not meet quality assurance criteria (4,035) or other, query-specific criteria were excluded from analysis.

[2] Density data were gathered from Reaxys® and other sources as noted. Reaxys® (http://www.elsevier.com/online-tools/reaxys) is an online database of chemistry literature and data. Direct density source, as provided by Reaxys®, is provided in Table C-7 in Appendix C.

[3] Reporting records to FracFocus 1.0 was required in six of the 20 states between January 1, 2011 and February 28, 2013. An additional three states required disclosure to either FracFocus or the state, and five states required reporting to the state. Reporting to FracFocus 1.0 was optional in other states. Some states changed their reporting requirements during the course of the study. The FracFocus 1.0 database therefore does not encompass all data on chemicals used in hydraulic fracturing. As stated in Text Box 4-2, this mix of voluntary versus mandatory disclosure requirements limits the completeness of data extracted from FracFocus 1.0 for estimating hydraulic fracturing fluid. According to a comparison between FracFocus reported fluid volumes and literature values, water use per well was reported to be about 86% of the actual used (median of estimated values. See Chapter 4, Text Box 4-1). If the fluid volume is underreported, then estimated chemical volumes based on fluid volume would be similarly underestimated. Using the underreporting of 86%, then the estimated median chemical volume would be 760 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 (see Chapter 4) (U.S. EPA, 2015a) and assume that up to 2% of that volume are 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.

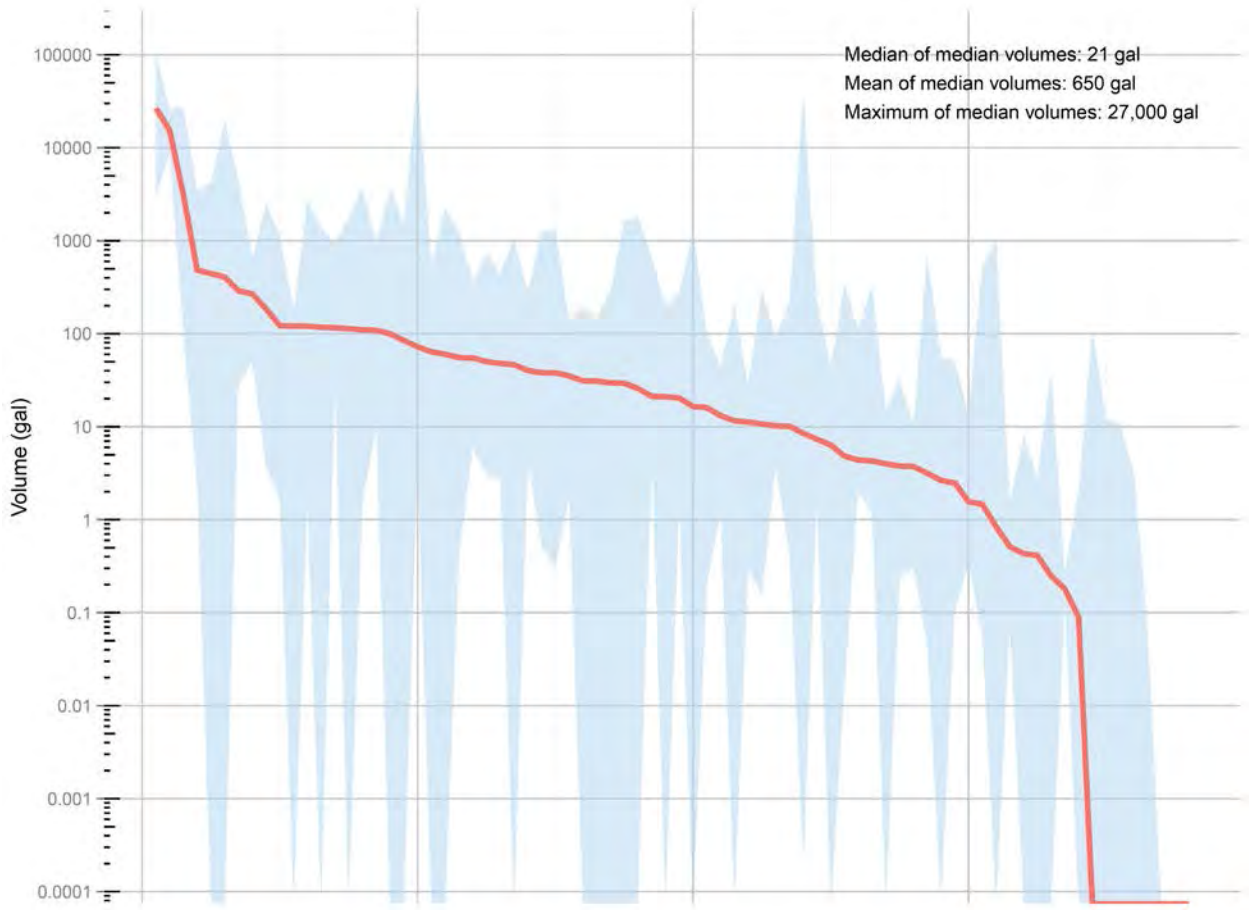

Figure 5-5. Estimated median volumes for chemicals reported in at least 100 FracFocus disclosures by February 28, 2013 for use in hydraulic fracturing from January 1, 2011 to February 28, 2013.

Shaded area represents the zone of 5% and 95% confidence limits. Derived from (U.S. EPA, 2015b).

Using the mean of the median chemical volumes from disclosures in FracFocus 1.0, 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 approximate 1,900 to 3,200 gal (7,400 to 12,000 L). On-site containers generally store 20% to

100% more additive volume than needed (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.

The volume that may be released during a spill depends on where in the chemical mixing process the spill occurs. Spills from chemical or additive containers may result in higher volume spills than the estimated volumes in Figure 5-5 suggest. However, if the spill is of the hydraulic fracturing fluid downstream of the blender, then the total volume of chemical spilled may be less than the estimated total volumes held on site.

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 approximately one-third of chemical spills on or near the well pad related to hydraulic fracturing resulted from equipment failure (U.S. EPA, 2015n). When possible, we describe documented spills associated with or attributed to specific pieces of equipment, in text boxes in the relevant subsections.

Hydraulic fracturing operations are mobile and must be assembled at each well site, and each assembly and disassembly presents a potential for spills. Equipment used in the chemical mixing and well injection processes 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. There are many potential sources for leaks and spills in this interconnected system.

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, reducing opportunities for human error. Information detailing the extent of technological and age differences in fracturing equipment across sites and operators is limited. Table 5-5 provides a description of typical hydraulic fracturing equipment.

Table 5-5. Examples of typical hydraulic fracturing equipment and their functions.

Equipment	Function
Acid transport truck	Transports acids to job sites, the truck has separate compartments for multiple acids or additives.
Chemical storage truck	Transport 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	Store the required volume of base fluid to be used in the hydraulic fracturing process.
Proppant storage units	Hold proppant and feed 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	Pressurize mixed fluids received from the blender and injected into the well.
Manifold trailer with hoses and pipes	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	A wellhead connection that allows fracture equipment to be attached to the well.

While the primary equipment and layout is 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):

- The size and type of the fracture treatment;
- The number of wells drilled per well pad;
- The location, depth, and length of the fractures;
- The volumes and types of additives, proppants, and fluids used; and
- The 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.

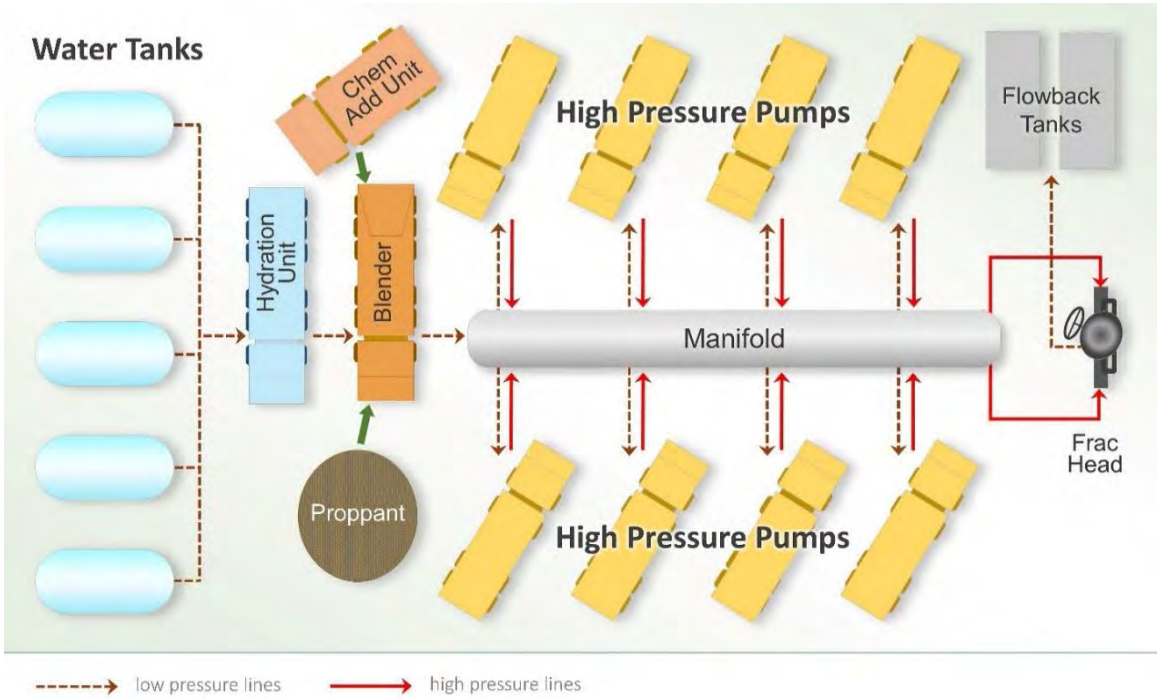

Figure 5-6. Typical hydraulic fracturing equipment layout.

This illustration shows how the various components of a typical hydraulic fracturing site fit together. 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. Malone and Ely (2007) indicate that companies typically store an excess of 20% of the required chemical inventories on location. Houston et al. (2009) recommends maintaining an on-site chemical reserve of 100% extra beyond what is necessary for the fracturing treatment (Houston et al., 2009). See Text Box 5-4 for documented spills from storage units.

Text Box 5-4. Spills from Storage Units.

Of the 151 spills of chemicals, additives, or fracturing fluid discussed and evaluated in (U.S. EPA, 2015n) (see Text Box 5-13 for more information), 54 spills were from storage units. Storage units include smaller totes or tanks used for storing individual chemicals or additives, and larger tanks containing 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 need for 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 (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. An example of a documented spill of hydraulic fracturing fluid is presented in Text Box 5-5.

Text Box 5-5. Spills of Fracturing Fluid Documented to Impact Surface Water.

In September 2009, two spills of hydraulic fracturing fluid occurred at the same site in Pennsylvania. A total of approximately 7,350 gal (28,000 L) of fluid comprised of a mixture of water, gel, and friction reducer leaked and migrated to Stevens Creek. While the causes of the spills are not clear, it appears that a pressurized line may have broken and a seal may have failed (U.S. EPA, 2015n, Appendix B Line 307; Lustgarten, 2009).

5.5.1.2. Chemical Additive Storage

Additives are typically stored on-site in the containers in which they were transported and delivered. The chemical 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 chemical additive trailers per site (ALL Consulting, 2012; NYSDEC, 2011). Additives constitute a relatively small portion of fluids used in a hydraulic fracturing fluid, although they can still be used in volumes ranging 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 5-6 for documented spills from an additive storage unit.

Text Box 5-6. Spill from Additive (Crosslinker) Storage Tote.

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 placed in a lined containment area (U.S. EPA, 2015n, Line 309).

The most commonly used chemical totes are 200–400 gal (760–1,500 L) capacity polyethylene containers that may be reinforced with steel or aluminum mesh (NYSDEC, 2011). Metal containers of the same capacity may also be used (ALL Consulting, 2012; UWS, 2008). The totes are typically equipped with bottom release ports, which enable the direct feed of the additives to the blending equipment (NYSDEC, 2011). 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) chemical additive units.

The image on the left depicts metal totes (industry source). The image on the right depicts plastic totes (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, 2011; UWS, 2008; Halliburton, 1988). Proppants are stored on-site in large tanks or bins with typical capacities of 220 to 440 lb (100 to 200 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 3,000 to 5,000 gal (11,400 to 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 CFR 173) designed to prevent or minimize spills.

Acid fracture treatments may use thousands of gallons (thousands of liters) 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. Eight spills (out of 105 spills from state data sources) of acid or fracturing fluid containing acid were reported to state data sources examined by the EPA (2015n). The median volume of these acid spills was approximately 1,600 gal (6,000 L) (Lines 240, 241, 248, 258, 264, 272, 278, and 281 in Appendix B of U.S. EPA (2015n)).

Details of a documented acid spill are presented in Text Box 5-7.

Text Box 5-7. Spill of Acid from Storage Container.

In July 2014, over 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 may pose different potential spill scenarios depending on whether the site is using batch or continuous mixing processes (BJ Services Company, 2009).

5.5.1.5. Batch Mixing

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 in large tanks (typically 20,000 gal or 76,000 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 may 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, which may 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 5-8.

Text Box 5-8. Spill of Gel during Mixing.

On April 9, 2010, 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 (U.S. EPA, 2015n, Appendix B Line 220).

5.5.1.6. Continuous Mixing (On-the-Fly)

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 BD, 1999), which may 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. The following photograph shows an example of hoses and lines at a hydraulic fracturing site.

Figure 5-8. A worker adjusts hoses at a hydraulic fracturing site near Mead, Colorado.

Source: AP Photo/Brennan Linsley.

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 may 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 potential for spills or 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 may result in a leak or spill. Safety restraints are typically used to prevent movement of flow lines 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 (48,300 L), with a median volume of 420 gal (1,600 L) (U.S. EPA, 2015n).

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). 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 may 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 comprised primarily of water with a low concentration (less than or equal to 2%) of chemicals. Details of a spill from a blender are presented in Text Box 5-9.

Text Box 5-9. Spill of Hydraulic Fracturing Fluid from Blender.

In May 2006, a blender malfunctioned during a fracture job in Oklahoma. Approximately 294 gal (1,100 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 (U.S. EPA, 2015n, Appendix B Line 249).

5.5.4. Manifold

A trailer-mounted manifold and pump system functions as a central transfer station for all fluids used to fracture the well. 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 it 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).

Figure 5-9. Manifold (pointed to by the white arrow).

Source: Halliburton.

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. The EPA (U.S. EPA, 2015n) identified seven spills sourced from manifolds. Three of these spills, out of the 105 chemical or hydraulic fracturing fluid spills reported to state data sources, were fracturing fluid that resulted from either human error of equipment failure. These three spills were responsible for approximately 5,000 gal (19,000 L) of spilled fluids (U.S. EPA, 2015n, Appendix B Lines 35, 141, 160).

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 may be larger. Smaller pumps may require more operators and more maintenance (BJ Services Company, 2009), and therefore may result in more frequent spills.

Figure 5-10. High-pressure pumps on either side of the manifold.

Source: http://drillingahead.com/roger-payne/gallery/14826/20000-psi-frac-near-caldwelltexas-2005#gallery_img.

The "fluid ends" of hydraulic fracturing pumps are the pump components through which fluids are moved and pressurized. Pump fluid ends must withstand enormous pressure and move a large volume of abrasive fluid high in solids content. They 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 5-10.

Text Box 5-10. Spill of Fluid from Fracture Pump.

In December 2011, 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 scheduled to be neutralized and taken to a landfill at the end of the job, after removal of the equipment (U.S. EPA, 2015n, Appendix B Line 14).

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 5-11. 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. Details of a documented frac head failure are presented in Text Box 5-11. Details on the Killdeer, ND, blowout and associated spill are presented in Text Box 5-12.

Text Box 5-11. Spill from Frac Head Failure.

On March 2, 2011, a frac head failed during fracturing operations in Colorado. 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. Some of the fluid was recovered, and saturated soils were scraped and stockpiled on the well pad (U.S. EPA, 2015n, Appendix B Line 75).

Text Box 5-12. The Killdeer Case Study.

In September 2010, a blowout occurred in the Franchuk 44-20 SWH well, in Dunn County near Killdeer, ND. Hydraulic fracturing fluids, oil, and flowback water spilled onto the land and possibly entered the Killdeer aquifer, which is a source of drinking water. The EPA investigated a reported blowout event at the Killdeer site as part of a retrospective case study. The study area is comprised of historical oil and gas production and current hydraulic fracturing. The discussion below was taken from the EPA Killdeer case study (U.S. EPA, 2015j).

Methods

Water quality samples were collected from three domestic wells, nine monitoring wells (installed by Terracon), two supply wells, one municipal well, and one state well during three rounds in July 2011, October 2011, and October 2012. The geochemistry of water samples was investigated by analyzing major ions, trace metals, methane/ethane gas concentrations, volatile organic compounds, semivolatile organic compounds, glycol ethers, diesel- and gasoline-range organics, low-molecular-weight acids, and selected stable isotopes. Data collected from this study were statistically compared with historical water quality data retrieved from the literature and national water quality databases. To help determine whether hydraulic fracturing processes were a cause of alleged impacts on water quality, detailed environmental record searches were conducted to help identify other potential contaminant sources.

Results

Three study wells, NDGW09, NDGW08, and NDGW07, were excluded from the comparisons with historical data. NDGW09 was excluded since it was screened in the Sentinel Butte aquifer so a comparison with historical Killdeer aquifer water quality data was not appropriate. NDGW08 and NDGW07 had significant differences in water quality compared to the remaining study wells. These two wells showed differences in ion concentrations (e.g., chloride, calcium, magnesium, sodium, strontium) as well as tert-butyl alcohol (TBA). The remaining study wells were then compared with historical data to determine if these wells represented background water quality of the Killdeer aquifer. This comparison between the remaining study wells and Killdeer aquifer historical water quality data indicated that these remaining study wells were in general consistent with the historical background data and then used for the data analysis as background wells. There were limited detections of other organic compounds in the study wells. In most cases, with the exception of TBA, the detected organic compounds could not be directly linked to the blowout or hydraulic fracturing, as these chemicals could have originated from other sources including vehicular traffic, generators used to power well pumps, flaring of methane from the pad production wells, and cement used to repair a well the day prior to sampling.

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. TBA data were compared with the background study wells and were found to be different. Based on the analysis of other potential sources of contamination, the EPA determined that the only other potential sources of TBA were gasoline spills, leaky underground storage tanks, and hydraulic fracturing fluids. The data from this study suggest the TBA resulted from the degradation of tert-butyl hydroperoxide used during the hydraulic fracturing of the Franchuk well since MTBE and other signature compounds associated with gasoline or fuels were not present in NDGW08 and NDGW07.

Conclusion

The analysis of data from NDGW008 and NDGW07 indicated that the main impact on water quality was from briny water and TBA mixing with Killdeer aquifer water in these wells. In all cases, the fingerprinting techniques used indicated that the impacts on NDGW07 and NDGW08 were consistent with deep formation brines underlying the Killdeer study location. Based on the data analysis performed for the Killdeer case study, the observed impacts on NDGW07 and NDGW08 were likely caused by the blowout that occurred at the Franchuk 44-20. This evidence, along with the absence of another plausible candidate cause, strongly suggests impact on a drinking water resource from the blowout during the hydraulic fracturing of the Franchuk 44-20 SWH well.

5.6. Spill Prevention, Containment, and Mitigation

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.

Hydraulic fracturing operating companies themselves may develop and implement spill prevention and containment procedures. The American Petroleum Institute has a guidance document *Practices for Mitigating Surface Impacts Associated with Hydraulic Fracturing* (API, 2011). The document describes practices currently used in the oil and natural gas industry to minimize potential surface environmental impacts. As another example, the province of New Brunswick, Canada, released rules for industry on responsible environmental management of oil and natural gas activities (GNB, 2013). It was beyond the scope of this assessment to evaluate the efficacy of the practices in these documents 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, 2015n). 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, 2015n). There was not enough information to detail the regularity 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 (U.S. EPA, 2015n). Other remediation methods reported by the EPA (U.S. EPA, 2015n) included the use of absorbent material, vacuum trucks, flushing the affected area with water, and neutralizing the spilled material.

5.7. 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, 2015n; Brantley et al., 2014; COGCC, 2014; Gradient, 2013). Spills may infiltrate drinking water resources by reaching surface water, or by leaching into the ground water. Potential impacts depend upon a variety of factors including the chemical spilled, environmental conditions, and actions taken in response to the spill. However, due to a lack of available data, little is known about the prevalence and severity of actual drinking water impacts.

5.7.1. EPA Analysis of Spills Associated with Hydraulic Fracturing

The EPA (2015n) (see Text Box 5-13 for additional information) evaluated 457 spills related to hydraulic fracturing activities on or near the well pad. Of these spills, 151 spills were 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.

Text Box 5-13. EPA Review of State and Industry Spill Data: Characterization of Hydraulic Fracturing-Related Spills.

The EPA (2015n) used data gathered from select 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 ground water 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 states 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. 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 and April 2012).

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. Figure 5-12 presents the percent distribution of chemical or fracturing fluid spills associated with each cause. Over half of the spills were collectively caused by equipment failure (34%) and human error (25%). Approximately one-quarter of the spill causes were unknown or not reported. A report analyzing spills in Colorado is generally consistent with the EPA's findings (COGCC, 2014).[1] Colorado found that equipment failure was the dominant spill cause, accounting for over 60% of spills between 2010 and 2013, followed by human error accounting for 20%–25% of spills.

[1] The COGCC report included all materials related to oil and gas production and were therefore not specific to chemical and fracturing fluid spills.

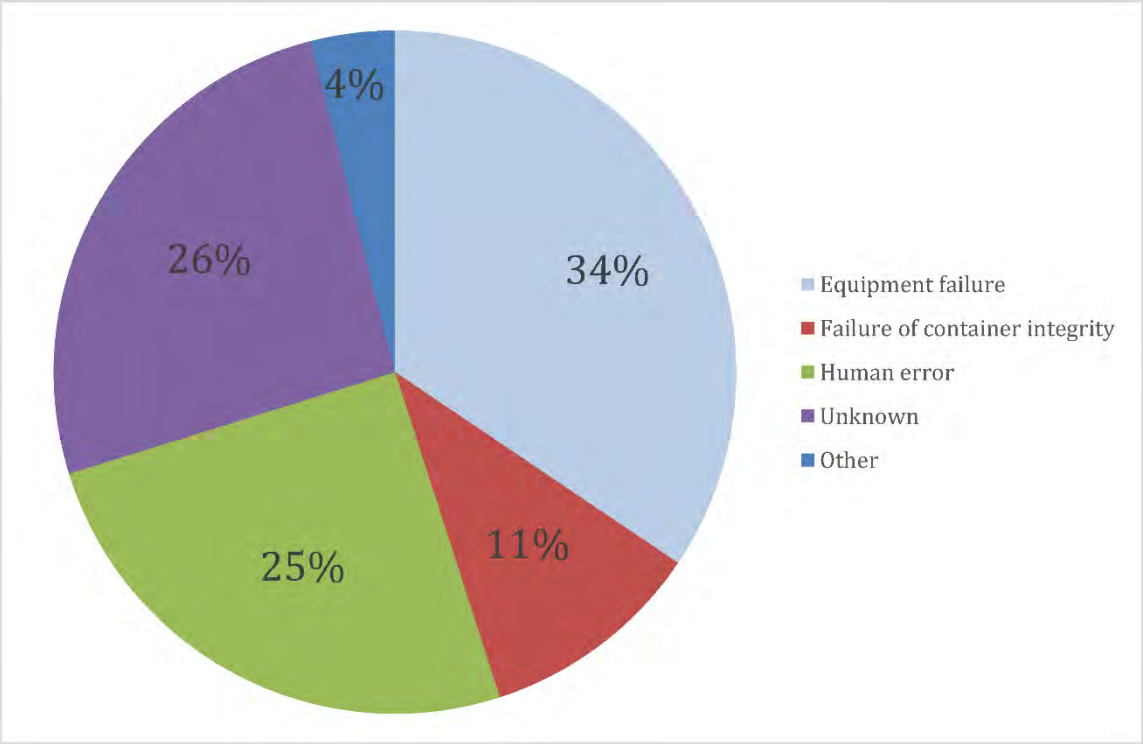

Figure 5-12. Distribution of the causes of 151 hydraulic fracturing-related spills of chemicals and fracturing fluid.

Data from U.S. EPA (2015n).

Spills in the EPA Spills Report were also categorized by the following sources: storage, equipment, well or wellhead, hose or line, and unknown. Figure 5-13 presents the percent distribution for the chemical or fracturing fluid spills associated with each source. Storage units (e.g., chemical totes, fracturing fluid tanks) were the predominant source of spills, accounting for 36% (54 spills) of spill sources. Spills from storage units were predominantly caused by human error (39%), followed by failure of container integrity (30%). Spills from equipment were the next most common known source (18%), followed by spills from hoses or lines (13%). Twenty-eight percent of spills had an unknown source.

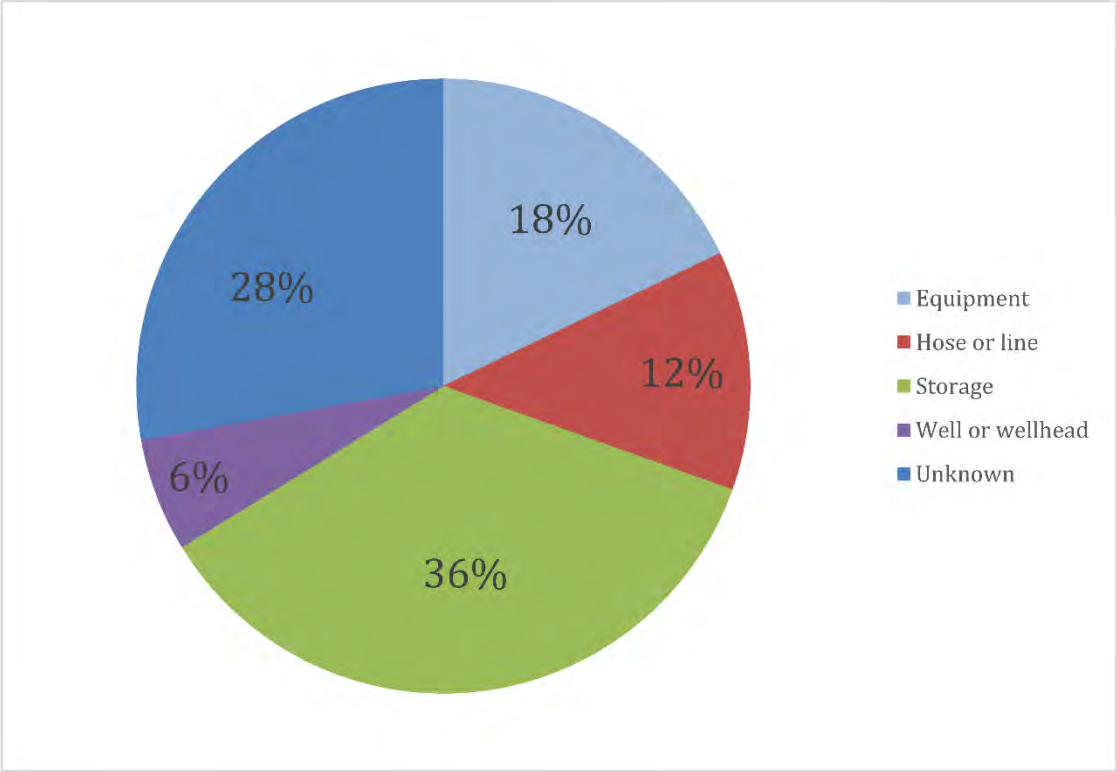

Figure 5-13. Percent distribution of sources of 151 hydraulic fracturing-related spills of chemicals or fracturing fluid.

Data from U.S. EPA (2015n).

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. The spills ranged in volume from 5 to more than 19,000 gal (19 to 72,000 L), with a median volume of 420 gal (1,600 L). The largest source of spills was storage containers, which released approximately 83,000 gal (314,000 L) of spilled fluid. Spills from wells or wellheads are often associated with high spill volumes. Nine instances of spills at the well or wellhead were associated with approximately 46,000 gal (174,000 L) of spilled fluid (see Figure 5-14). The high pressure associated with frac head blowouts has led to large, high-volume spills (see Text Box 5-11).

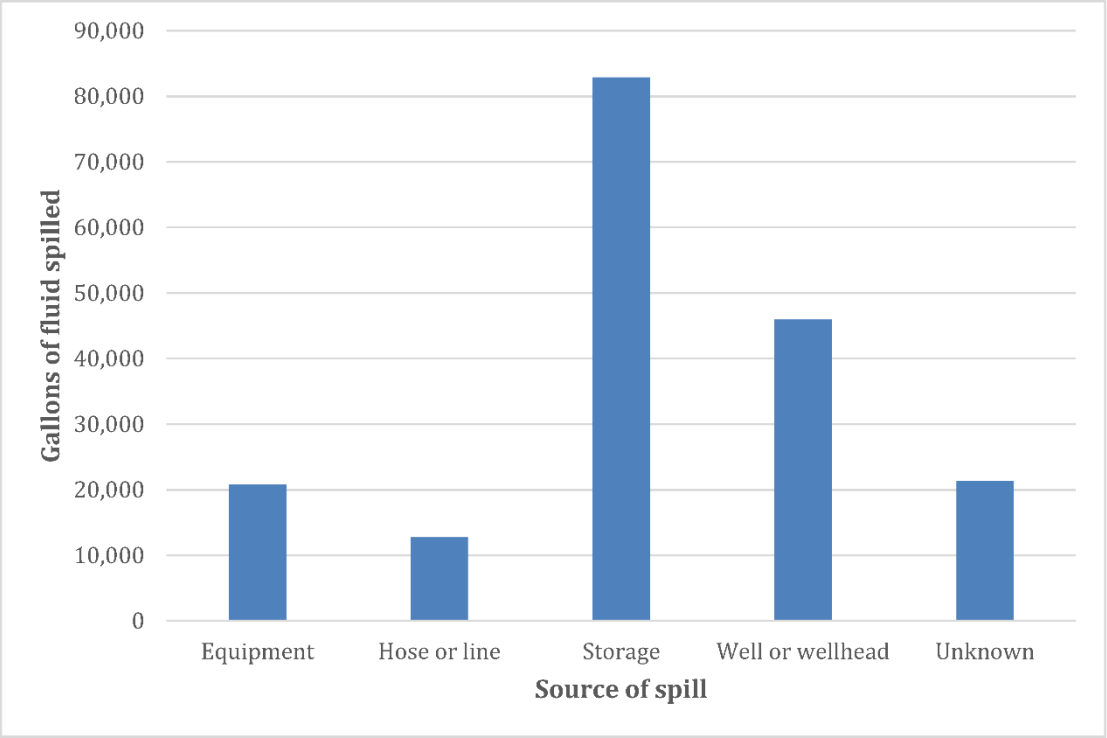

Figure 5-14. Total volume of fluids spilled for 151 hydraulic fracturing-related spills of chemicals and fracturing fluid, by spill source.

Data from U.S. EPA (2015n).

Figure 5-15 presents the number of chemical or fracturing fluid spills that reached environmental receptors, by receptor type. Environmental receptors (i.e., surface water, ground water, soil) were identified for 101 of the 151 spills, or 67% of the spills in the EPA's analysis (U.S. EPA, 2015n). Soil was by far the dominant environmental receptor, with 97 spills reaching soil. Thirteen spill reports indicated that the spilled fluid had reached surface water. Nine spill reports identified both soil and surface water as a receptor. No spill report identified ground water as a receptor. The data contain few post-spill analyses, so ground water contamination may have occurred but have not been identified. Additionally, several years may be required for a spilled fluid to leach into the ground water and therefore impact on a ground water receptor may not be immediately apparent. Storage units were the predominant sources of spills reaching an environmental receptor.

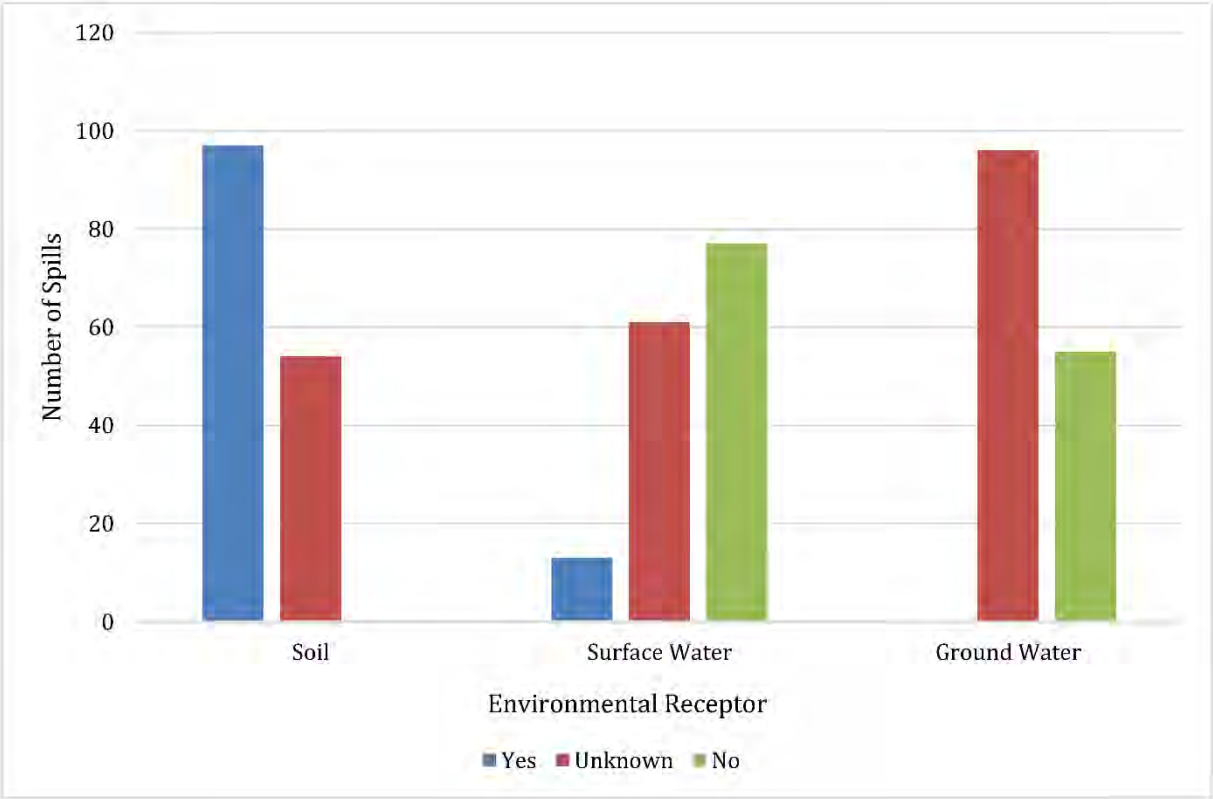

Figure 5-15. Number of hydraulic fracturing-related spills of chemicals or fracturing fluid that reported whether an environmental receptor was reached.

"Unknown" refers to hydraulic fracturing related spill events for which environmental receptors were specified as unknown or not identified (positively or negatively).
Data from U.S. EPA (2015n).

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.

The EPA analysis demonstrates that spills of chemicals, additives, and fracturing fluids do occur at well sites and reach both soil and surface water receptors.

5.7.2. Other Spill Reports

Surface spills related to hydraulic fracturing activities are not well documented in the scientific literature, though some evidence of spills and impacts to environmental media exists (e.g., U.S. EPA,

2015j; Brantley et al., 2014; Gross et al., 2013; Papoulias and Velasco, 2013). For example, Papoulias and Velasco (2013) demonstrated that fracturing fluid spilled into surface water likely contributed to the distress and deaths of the 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 in ground water samples, which the authors attributed to numerous hydraulic fracturing-related spills. The COGCC (2014) published a report analyzing all spills reported to the state of Colorado between 2010 and 2013, and found that approximately 8% of them were related to hydraulic fracturing. Based on the EPA's analyses (U.S. EPA, 2015n) and available scientific data, we estimate spill rates of chemicals and hydraulic fracturing fluid range from 0.4 and 12.2 spills for every 100 wells. (See Text Box 5-14 for additional information.)

Text Box 5-14. Spill Rates.

Several studies have estimated the frequency of hydraulic fracturing-related spills. Three studies (Rahm et al., 2015; Brantley et al., 2014; Gradient, 2013) calculated a spill rate for the Marcellus Shale in Pennsylvania using reports from the Pennsylvania Department of Environmental Protection (PA DEP) Oil and Gas Compliance Report Database, and here we estimate an on-site spill rate for Colorado. The PA DEP database provides a searchable format based on Notices of Violations from routine inspections or investigations of spill reports or complaints. Each study had different criteria for inclusion, presented in Table 5-6, resulting in a range of rates even when using the same data source. Spills of hydraulic fracturing fluids, flowback/produced water are estimated to occur at a rate of 0.4 per 100 wells fractured. Spills related to hydraulic fracturing activity are estimated to occur at a rate between 3.3 to 12.2 spills per 100 wells installed (PA DEP data) (see Table 5-6).

In its study of spills related to hydraulic fracturing, the EPA determined that spill reports from the Colorado Oil and Gas Conservation Commission (COGCC) Information System were the most detailed spill reports from among the nine state data sources investigated and generally provided more of the information needed to determine whether a spill was related to hydraulic fracturing (U.S. EPA, 2015n). Here, we estimate the spill rate in Colorado by dividing the number of hydraulic fracturing-related spills identified by the EPA (U.S. EPA, 2015n, Appendix B)(Appendix B in U.S. EPA, 2015b) by the number of wells hydraulically fractured in Colorado for specific time periods between January 2006 and April 2012. We used three data sources to estimate the number of wells: (1) there were 172 reported spills in Colorado for the 15,000 wells fractured from January 2006 to April 2012 (DrillingInfo, 2012), (2) there were 50 reported spills in Colorado for the 3,559 wells fractured from January 2011 to April 2012 (U.S. EPA, 2015b), and (3) there were 41 reported spills in Colorado for the 3,000 wells fractured from September 2009 to October 2010 (U.S. EPA, 2013a). From these data we estimate an average of 1.3 reported spills on or near the well pad for every 100 hydraulically fractured wells.

Table 5-6. Estimations of spill rates.

Spill rates from four different sources. Each source used different criteria to identify and include spills in their analysis.

Spill rate[a]	Data source	Time period	Inclusion criteria	Information source
0.4	PA DEP[b] Media	2008–2013	Volume spilled > 400 gal; Spill reported to reach water body.	Brantley et al. (2014)[d]
3.3	PA DEP[b]	2009-2012	"Unconventional" well; Spills with unknown volumes not included, Includes any spill during HF activities	Gradient (2013)[e]
12.2	PA DEP[b]	2007-July 2013	"Unconventional" well based on environmental violation rates.	Rahm et al. (2015)[e]
1.3	COGCC[c]	Jan 2006 – May 2012	Specifically related to hydraulic fracturing on or near well pad	U.S. EPA (2013a)[d]

[a]Spill rate is the number of reported spills per 100 wells.

[b]PA DEP (http://www.depreportingservices.state.pa.us/ReportServer/Pages/ReportViewer.aspx?/Oil_Gas/OG_Compliance)

[c]COGCC (https://cogcc.state.co.us/cogis/IncidentSearch.asp)

[d]Spill rate is calculated as the number of spills per 100 wells fractured.

[e]Spill rate is calculated as the number of spills per 100 wells installed.

Text Box 5-14 (Spill Rates), continued:

The spill rates presented in Table 5-6 are based on spill reports found in two state data sources and are limited by both the spills reported in the state data sources and the inclusion criteria defined by each of the studies. Spills identified from state data sources are likely a subset of the total number of spills that occurred within a state for a specified time period. Some spills may not be recorded in state data sources because they do not meet the spill reporting requirements in place at the time of the spill. Additionally, the PA DEP Notices of Violation may include spills not specifically related to hydraulic fracturing, such as spills of drilling fluids.

The inclusion criteria used by each of the studies affects which spills are used to calculate a spill rate. More restrictive criteria, such as only counting spills that were greater than 400 gallons, results in a lower number of spills being used for estimating spill rates, while less restrictive criteria, such as all spills from wells marked unconventional in the PA DEP database, results in a greater number of spills being used for estimating spill rates. Rahm et al. applied the least restrictive criteria of the four studies (i.e., spills from unconventional wells) when identifying spills, while Brantley et al. applied more restrictive criteria (i.e., spills of >400 gallons in which spilled fluids reached a surface water body). This may account for the different spill rates calculated by these two studies.

Based on previous studies and the analysis here, hydraulic fracturing-related spills rates in Pennsylvania and Colorado range from 0.4 and 12.2 per 100 wells. These numbers may not be representative of national spill rates or rates in other regions. If this range is applied nationally however, assuming between 25,000 and 30,000 wells are fractured each year, we would expect between approximately 100 and 3,700 spills annually from hydraulic fracturing.

5.8. Fate and Transport of Chemicals

This section provides an overview of fate and transport of the range of chemicals used in hydraulic fracturing fluid, including the physicochemical properties of these chemicals, and an overview of the potential for a spilled chemical to affect drinking water resources. A general overview of the processes governing the fate and transport of a chemical spill is shown in Figure 5-16. 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 may undergo. Chemicals may react and transform into other chemicals, volatilize, travel to surface water, leach into and partition to soils, and/or reach ground water. The potential path and the severity of the impact of a spill depend on different factors, including the site conditions; environmental conditions; climate; weather; and chemical properties, concentration, and volume of the release. The point in the chemical mixing process where the spill occurs affects potential impact. If the spill occurs before chemicals are mixed into the base fluid, the chemicals will spill in their most concentrated form. If the hydraulic fracturing fluid spills, then the chemicals will be more diluted, and there may be effects on persistence and mobility due to interactions among chemicals present.

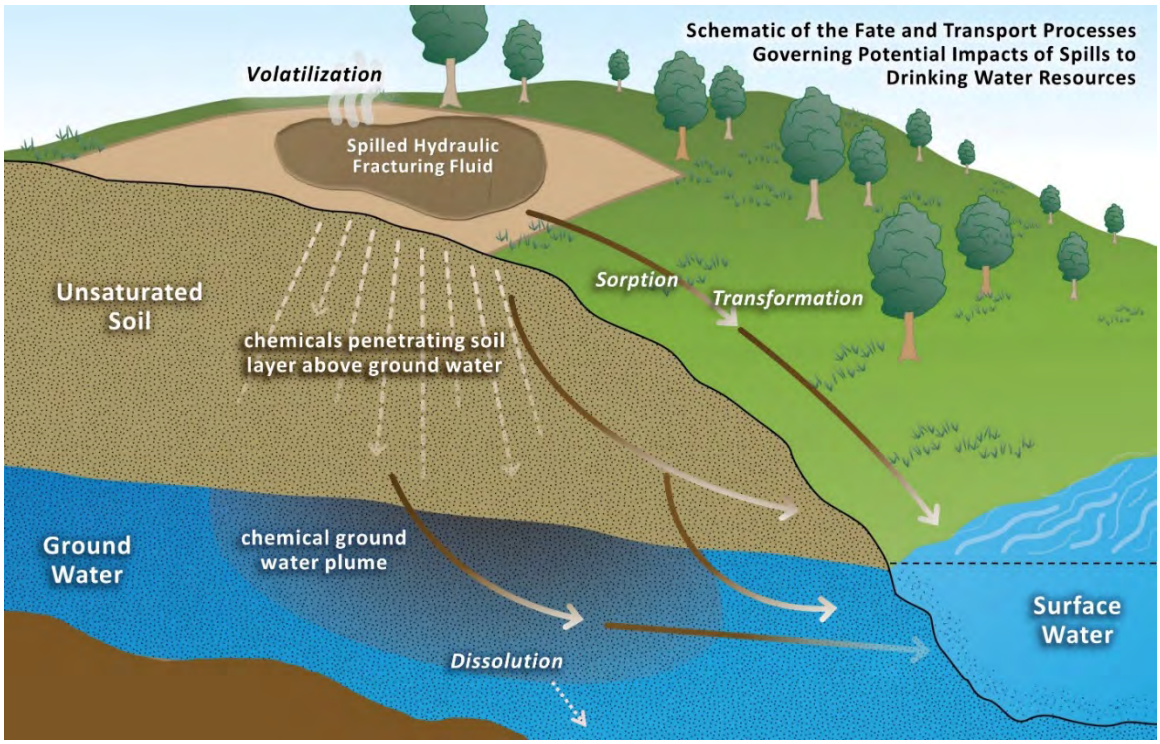

Figure 5-16. Fate and transport schematic for a spilled hydraulic fracturing fluid.

Schematic shows the potential paths and governing processes that spilled chemicals, which may lead to potential impacts to 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 ground water depends on the nature of ground water flow and flow through the unsaturated zone above the water table. Potential transformations of inorganic chemicals differ from those of organic chemicals.[2] 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) that can have an

[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, hence "unsaturated zone."
[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.

impact. Unlike inorganic chemicals, organic chemicals degrade, which may 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 compounds 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, 1979).

5.8.1. Potential Paths

Chemicals, additives, and hydraulic fracturing fluids that are released into the environment travel along different potential paths, as detailed in Figure 5-16. Liquids may flow overland to nearby surface water or infiltrate the subsurface, where they may eventually reach the underlying ground water or travel laterally to reach surface water. Movement can occur quickly or be delayed and have a later or longer-term impact. Surface water and ground water gain or lose flow to each other, and may transport chemicals in the process.

A dry chemical (e.g., gelling agents, biocides, friction reducers) released to the environment will generally 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, or rain could dissolve a soluble chemical. Dissolved chemicals may 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 chemicals in the fluid may sorb to the soil particles and the vegetation, and then these chemicals may be mobilized during rainfall, runoff, or erosion. As rainwater percolates through the soil, it may dissolve stored chemicals, which can then migrate toward ground water.

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. If a more rapid release occurs, like a blowout or tank failure, then momentum may result in greater overland movement and less soil infiltration during the event.

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 may move quickly through the subsurface. In low permeability soil, the movement of the fluid is slower. As chemicals pass through the subsurface, some may sorb to soil or remain in the open spaces between soil particles, effectively slowing their movement. Chemicals may again be

[1] Capillarity occurs because of the forces of attraction of water molecules to themselves (cohesion) and to other solid substances such as soils (adhesion).

mobilized during future precipitation events, resulting in infiltration towards ground water 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 ground water. Generally, fluids travel further in systems with high ground water flow rates and high recharge (e.g., sandy aquifers in humid climates) than in systems with low flow and low recharge. Chemicals may sorb to suspended soil particles or complex with naturally occurring chemicals (e.g., dissolved organic carbon) and be transported with the flowing water.[1] These mechanisms can mobilize sparingly soluble chemicals that would otherwise be immobile.

5.8.2. Physicochemical Properties

Three physicochemical properties are useful to describe the movement of chemicals in the environment: (1) K_{ow}, the octanol-water partition coefficient, (2) the aqueous solubility, and (3) the Henry's law constant.[2] These properties describe whether a chemical will sorb to soil and organic 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).[3]

The K_{ow} measures the relative hydrophobicity (chemical prefers to be in oil, log K_{ow} >0) and hydrophilicity (chemical prefers 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 Suite 4.1 (see Appendix C).[4] Of the 1,076 chemicals the EPA listed as used in hydraulic fracturing (see Appendix A), EPI Suite™ has estimated properties for 453 (42%). EPI Suite™ does not have data available for the remaining 58% of the chemicals. The 453 chemicals with physicochemical property data were chemicals with structures that are considered suitably representative of the substance to compute properties within the constraints of EPI Suite™ software. Only unique defined organic desalted structures were submitted for property calculation. Figure 5-17 presents histograms of all 453 of the chemicals, sorted by four physicochemical parameters: measured log K_{ow} (n = 247, 23%), estimated log K_{ow} (n=453, 42%) estimated log of the

[1] 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.
[2] 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.
[3] We present the physicochemical parameter values using $\log_{10}$ because of the wide range of values that these parameters cover.
[4] EPI Suite™, version 4.1, http://www.epa.gov/opptintr/exposure/pubs/episuite.htm (U.S. EPA, 2012b). 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.

aqueous solubility (n = 453, 42%), and estimated log of Henry's law constant (at 25°C, n = 453, 42%).

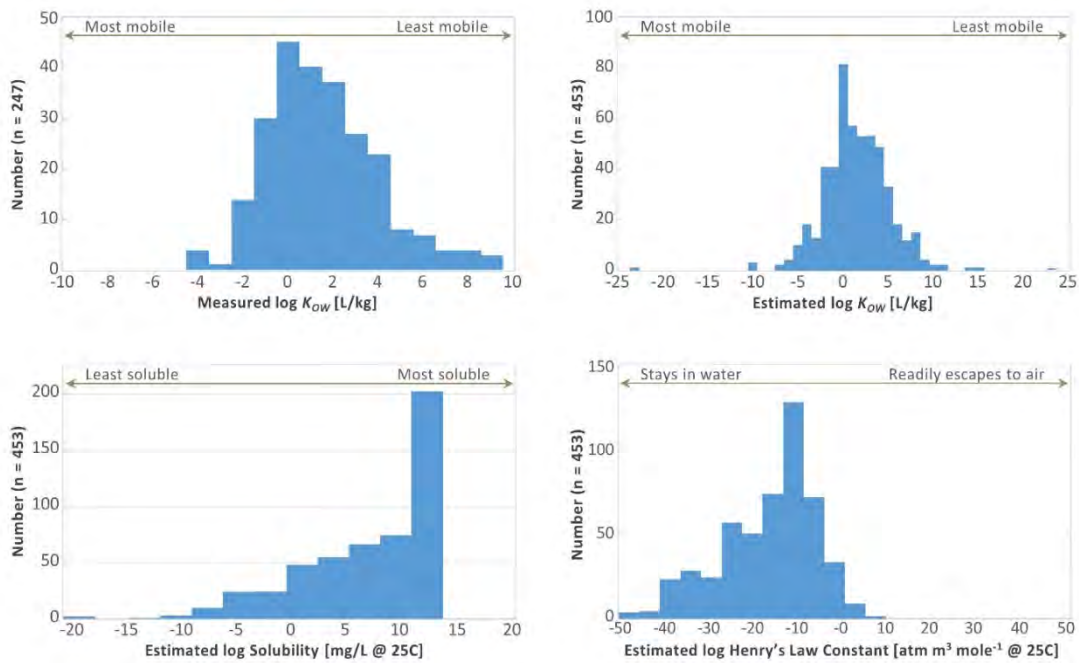

Figure 5-17. Histograms of physicochemical properties of chemicals used in the hydraulic fracturing process.

Measured values of log K_{ow} (upper left). Estimated physicochemical properties for log K_{ow} (upper right), log Solubility (lower left), and log Henry's law constant (lower right) for all chemicals. Physicochemical properties (log K_{ow}, solubility, and Henry's Law constant) estimated by EPI Suite™.

The EPA also used EPI Suite™ to determine the physicochemical properties for 19 chemicals provided to the EPA as confidential business information (CBI) (See Text Box 5-3 for discussion on CBI).[1] The CBI chemical physicochemical properties are plotted as histograms in Figure 5-18. The values of the physicochemical properties of known and CBI chemicals are similar, covering similar ranges 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 means that their fate and transport would not be appreciably different than the chemicals that are publicly known.

[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 USEPA by 9 service companies.

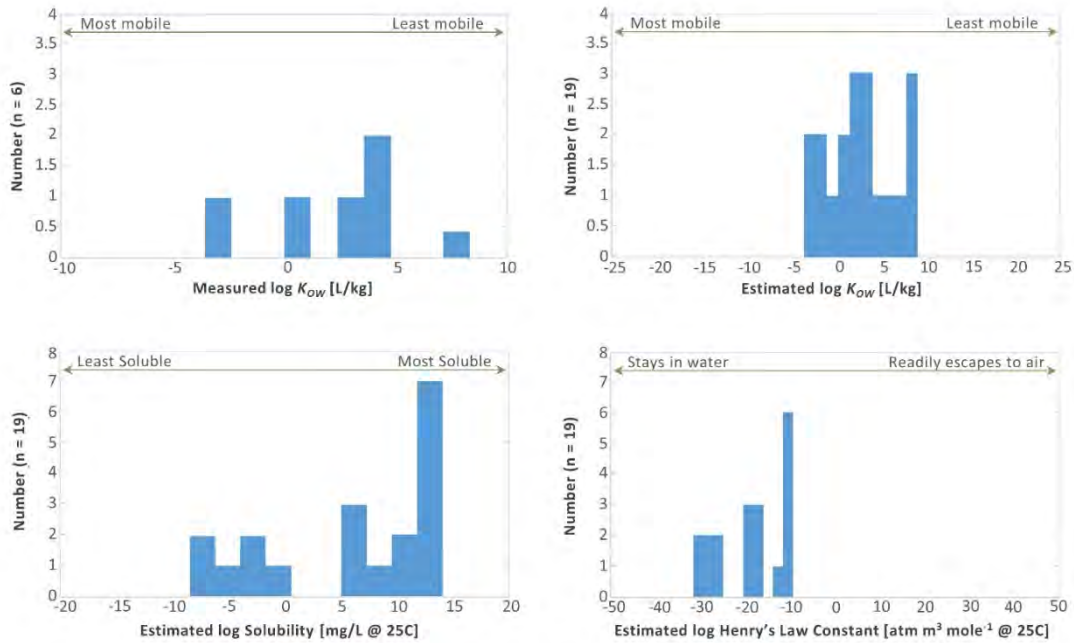

Figure 5-18. Histograms of physicochemical properties of confidential chemicals used in the hydraulic fracturing process.

Source: (U.S. EPA, 2013a)
Measured values of log K_{ow} (upper left). Estimated physicochemical properties for log K_{ow} (upper right), log solubility (lower left), and log Henry's law constant (lower right) for all chemicals. Physicochemical properties (log K_{ow}, solubility, and Henry's Law constant) estimated by EPI Suite™.

5.8.3. Mobility of Chemicals

Figure 5-17 shows the distribution of the three properties. The log K_{ow} distribution demonstrates that the chemicals cover a wide range from the more mobile to the less mobile. The more hydrophilic chemicals are more mobile (i.e., they move with water). The more hydrophobic chemicals tend to associate with organic matter and soil particles and to be less mobile in the environment, and they may serve as long-term sources of contamination. A large number of the chemicals fall near log K_{ow} = 0, which indicates that these chemicals are likely to associate roughly equally with organic or aqueous phases. However, overall the log K_{ow} values are skewed positively, indicating less mobile chemicals, which may result in their being later-term or long-term sources of impact to drinking water. The log S values span a wide range from fully miscible to sparingly soluble. Many of the chemicals have high aqueous solubilities, with a large number being fully miscible. Most of the chemicals have log Henry's law constants less than 0, indicating that most are not volatile. Once these chemicals dissolve into water they will tend to stay there rather than volatilize. Therefore, volatilization does not generally serve as a loss process for most hydraulic fracturing chemicals.

Table 5-7 and Table 5-8 present the 20 most mobile and least mobile chemicals, known to be used in hydraulic fracturing fluids, respectively, as ranked by log K_{ow}. These were taken from the list of

515 chemicals with estimated values for physicochemical properties. These tables also include values for aqueous solubility and Henry's law constant, as well as frequency of use, based on FracFocus disclosures (U.S. EPA, 2015a).

Table 5-7 shows the chemicals that have the *lowest* log K_{ow} and are, thus, the *most* mobile. These chemicals are fully miscible (i.e., they will mix completely with water), which means they may move through the environment at high concentrations, leading to greater severity of impact. These chemicals generally have low volatility, based on their negative log Henry's law constants (i.e., will remain in water and will not be lost to the air). These chemicals will dissolve in water and move rapidly through the environment (e.g., via infiltration into the subsurface or via overland flow to surface waters). Chemicals exhibiting this combination of properties have greater potential to cause immediate impacts to drinking water resources. Most of the chemicals in the table were infrequently reported (≤2% of wells) in FracFocus (U.S. EPA, 2015a). However, choline chloride (14% of wells), used for clay control, and tetrakis(hydroxymethyl)phosphonium sulfate (11% of wells), a biocide, were more commonly reported.

Table 5-7. Ranking of the 20 most mobile organic chemicals, as determined by the largest log K_{ow}, with CASRN, percent of wells where the chemical is reported from January 1, 2011 to February 28, 2013 (U.S. EPA, 2015b), and physicochemical properties (log K_{ow}, solubility, and Henry's Law constant) as estimated by EPI Suite™.

(U.S. EPA, 2015b)
For organic salts, parameters are estimated using the desalted form.

Rank	Chemical Name	CASRN	Percent of wells (U.S. EPA, 2015b)[a]	Estimated Log K_{ow} (unitless)[b]	Estimated Water Solubility (mg/L @ 25°C)[c]	Estimated Henry's Law Constant (atm m^3/mole @ 25°C)[d]
1	1,2-Ethanediaminium, N,N'-bis[2-[bis(2-hydroxyethyl)methylammonio]ethyl]-N,N'-bis(2-hydroxyethyl)-N,N'-dimethyl-, tetrachloride	138879-94-4	2%	-23.19	1.00×10^6	2.33×10^{-35}
2	Phosphonic acid, [[(phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-	15827-60-8	0.2%	-9.72	1.00×10^6	NA
3	Phosphonic acid, [[(phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-, sodium salt	22042-96-2	0.07%	-9.72	1.00×10^6	NA

Rank	Chemical Name	CASRN	Percent of wells (U.S. EPA, 2015b)[a]	Estimated Log K_{ow} (unitless)[b]	Estimated Water Solubility (mg/L @ 25°C)[c]	Estimated Henry's Law Constant (atm m^3/mole @ 25°C)[d]
4	Phosphonic acid, [[(phosphonomethyl)imino]bis [2,1-ethanediylnitrilobis (methylene)]]tetrakis-, ammonium salt (1:x)	70714-66-8	NA	-9.72	1.00×10^6	NA
5	Phosphonic acid, (((2-[(2-hydroxyethyl)(phosphonomethyl) amino)ethyl)imino]bis(methylene))bis-, compd. with 2-aminoethanol	129828-36-0	NA	-6.73	1.00×10^6	5.29×10^{-42}
6	2-Hydroxy-N,N-bis(2-hydroxyethyl)-N-methylethanaminium chloride	7006-59-9	NA	-6.7	1.00×10^6	4.78×10^{-19}
7	N-(3-Chloroallyl)hexaminium chloride	4080-31-3	0.02%	-5.92	1.00×10^6	1.76×10^{-8}
8	3,5,7-Triazatricyclo(3.3.1.1 (superscript 3,7))decane, 1-(3-chloro-2-propenyl)-, chloride, (Z)-	51229-78-8	NA	-5.92	1.00×10^6	1.76×10^{-8}
9	(2,3-dihydroxypropyl) trimethylammonium chloride	34004-36-9	NA	-5.8	1.00×10^6	9.84×10^{-18}
10	Phosphonic acid, [[(phosphonomethyl)imino]bis [6,1-hexanediylnitrilobis (methylene)]]tetrakis-	34690-00-1	0.006%	-5.79	1.00×10^6	NA
11	[Nitrilotris(methylene)]tris-phosphonic acid pentasodium salt	2235-43-0	0.5%	-5.45	1.00×10^6	1.65×10^{-34}
12	Aminotrimethylene phosphonic acid	6419-19-8	2%	-5.45	1.00×10^6	1.65×10^{-34}
13	Choline chloride	67-48-1	14%	-5.16	1.00×10^6	2.03×10^{-16}
14	Choline bicarbonate	78-73-9	0.2%	-5.16	1.00×10^6	2.03×10^{-16}
15	alpha-Lactose monohydrate	5989-81-1	NA	-5.12	1.00×10^6	4.47×10^{-22}
16	Lactose	63-42-3	NA	-5.12	1.00×10^6	4.47×10^{-22}

Rank	Chemical Name	CASRN	Percent of wells (U.S. EPA, 2015b)[a]	Estimated Log K_{ow} (unitless)[b]	Estimated Water Solubility (mg/L @ 25°C)[c]	Estimated Henry's Law Constant (atm m^3/mole @ 25°C)[d]
17	Tetrakis(hydroxymethyl)phosphonium sulfate	55566-30-8	11%	-5.03	1.00×10^6	9.17×10^{-13}
18	Disodium ethylenediaminediacetate	38011-25-5	0.6%	-4.79	1.00×10^6	1.10×10^{-16}
19	Nitrilotriacetamide	4862-18-4	NA	-4.75	1.00×10^6	1.61×10^{-18}
20	1,3,5-Triazine-1,3,5(2H,4H,6H)-triethanol	4719-04-4	0.2%	-4.67	1.00×10^6	1.08×10^{-11}

[a] Some of the chemicals in these tables have NA (not available) listed as the number of wells, which means that these chemicals have been used in hydraulic fracturing, but they were not reported to FracFocus program for the time period of the study (January 1, 2011, to February 28, 2013) (U.S. EPA, 2015b). 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.
[b] Log K_{ow} is estimated using the KOWWIN™ model, which uses an atom/fragment contribution method.
[c] Water solubility is estimated using the WSKOWWIN™ model, which estimates a chemical's solubility from K_{ow} and any applicable correction factors.
[d] Henry's Law constant is estimated using the HENRYWIN™ model using the bond contribution method.

Table 5-8 shows the chemicals that have the *highest* log K_{ow} and are, thus, the *least* mobile. The estimated aqueous solubilities for some of these chemicals are extremely low, with highest solubilities of <10 µg/L. Therefore, the concentration of these chemicals dissolved in water will be low. The estimated Henry's law constants are more variable for these low-mobility chemicals. Chemicals with high log K_{ow} values (>0) and high Henry's law constants will sorb strongly to organic phases and solids and may volatilize. However, their strong preference for the organic or solid phase may slow or reduce volatilization. The chemicals with low Henry's law constants will readily sorb to organic phases and solids. Less mobile chemicals will move slowly through the soil and have potentially delayed and longer-term impacts to drinking water resources. Seven of the chemicals in Table 5-8 were reported to FracFocus (U.S. EPA, 2015b). 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. The least mobile organic chemical is

sorbitan, tri-(9Z)-9-octadecenoate, a mineral oil co-emulsifier (0.05% of wells), with an estimated log K_{ow} of 22.56.[1]

Table 5-8. Ranking of the 20 least mobile organic chemicals, as determined by the largest log K_{ow}, with CASRN, percent of wells where the chemical is reported from January 1, 2011 to February 28, 2013 (U.S. EPA, 2015b), and physicochemical properties (log K_{ow}, solubility, and Henry's Law constant) as estimated by EPI Suite™.

Source: (U.S. EPA, 2015b)
For organic salts, parameters are estimated using the desalted form.

Rank	Chemical Name	CASRN	Percent of wells (U.S. EPA, 2015b)[a]	Estimated Log K_{ow} (unitless)[b]	Estimated Water Solubility (mg/L @ 25°C)[c]	Estimated Henry's Law Constant (atm m^3/mole @ 25°C)[d]
1	Sorbitan, tri-(9Z)-9 octadecenoate	26266-58-0	0.05%	22.56	1.12×10^{-19}	4.02×10^{-11}
2	Fatty acids, C18-unsatd., dimers	61788-89-4	NA	14.6	2.31×10^{-10}	4.12×10^{-08}
3	Sorbitan sesquioleate	8007-43-0	0.02%	14.32	2.31×10^{-11}	7.55×10^{-12}
4	Tri-n-butyltetradecyl-phosphonium chloride	81741-28-8	6%	11.22	7.90×10^{-7}	2.61×10^{-1}
5	Sodium bis(tridecyl) sulfobutanedioate	2673-22-5	NA	11.15	7.46×10^{-9}	8.51×10^{-11}
6	1-Eicosene	3452-07-1	NA	10.03	1.26×10^{-5}	1.89×10^{1}
7	D&C Red 28	18472-87-2	NA	9.62	1.64×10^{-8}	6.37×10^{-21}
8	C.I. Solvent Red 26	4477-79-6	NA	9.27	5.68×10^{-5}	5.48×10^{-13}
9	1-Octadecene	112-88-9	NA	9.04	1.256×10^{-4}	1.07×10^{1}
10	Alkenes, C>10 alpha-	64743-02-8	8%	8.55	3.941×10^{-4}	8.09×10^{0}
11	Dioctyl phthalate	117-84-0	NA	8.54	4.236×10^{-4}	1.18×10^{-5}
12	Benzene, C10-16-alkyl derivs.	68648-87-3	0.5%	8.43	2.099×10^{-4}	1.78×10^{-1}

[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).

Rank	Chemical Name	CASRN	Percent of wells (U.S. EPA, 2015b)[a]	Estimated Log K_{ow} (unitless)[b]	Estimated Water Solubility (mg/L @ 25°C)[c]	Estimated Henry's Law Constant (atm m^3/ mole @ 25°C)[d]
13	Di(2-ethylhexyl) phthalate	117-81-7	NA	8.39	1.132×10^{-3}	1.18×10^{-5}
14	1-Octadecanamine, N,N-dimethyl-	124-28-7	NA	8.39	8.882×10^{-3}	4.51×10^{-3}
15	N,N-dimethyloctadecylamine hydrochloride	1613-17-8	NA	8.39	8.882×10^{-3}	4.51×10^{-3}
16	Butyryl trihexyl citrate	82469-79-2	0.03%	8.21	5.56×10^{-5}	3.65×10^{-9}
17	1-Hexadecene	629-73-2	NA	8.06	1.232×10^{-3}	6.10×10^{0}
18	Benzo(g,h,i)perylene	191-24-2	NA	7.98	7.321×10^{-4}	1.26×10^{-2}
19	Dodecylbenzene	123-01-3	NA	7.94	1.015×10^{-3}	1.34×10^{-1}
20	Isopropanolamine dodecylbenzene	42504-46-1	0.02%	7.94	1.015×10^{-3}	1.34×10^{-1}

[a] Some of the chemicals in these tables have NA (not available) listed as the number of wells, which means that these chemicals have been used in hydraulic fracturing, but they were not reported to FracFocus program for the time period of the study (January 1, 2011, to February 28, 2013) (U.S. EPA, 2015b). 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.
[b] Log K_{ow} is estimated using the KOWWIN™ model, which uses an atom/fragment contribution method.
[c] Water solubility is estimated using the WSKOWWIN™ model, which estimates a chemical's solubility from Kow and any applicable correction factors.
[d] Henry's Law constant is estimated using the HENRYWIN™ model using the bond contribution method.

Table 5-9 shows the EPI Suite™ estimated physicochemical property values of the 20 chemicals most frequently reported to FracFocus nationwide, with estimated mean and median volumes based on FracFocus data. 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 and go where the water goes. These chemicals have the potential for immediate impacts to drinking water resources. Naphthalene 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 have the potential to act as long-

term sources of contamination.[1] All of these chemicals have low Henry's law constants, so they tend not to volatilize.

[1] Chemicals may have the potential to be long-term sources of contamination because 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 the right conditions, for example, naphthalene is biodegradable, which may reduce or remove it from the environment, and thus may not be a long-term source of contamination.

Table 5-9. The 20 chemicals reported most frequently nationwide for hydraulic fracturing based on reported FracFocus 1.0 disclosures (U.S. EPA, 2015b), with EPI Suite™ physicochemical parameters where available, and estimated mean and median volumes of those chemicals, where density was available.

Source: (U.S. EPA, 2015b)
Excludes water, sodium chloride, and quartz. NA means that the physicochemical parameter is not provided by EPI Suite™. For organic salts, parameters are estimated using the desalted form.

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	64742-47-8	22,463 (65%)	NA	NA	NA	NA	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

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
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
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.	64742-94-5	7,108 (21%)	NA	NA	NA	NA	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

Note: 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.

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5.8.4. Transformation Processes

It is important to understand the processes governing transformation of chemicals in the environment. The transformation of a chemical reduces its concentration over time. Chemicals may completely degrade before reaching a drinking water resource. Transformation processes may be biotic or abiotic. The transformation process may transform a chemical into a less or more harmful chemical.

Biodegradation is a biotic process where microorganisms transform a chemical from its original form into another chemical. For example, the biodegradation pathway of methanol is $CH_3OH \rightarrow CH_2O \rightarrow CHOOH \rightarrow CO_2$, or methanol → formaldehyde → formic acid → carbon dioxide. 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 highly biodegradable chemical could biodegrade quickly under the right conditions, before it can impact a water resource. The relationship between mobility and biodegradability is complex, and therefore a variety of factors can influence a particular compound's movement through the environment.

Abiotic processes, such as oxidation, reduction, photochemical reaction, and hydrolysis, can transform or break apart chemicals. In hydrolysis, for example, a water molecule substitutes for a group of atoms. The typical results are products that are more polar than the original, and thus have different physicochemical properties than the original compounds (Schwarzenbach et al., 2002).[1]

5.8.5. Fate and Transport of Chemical Mixtures

Chemicals at hydraulic fracturing sites are often present as mixtures, which may act differently in the environment than individual chemicals do. Individual chemicals can affect the fate and transport of other chemicals in a mixture primarily by changing their solubility and biodegradation rates.

Mixtures of chemicals may 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,

[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.

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 compounds, and can mobilize less soluble/less mobile organic compounds. Two common surfactants reported to FracFocus 1.0 from January 1, 2011 to February 2013 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 may decrease or enhance the biodegradability of another through inhibition or co-metabolism. The process of inhibition can occur when multiple chemicals compete for the same enzyme, so only one chemical is degraded at a time, which can ultimately slow biodegradation of each of the chemicals present. For example, the biodegradation of ethanol and methanol may inhibit the biodegradation of BTEX or other organic compounds present (Rasa et al., 2013; Powers et al., 2001). Co-metabolism may increase the biodegradation rate of other compounds. 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. A chemical that may have otherwise been biodegradable may be inhibited and act as a long-term source.

5.8.6. Site and Environmental Conditions

Environmental conditions at and around the spill site affect the movement and transformation of the chemical. We discuss 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 an aquifer, affects the potential for impact. Land cover will affect how readily a fluid moves over land. For example, more rugged land cover such as forest will impede flow, and an asphalt road will facilitate flow. A spill that occurs on or near a sloped site may move overland faster, making it more likely to reach a nearby surface water body. Flatter surfaces would result in a greater chance for infiltration to the subsurface, which could increase the potential for a ground water 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.[1,1] Fluids will move more

[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.

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 adhere to. 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 move insoluble chemicals across the surface and through the subsurface. Chemicals may also associate with particulates and colloids, which may act as an important transport mechanism.

Weather and climate conditions also affect the fate and transport of a spilled chemical. After a spilled chemical stops moving, rainfall may remobilize the chemical. The amount, frequency, and intensity of precipitation will impact volume, distance, and speed of chemical movement. Precipitation may carry chemicals downward or overland, and it can cause erosion, which may 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 amongst different phases: air, water, soil, and biota.[2] They presented a ranking of 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 also suggested that after a spill, a large fraction would enter the air and leave the soil; however, some constituents would be left behind in the water, soil, and biota compartments, which could effectively 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 with greater impacts.

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. In this section, we highlight the potential and documented impacts for three documented spills (U.S. EPA, 2015n). In each case, we provide the documented and potential paths (surface, subsurface, or combination) and the associated fate and transport governing processes by which a spill has been

[1] 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.
[2] 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.

documented to or has the potential to have an impact on drinking water resources. The three cases involve a tank overflow with a surface water impact, a human error blender spill with a soil impact, and an equipment failure that had no impact. These three spills were chosen to highlight cases where there was a documented impact, a potential impact, and no impact.

In the first documented spill, shown in Figure 5-19, a tank overflowed twice, releasing a total of 7,350 gal (980 ft^3 or 28 m^3).[1] The spilled fluid was documented as containing a friction reducer and gel. The spill traveled across the land surface, crossed a road, and then continued to a nearby stream. The spill affected wetlands and a stream, where fish were killed. The fish kill indicates that the chemicals present were in high enough concentrations to have an adverse impact.

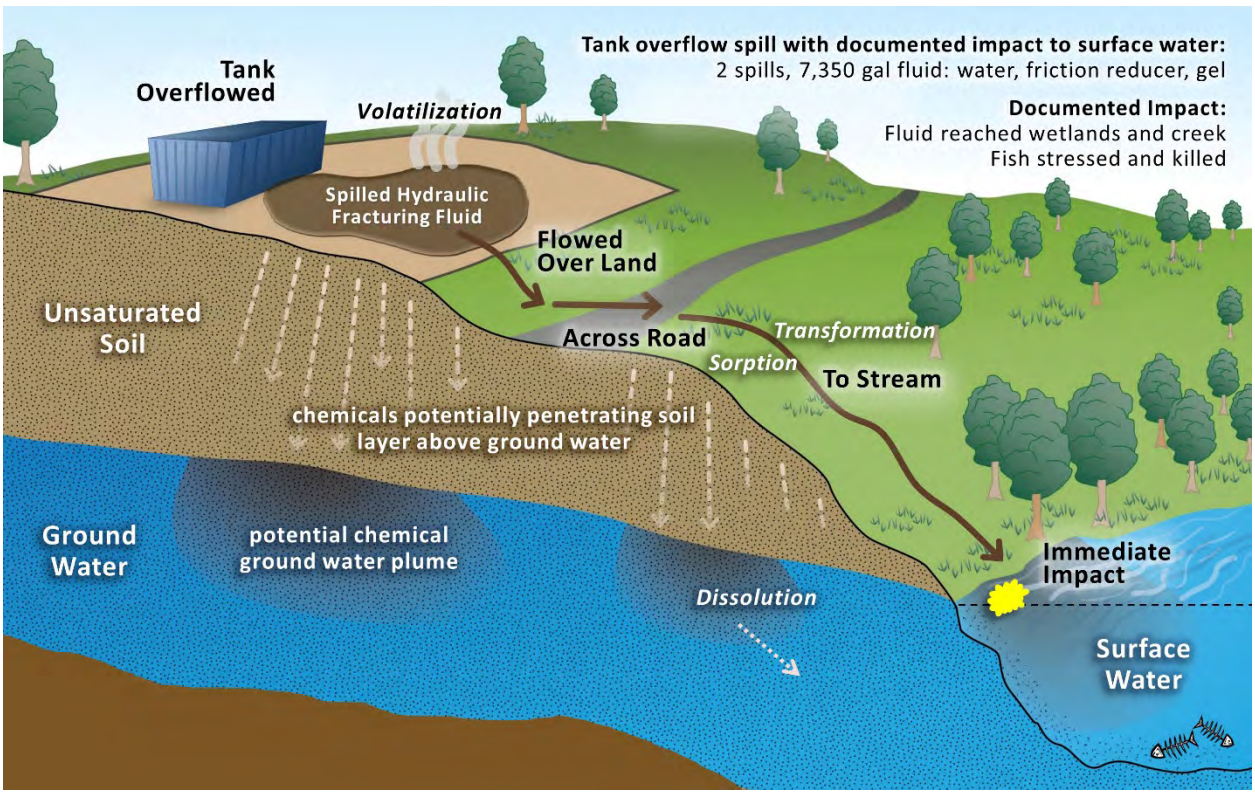

Figure 5-19. Fate and Transport Spill Example: Case 1.

Spills information from U.S. EPA (2015n).

For this first spill, the documented path was overland flow from the tank to the stream with a documented, immediate impact. In addition to this documented path, there are potential paths for potential impacts to drinking water resources. The spilled chemicals may have penetrated into the soils or sorbed to soils and vegetation as the fluid moved across the ground towards the stream.

[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 might travel.

Chemicals could be mobilized during later rainfall, runoff, or erosion events. Chemicals that infiltrated the subsurface could serve as long-term sources, as well as travel laterally across the unsaturated zone, or continue downwards to the ground water. Additionally, some chemicals could be lost to transformation processes. The lack of reported soil or ground water sampling data prevents the ability to know if these potential paths occurred or not.

The second documented spill (U.S. EPA, 2015n, line 144), shown in Figure 5-20, 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; 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. However, 210 gal (28 ft^3 or 0.8 m^3) did run off-site and were vacuumed up. There was no documented impact to surface or ground water.

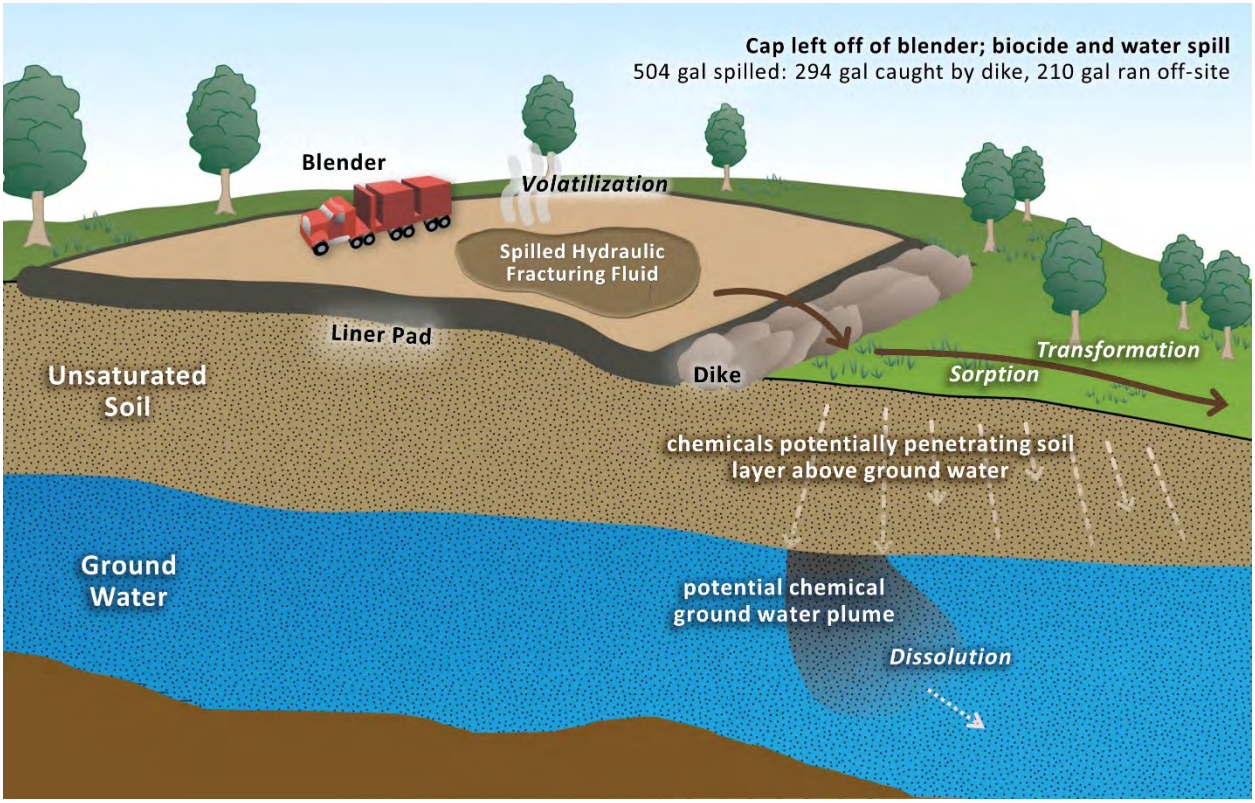

Figure 5-20. Fate and Transport Spill Example: Case 2.

Spills information from U.S. EPA (2015n).

In this second case, the uncontained 210 gal could have infiltrated the subsurface, creating a potential path to ground water. There is no documented information on the composition of the spilled fluid. Highly mobile chemicals would 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 water table

and moved with the ground water. These chemicals could have served as a long-term source. These chemicals 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 demonstrate whether chemicals did or did not follow this path.

In the third documented spill (U.S. EPA, 2015n, line 188), shown in Figure 5-21, 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. The spill was contained in the berm and an on-site vacuum truck was used to clean up the spill. No impact to soil or water was reported.

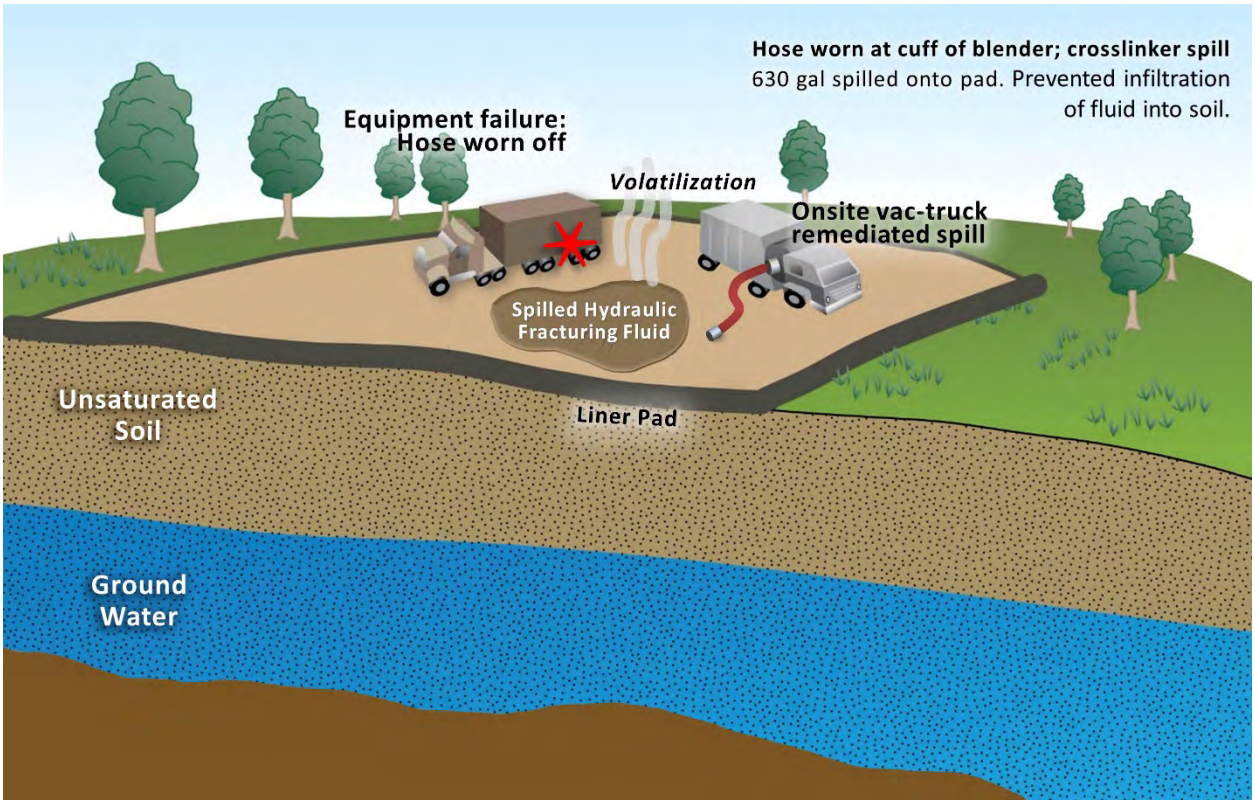

Figure 5-21. Fate and Transport Spill Example: Case 3.

Spills information from U.S. EPA (2015n).

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, not infiltrated the subsurface, and been fully cleaned up. Without a liner or if the liner was not completely successful (e.g., had a tear), the potential paths would have been similar to those above in the second case, where the chemicals may sorb to the soils and penetrate into the subsurface. There was no reported sampling of soil or ground water to determine whether or not chemicals migrated into the soil.

5.9. Trends in Chemicals Use in Hydraulic Fracturing

This section provides an overview of ongoing changes in chemical use in hydraulic fracturing, with an emphasis on efforts to reduce potential impacts from surface spills by using fewer and safer chemicals.

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, 2014a; 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 report, toxicity and a methodology to rank chemical hazards of hydraulic fracturing chemicals is discussed in Chapter 9.

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), and
- The recovery and reuse of flowback and produced water as hydraulic fracturing fluids, which may reduce need to add additional chemicals (Horn et al., 2013).

In addition to efforts to address environmental concerns, the oil and gas industry continues to research and develop less expensive and more effective fracturing fluid additives. 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 hydraulic fracturing fluid 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 those chemicals are now used commercially.

The FracFocus 1.0 data extracted by the EPA cannot be used to identify temporal trends in additive usage. A data set with a much longer duration of data collection would be needed to distinguish actual temporal trends from the normal diversity of chemicals in use as a result of geologic and geographic variability. However, the current FracFocus 1.0 database provides a point of comparison for use in the future.

5.10. Synthesis

Chemical mixing is the process by which a base fluid, chemicals, and proppant are mixed prior to injection into the well. This chapter addressed the potential for on-site spills of chemicals used in the hydraulic fracturing process to affect the quality of drinking water resources, which is governed by three overarching factors: (1) fluid characteristics, (2) chemical management and spill characteristics, and (3) chemical fate and transport.

5.10.1. Summary of Findings

Documented on-site chemical spills have occurred during the chemical mixing process and reached soil and surface water receptors, with potential impacts to drinking water resources. The EPA analysis of 497 spills reports found no documented impacts to ground water from those particular chemical spills, though there was little information on post-spill testing and sampling (U.S. EPA, 2015n). The EPA's case study in Killdeer, ND strongly suggests that there was impact to ground water, but it is unclear if the path was via the surface spill caused by the blowout (U.S. EPA, 2015j). The EPA found 151 spills of chemicals or fracturing fluid on or near the well pad in a six-year time period. The chemical spills were primarily caused by equipment failure (34%), closely followed by human error (25%). The remaining spills were caused by a failure of container integrity, weather, vandalism, well communication, or unknown causes. Reported spills cover a large range of volumes, from five to 19,000 gal (19 to 72,000 L), with a median of 420 gal (1,700 L).

If a spilled fluid reaches a drinking water resource, the potential to affect the water quality is largely governed by the fluid characteristics. A typical water-based fracturing fluid is composed of 90%–94% water, 5%–9% proppant, and less than 2% chemical additives (Carter et al., 2013; Knappe and Fireline, 2012). According to the EPA's analysis of disclosures to FracFocus 1.0, approximately 93% of hydraulic fracturing fluids are inferred to use water as a base fluid (U.S. EPA, 2015a). Non-aqueous constituents, such as nitrogen, carbon dioxide, and hydrocarbons, are also used as base fluids or used in combination with water as base fluids.

The EPA has identified 1,076 unique chemicals used in hydraulic fracturing fluids. The chemicals include acids, aromatic hydrocarbons, bases, hydrocarbon mixtures, polysaccharides, and surfactants. Of the 1,076 chemicals, 453 have physicochemical properties in the EPI Suite™ database. These chemicals range from fully miscible to insoluble, and from highly hydrophobic to highly hydrophilic. The majority of the chemicals are not volatile.

According to the EPA's analysis of FracFocus, a median of 14 chemicals are used per well, with a range of four to 28 (5th and 95th percentiles). The volumes used range from tens to tens of thousands of gallons (tens to tens of thousands of liters) per well; therefore, operators typically

store chemicals on-site in large volumes (typically 200 to 400 gal (760–1,500 L) totes), often in multiple containers. 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. These chemicals are present in multiple additives. Methanol was reported in 72% of the FracFocus disclosures, and hydrotreated light petroleum distillates and hydrochloric acid were both reported in over half the disclosures (U.S. EPA, 2015b).

5.10.2. Factors Affecting the Frequency or Severity of Impacts

The potential for spills from the chemical mixing process to affect drinking water resources depends on three factors: fluid characteristics, chemical management and spill characteristics, and chemical fate and transport. Specific factors affecting the frequency and severity of impacts include size and type of spill, volume of chemicals spilled, type of chemicals and their properties, combinations 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 horizontal leg, and the number of stages and phases, affect the likelihood and potential impacts of spills. Larger operations may 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, and additional transfers between equipment increase the possibility of human error.

The type of chemical spilled governs how it will move and transform in the environment. More mobile chemicals move faster through the environment, causing a quicker impact. More mobile chemicals are also generally more soluble and may reach the drinking water resource at higher concentrations. Less mobile chemicals will move more slowly, and may have delayed and longer-term impacts, at lower concentrations. The severity of impact is also governed by how the chemical adversely impacts water quality. Water quality impacts may 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. These conditions include soil properties, climate, weather, and terrain. Permeable soils may allow for rapid transport of the spilled fluid through the soil and into a nearby drinking water resource. 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 a resource, the higher potential to reach it. Also, as a fluid moves toward a drinking water resource, it may decrease in concentration, which will affect the severity of an impact. More concentrated chemicals have the potential to have a bigger impact on

water quality. The characteristics of the drinking water resource will also influence the magnitude of the impact of a spill.

The most successful way to prevent impacts to drinking water resources is to prevent spills from occurring in the first place and to quickly and effectively contain spills. 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 may limit the severity of a spill. Implementation of these measures varies from site-to-site and may not always be effective.

5.10.3. Uncertainties

The lack of information regarding the composition of chemical additives and fracturing fluids, containment and mitigation measures in use, and the fate and transport of spilled fluids greatly limits our ability to assess potential impacts to drinking water resources.

There is no standard design for hydraulic fracturing fluids. Detailed information on the chemicals used is limited, and volumes of chemicals stored on-site are generally not publicly available. These limitations in data preclude the ability to know what volumes of chemicals may be spilled. FracFocus, which currently holds the most comprehensive information on water and chemicals used in hydraulic fracturing fluids, identifies well-specific chemicals and the concentration of those chemicals as a maximum percentage of the mass of fracturing fluid. Accuracy and completeness of original FracFocus disclosure information was not verified. In applying the EPA-standardized chemical list to the ingredient records in the FracFocus 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 to FracFocus contained at least one CBI chemical. Of disclosures with at least one CBI chemical, the average number of CBI chemicals was five. Approximately 11% of all ingredients were reported to FracFocus as CBI (U.S. EPA, 2015a). No data are available in FracFocus for any chemical listed as CBI. Therefore, FracFocus CBI chemicals are not included in analyses of volume, physical properties, or any other analysis in this assessment, although we were able to do limited physicochemical analysis of 19 CBI chemicals.

Of the 1,076 hydraulic fracturing fluid chemicals identified by the EPA, 623 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).

In order to determine the potential impact of a spill, the physicochemical properties, the site-specific environmental conditions, and proximity to drinking water resources must be known. This information is generally lacking.

There is a lack of baseline surface water and ground 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.

In addition to limited information on chemical usage, we cannot complete a thorough assessment of the potential impact of chemical spills due to limited information on actual spills. Data sources used in the EPA's spills analysis do not cover all states with hydraulic fracturing activity. The available data provide limited information on the types and volumes of chemicals spilled, spill causes, containment and mitigation measures, and sources of spills. In addition, there is 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 to drinking water resources from chemical spills, based on available current information. To improve our understanding we need: more information on the chemical composition of additives and fracturing fluid; the physicochemical properties of chemicals used; baseline monitoring and field studies of spilled chemicals; drinking water resources quality conditions before and after hydraulic fracturing is performed; detailed site-specific environmental conditions; more information on the containment and mitigation measures and their effectiveness; and the types and volumes of spills.

5.10.4. Conclusions

The chemical mixing stage of the hydraulic fracturing process has the potential to cause impacts to drinking water resources by way of surface spills of chemicals and fracturing fluids. There are documented chemical spills at fracturing sites, but a lack of available data limits our ability to determine impacts. Potential impacts to drinking water resources are governed by the fluid characteristics, chemical management and spill characteristics, and the fate and transport of spilled chemicals through the environment.

Text Box 5-16. Research Questions Revisited.

What is currently known about the frequency, severity, and causes of spills of hydraulic fracturing fluids and additives?

- The frequency of on-site spills from hydraulic fracturing operations could be obtained for two states. Frequency estimates from data and literature ranged from 0.4 to 1.3 spills for every 100 wells hydraulically fractured in Pennsylvania and Colorado, respectively, and between 3.3 and 12.2 spills for every 100 wells installed in Pennsylvania (Rahm et al., 2015; U.S. EPA, 2015n; Brantley et al., 2014; Gradient, 2013).[1] These estimates include spills of hydraulic fracturing chemicals and fluids, and flowback and produced water reported in state databases. It is unknown whether these spill estimates are representative of national occurrences. Estimates of the frequency of on-site spills from hydraulic fracturing operations were unavailable for other areas. If the estimates are representative, the number of spills nationally could range from 100 to 3,700 spills annually, assuming 25,000 to 30,000 new wells are fractured per year.

- In an analysis of spills, EPA characterized volumes and causes of hydraulic fracturing-related spills identified from selected state and industry data sources. The spills occurred between January 2006 and April 2012 in 11 states and included 151 cases in which fracturing fluid or additives spilled on or near a well pad (U.S. EPA, 2015n). These cases were likely a subset of all chemical and fracturing fluid spills during the study's time period. The reported volume of chemicals or fracturing fluid spilled ranged from 5 gal to more than 19,000 gal (19 to 72,000 L), with a median volume of 420 gal (1,600 L) per spill. Spill causes included equipment failure, human error, failure of container integrity, and other causes (e.g., weather and vandalism). The most common cause was equipment failure. Specific causes of equipment failure included blowout preventer failure, corrosion, and failed valves. More than 30% of the chemical or fracturing fluid spills characterized by the EPA came from fluid storage units (e.g., tanks, totes, and trailers) (U.S. EPA, 2015n).

[1] Spill frequency estimates are for a given number of wells over a given period of time. These are not annual estimates nor are they for over a lifetime of the wells.

What are the identities and volumes of chemicals used in hydraulic fracturing fluids, and how might this composition vary at a given site and across the country?

- In this assessment, we compiled a list of 1,076 chemicals used to formulate hydraulic fracturing fluids. These chemicals include acids, alcohols, aromatic hydrocarbons, bases, hydrocarbon mixtures, polysaccharides, and surfactants. This is a cumulative list over multiple wells and years. Operators used an median of 14 unique chemicals per well according to the EPA's analysis of disclosures to FracFocus (U.S. EPA, 2015a).

- Our analysis showed that chemical use varies and that no single chemical is used at all well sites across the country, although several chemicals are widely used. Methanol, hydrotreated light petroleum distillates, and hydrochloric acid were reported in 65% or more of FracFocus disclosures analyzed by the EPA (U.S. EPA, 2015a). The composition of hydraulic fracturing fluids varies by state, by well, and within the same service company and geologic formation. This variability likely results from several factors, including the geology of the formation, the availability and cost of different chemicals, and operator preference (U.S. EPA, 2015a).

- Estimates from the EPA's database developed from disclosures made to FracFocus suggest median volumes of individual chemicals injected per well ranged from a few gallons to thousands of gallons, with a median of 650 gal (2,500 L) per chemical per well (U.S. EPA, 2015b). If 14 unique chemicals are used per well, then an estimated 9,100 gal (34,000 L) of chemicals may be injected per well (U.S. EPA, 2015a).

What are the chemical and physical properties of hydraulic fracturing chemical additives?

- Measured or estimated physicochemical properties were obtained for 453 of the 1,076 chemicals reported in hydraulic fracturing fluids. The wide variety of chemicals results in a wide range of physicochemical properties.

- Many hydraulic fracturing chemicals fully dissolve in water, but the aqueous solubilities range from fully miscible to sparingly soluble.

- The octanol-water partition coefficient ranges from the highly hydrophilic to the highly hydrophobic. Many chemicals used in hydraulic fracturing fluid fall in the middle of this range, suggesting that they will divide equally between water and solid phase, so that they may move slower through the environment than those that associate more with water. More chemicals will associate strongly with soils and organic materials, suggesting the potential of these chemicals to be long-term contaminants if they are spilled.

- There are few hydraulic fracturing chemicals that are volatile. Most hydraulic fracturing chemicals will tend to remain in water as opposed to volatilizing to the air.

- The chemicals for which we know physicochemical properties are not necessarily the chemicals most frequently reported as used in hydraulic fracturing activities. Of the 453 chemicals for which physicochemical properties were available, 18 of the top 20 most mobile chemicals were included in 2% or less of disclosures (U.S. EPA, 2015b). However, two more common, but highly mobile chemicals, choline chloride and tetrakis (hydroxymethyl) phosphonium sulfate were reported in 14% and 11% of disclosures, respectively. These two chemicals are thus relatively more common, and, if spilled, their properties of high mobility means they would move quickly through the environment with the flow of water.

If spills occur, how might hydraulic fracturing chemical additives contaminate drinking water resources?

- When chemicals are spilled, there are several paths by which a chemical could contaminate drinking water resources. The chemical could flow overland to nearby surface water, penetrate into the soil that could travel laterally and impact surface waters, or infiltrate and contaminate the underlying ground water.
- Of the 151 spills characterized by the EPA, fluids reached surface water in 13 (9%) and soil in 97 (64%) of those cases. None of the spills reportedly reached ground water (U.S. EPA, 2015n), but it could take several years for spilled fluids to infiltrate soil and leach into ground water. Thus, it may not be immediately known whether a spill reaches ground water or not
- The timing of a potential impact varies, but it could occur quickly, be delayed, have a continual impact over time, or occur much later. Which path the spill takes depends on different conditions, such as distance to a water receptor, spill volume, soil characteristics, and the physicochemical properties of the chemical.

5.11. References for Chapter 5

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Chapter 6

Well Injection

6. Well Injection

6.1. Introduction

To conduct hydraulic fracturing, fluids (primarily water, mixed with the types of chemicals and proppant described in Chapter 5) are injected into a well under high pressure.[1] These fluids flow under pressure through the well (sometimes thousands of feet below the surface), 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 laterally from the well, are designed to remain within the production zone to access as much oil or gas as possible, while using no more water or chemicals than necessary 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 and those containing the hydrocarbons to be exploited from each other. This isolation can also protect drinking water resources. Appropriately sited, designed, constructed, and operated wells and hydraulic fracturing treatments can reduce the potential for impacts to drinking water resources. However, problems with the well's components or improperly sited, designed, or executed hydraulic fracturing operations (or combinations of these) could lead to adverse effects on drinking water resources.

The well and the geologic environment in which it is located are a closely linked system, often designed with multiple barriers (i.e., isolation afforded by the well's casing and cement and the presence of multiple layers of subsurface rock) to prevent fluid movement between oil/gas zones and drinking water resources. Therefore, in this chapter we discuss (1) the well (including its construction and operation) and (2) 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 drinking water resources throughout the life of the well, including during and after hydraulic fracturing.[4]

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 (see Section 6.2). While wells are designed and constructed to isolate fluids and maximize the production of oil and gas,

[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 create blockage and 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) 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] 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.

inadequate construction or degradation of the casing or cement can allow fluid movement that can change the quality of drinking water resources. Potential issues associated with wells may be related to the following:

- Casing (e.g., faulty, inadequate, or degraded casing or other well components, as influenced by the numbers of casings; the depths to which these casings are set; compatibility with the geochemistry of intersected formations; the age of the well; whether re-fracturing is performed; and other operational factors) and
- Cement (e.g., poor, inadequate, or degraded cement, as influenced by a lack of cement in key intervals; poor-quality cement; improper or inadequate placement of cement; or degradation of cement over time).

Fluid movement can also occur **via induced fractures and/or other features within subsurface formations** (see 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 the 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 abandoned or active (producing) offset wells near the well that is being stimulated (i.e., well communication) or abandoned or active mines.[1]
- Fractures intersecting geologic features that can act as conduits, such as existing permeable faults and fractures.

In this chapter, we describe the conditions that can contribute to or cause the development of the pathways listed above, the evidence for the existence of these pathways, and potential impacts or impacts on drinking water resources associated with these pathways.

The interplay between the well and the subsurface features is complex, and sometimes it is not possible to identify what specific element is contributing to or is the primary cause of an impact to drinking water resources. For example, concerns have been raised regarding stray gas detected in ground water in natural gas production areas (for additional information about stray gas, see Sections 6.2.2 and 6.3.2.4).[2] Stray gas migration is a technically complex phenomenon, because

[1] An abandoned well refers to a well that is no longer being used or cannot be used because of its poor condition.
[2] Stray gas refers to the phenomenon of natural gas (primarily methane) migrating into shallow drinking water resources or to the surface.

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), and it is 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. Where such data does exist and provides 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.

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 at any time within any well, the repeated high pressure stresses exerted during hydraulic fracturing operations may make maintaining integrity of the well more difficult (Council of Canadian Academies, 2014). In Section 6.2.1, we present 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 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 convey hydrocarbon resources from the reservoirs in which they are found to the surface and also to isolate fluid-bearing zones (containing oil, gas, or fresh water) from each other. Multiple barriers are often present, and they act together to prevent both horizontal movement (in or out of the well) and vertical movement (along the wellbore from deep 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 fracturing fluids, formation fluids, and hydrocarbons 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.[1] 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 one pathway for fluid movement does not necessarily mean that an impact to a drinking water resource has occurred or will occur.

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 6-1 illustrates the configurations of casing and cement that may occur in oil and gas production wells, including the types of casing strings that may be present, the potential locations of cement, and other features. 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, 2015o), 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 may be present in a well. Surface casing often extends from the wellhead down to the base (bottom) of the drinking water resource to be protected. Wells also may be constructed with liners, which are anchored or suspended from inside the bottom of the previous casing string, rather than extending all the way to the surface, and production tubing, which is used to transport the hydrocarbons to the surface.

[1] For the purposes of this assessment, a well's "orientation" refers to the direction in which the well is drilled, and "deviation" is used to indicate an orientation that is neither strictly vertical nor strictly horizontal. However, in industry usage, "deviation" is also used as a generic term to indicate well orientation.

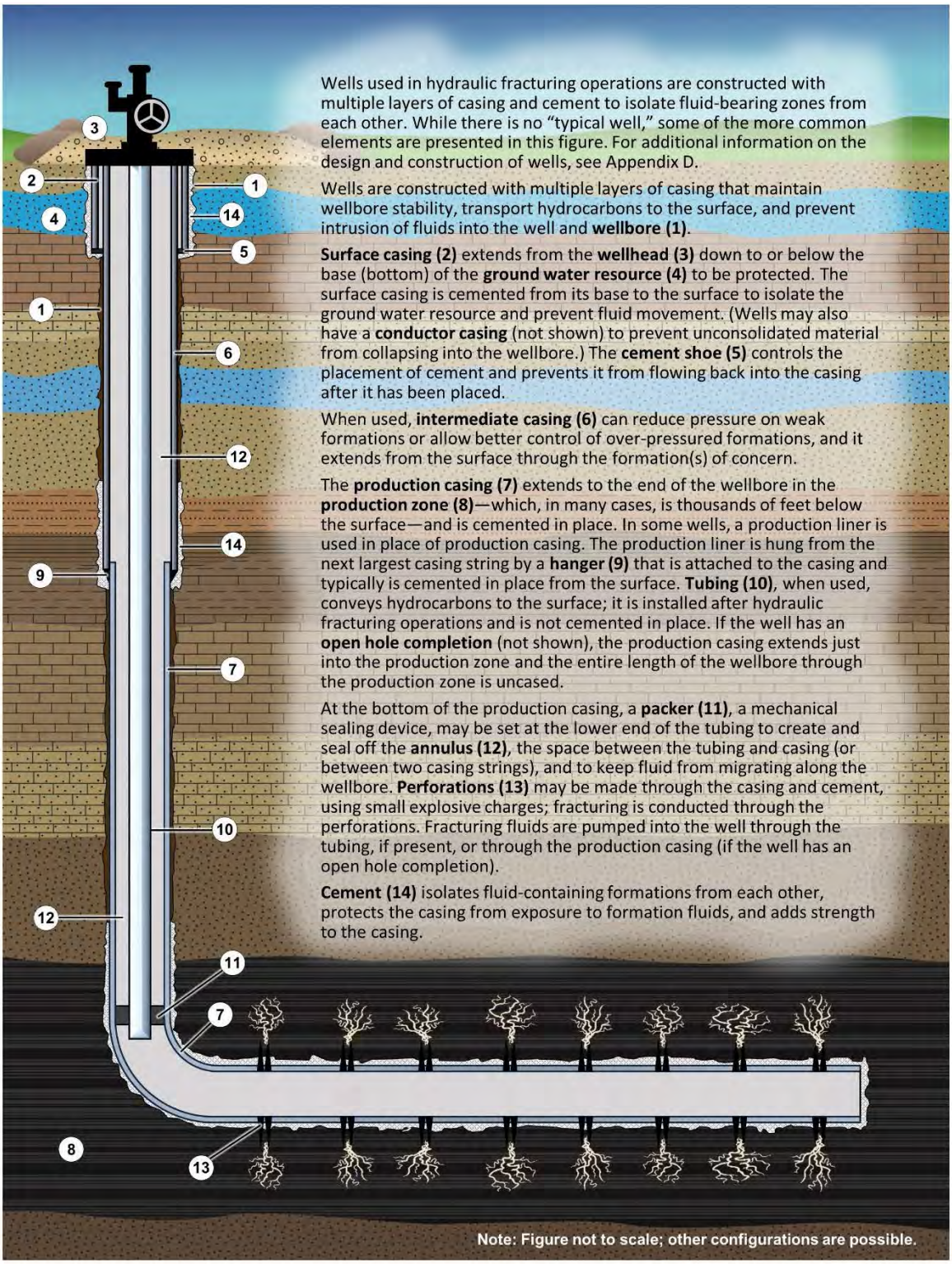

Figure 6-1. Overview of well construction.

Among the wells represented by the Well File Review (see Text Box 6-1), between one and three 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, 2015o).

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. The *Review of Well Operator Files for Hydraulically Fractured Oil and Gas Production Wells: Well Design and Construction* (U.S. EPA, 2015o), referred to as the Well File Review, presents the results of the survey and describes, for these wells: well design and construction characteristics, the relationship of well design and construction characteristics to drinking water resources, and the number and relative location of well construction barriers (i.e., casing and cement) that can block pathways for potential subsurface fluid movement.

The results of the survey are based on information provided by well operators for a statistically representative sample of 323 hydraulically fractured oil and gas production wells. The EPA did not attempt to independently and systematically verify data supplied by well operators. Consequently, results from analyses based on these data are of the same quality as the supplied data.

Results of the survey are presented as rounded estimates of the frequency of occurrence of hydraulically fractured production well design or construction characteristics with 95% confidence intervals. The results are statistically representative of an estimated 23,200 (95% confidence interval: 21,400-25,000) onshore oil and gas production wells hydraulically fractured in 2009 and 2010 by the nine service companies.

Hydraulic fracturing operations impose a variety of stresses on the well components. The casing should be designed with sufficient strength to withstand the stresses it will encounter during the installation, cementing, fracturing, production, and postproduction phases of the life of the well. These stresses, illustrated in Figure 6-2, 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 cyclical stress (the stress caused by frequent or rapid changes in temperature or pressure). Casing strength can be increased by using high-strength alloys or by increasing the thickness of the casing. 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.

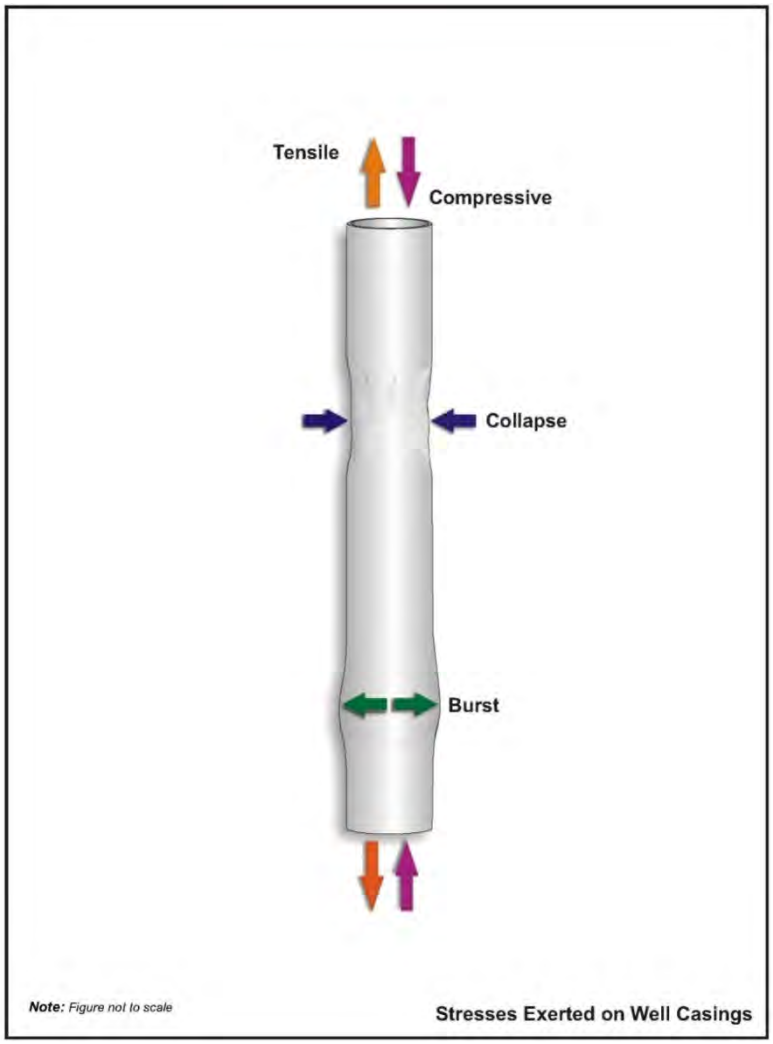

Figure 6-2. The various stresses to which the casing will be exposed.

In addition to the stresses illustrated, the casing will be subjected to bending and cyclical stresses. Source: U.S. EPA (2012c).

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 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 formations and fluids encountered are important for maintaining well integrity through the life of the well.

The cement does not always need to be continuous along the entire length of the well in order 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 in the Gulf of Mexico found that there was no breakdown in isolation

between geologic zones with pressure differentials as high as 14,000 psi as long as there was at least 50 ft (15 m) of high-quality cement between the 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.[1] 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; 25 out of 27 oil and gas producing states surveyed by the Ground Water Protection Council require some minimum amount of cementing on the production casing above the producing zone (GWPC, 2014). In general, the intermediate casings of the wells studied in the Well File Review were fully cemented; while 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%). Production casings were partially cemented in 47% of the wells, or approximately 10,900 wells (U.S. EPA, 2015o).

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 ground surface. 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, 2015o).

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

[1] 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.

pressure associated with standard cement placement could damage weak zones in the formation (Crook, 2008).

Deficiencies in the cementing process can result from poor centering or lost cement.[1] Poor centering of the casing within the wellbore can cause uneven cement placement around the wellbore, leading to the formation of thin weak spots that are prone to creation of uncemented channels around the casing and loss of integrity (Kirksey, 2013). If any deficiencies or defects in the primary cement job are identified, remedial cementing may be performed.

In over 90% of wells studied in the Well File Review, the casing strings were cemented using primary cement methods. Secondary or remedial cementing was used on an estimated 4,500 casings (8%) most often on surface and production casings and less often on intermediate casings. The remedial cementing techniques employed in these wells included cement squeezes, cement baskets, and pumping cement down the annulus (U.S. EPA, 2015o). See Appendix D for more information on remedial cementing techniques.

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, 2015o). 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.[2] 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 (1,524 m) above the hydraulic fracturing zone (U.S. EPA, 2015o). 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 five feet 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 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 that is three times the length that would otherwise be considered adequate for zonal isolation (Fitzgerald et al.,

[1] 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.
[2] 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.

1985). Conversely, King and King (2013) concluded that 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.

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 below, 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 drilled vertically but are designed to deviate 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 (see Figure 6-1).

The use of horizontal wells, particularly in unconventional reservoirs, is increasing (DrillingInfo, 2014b; Valko, 2009). Among wells evaluated in the Well File Review (i.e., over the period of September 2009 to September 2010), about 66% were vertical, 11% were horizontal, and about 23% were deviated wells (U.S. EPA, 2015o).[1] 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). Note that among natural gas wells used in hydraulic fracturing operations, 49.5% of wells in the DrillingInfo database were horizontal. The use of horizontal wells in hydraulic fracturing operations has also been steadily increasing; in 2012, 63.7% of all wells used in hydraulic fracturing operations were horizontal, compared to just 4% in 2003 (DrillingInfo, 2014b). See Figure 2-16 for a map presenting the locations of horizontal wells in the United States.

6.2.1.4. Well Completion

Another important aspect of well construction is how the well is completed into the production zone, because the well's completion is part of the system of barriers and must be intact to provide a fully functioning system.[2] 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, 2015o; George et al., 2011; Renpu, 2011). 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 frac string, is inserted inside the production casing to protect it from the high pressures imposed during hydraulic fracturing operations. Another method of completion is an open hole completion,

[1] 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.
[2] 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.

where the production casing extends into the production zone and the entire length of the drilled horizontal wellbore through the production zone is left uncased. With open hole completions, the entire production zone can either be fractured all at once in a single stage, or in stages using a casing string set on formation packers, which separate the annulus into stages.[1] A special casing with retractable sleeves is used to fracture each stage separately. 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, 2015o).

In some cases, wells may be recompleted after the initial construction, with re-fracturing if production has decreased (Vincent, 2011). Recompletion 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.

6.2.2. Evidence of the Existence of Fluid Movement Pathways or of Fluid Movement

The following sections describe the pathways for fluid movement that can develop within the production well and wellbore. We also describe the conditions that lead to the development of fluid movement pathways and, where available, evidence that a pathway has allowed fluid movement to occur within the casing or cement, and—in the case of sustained casing pressure (see Section 6.2.3)—a combination of factors within the casing and cement. (See Figure 6-3 for an illustration of potential fluid movement pathways related to casing and cement.) We describe available information regarding the rate at which these pathways have been identified in hydraulic fracturing wells or, where such information does not exist, present the results of research on oil and gas production wells in general or on injection wells.[2] Insufficient publicly accessible information exists to determine whether wells intended for hydraulic fracturing are constructed differently from production wells where no fracturing is conducted. 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, this information is considered relevant to the research questions (see Section 6.4).

While new wells can be specifically designed to withstand the stresses associated with hydraulic fracturing operations, older wells, which are sometimes used in hydraulic fracturing operations, may not have been designed to the same specifications. Where older wells were not designed specifically to withstand the stresses associated with hydraulic fracturing, their reuse for this purpose could be a concern. Frac strings, which are specialized pieces of casing inserted inside the production casing, may be used to protect older casing during fracturing. However, the effect of 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 fracturing (Vincent, 2011). An estimated 6% of wells (1,400 wells)

[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 casing and formation, preventing migration of fluids.
[2] An injection well is a well into which fluids are being injected (40 CFR 144.3).

represented in the Well File Review were more than 10 years old before they were fractured between 2009 and 2010 (U.S. EPA, 2015o).

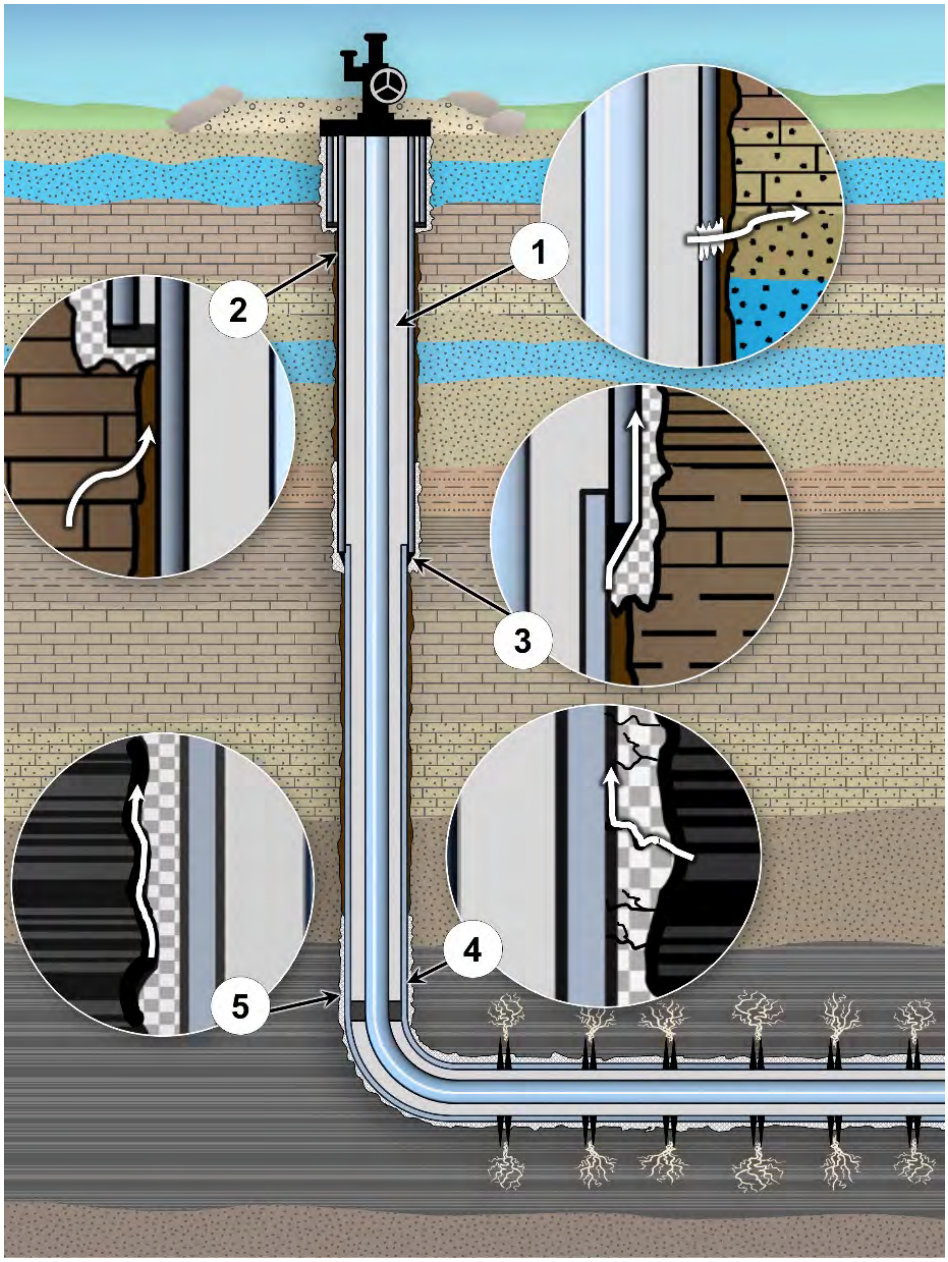

Figure 6-3. Potential pathways for fluid movement in a cemented wellbore.

These pathways include: (1) casing/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, or (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.

Note that there are also potential issues related to *where* older wells are sited. For example, some wells may 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. See Section 6.3.2.

6.2.2.1. Pathways Related to Well Casing

High pressures associated with hydraulic fracturing operations can damage the casing and lead to fluid movement that can change the quality of drinking water resources. The casing string through which fracturing fluids are injected is subject to higher pressures during 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 (see Figure 6-2), a casing failure may result. If undetected or not repaired, casing failures will serve as pathways for fracturing fluids to leak out of the casing.[1] Below we present indicators that pathways along the casing are present or allowing fluid movement.

Fracturing fluids or fluids naturally present in the subsurface could flow into other zones in the subsurface if inadequate or no cement is present and the pressure in the casing is greater than the formation pressure. As we describe below, pathways for fluid movement associated with well casing may 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 may also occur if the wellbore passes through a structurally weak geologic zone that fails and deforms the well casing. Such failures are common when drilling through zones containing salt (Renpu, 2011). This type of well damage may also be possible if hydraulic fracturing causes stress failure along a fault. Investigation of a well following a seismic event in England that was attributed to hydraulic fracturing found that the casing had been deformed by the stress from the formation (De Pater and Baisch, 2011). While it is not known if the casing deformation occurred before or after the seismic event, such damage is possible if mechanically weak formations are present. 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 fail, potentially damaging the well. Palmer et al. (2005) demonstrated through modeling that hydraulic fracturing within coal that had a low unconfined compressive strength could cause shear failure of the coalbeds surrounding the wellbore.

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

[1] Internal mechanical integrity tests (MITs), such as casing inspection logs or caliper logs, annulus pressure monitoring, and pressure testing, can provide early warning of a problem, such as a leak, within the casing. 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 integrity is an event that may result in fluid movement from the well if remediation is not performed.

at other places where other equipment is attached to the casing. Corrosion at collars may exacerbate problems with loose or poorly designed connections, which are another common cause of casing leaks (King and King, 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 6-3.

Aging and use of the well contribute to casing degradation. Casing corrosion and degradation can occur over time and with extended use. Also, exposure to corrosive chemicals such as hydrogen sulfide, carbonic acid, and brines can accelerate corrosion. Therefore, the potential for fluid migration related to compromised casing tends to be higher in older wells. Ajani and Kelkar (2012) studied wells in Oklahoma and found a correlation between well age and integrity, specifically in wells spaced between 1,000 and 2,000 ft (305 and 610 m) from a well being fractured, the likelihood of impact to the well 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 well integrity problems in a study of wells in the Gulf of Mexico (Brufatto et al., 2003). The studies mentioned did not look for evidence of such fluid movement pathways, however. Because of this potential for degradation of well components in older wells and the related potential for fluid movement, reentering older wells for re-fracturing may contribute to the development of fluid movement pathways within those wells.

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 or if the uncemented section is in contact with fluid-containing zones (including the zone being fractured). Sections of well casing that are uncemented may allow fluid migration into the annulus between the casing and formation. Fluid is free to migrate between formations in contact with the uncemented well section in any uncemented annulus without significant hole sloughing or wellbore swelling. If the uncemented section extends through a drinking water resource, fluid migration into the drinking water resource may occur.

Other well 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 (King and King, 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 7 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 6 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 drinking water wells with alleged water quality problems in the Wind River and Fort Union formations in Wyoming

(WYOGCC, 2014). The state found that the surface casing of oil and gas wells was shallower than the depth of 3 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, 2014).

During hydraulic fracturing operations 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 stages of hydraulic fracturing when the pressure spiked to over 8,390 psi (58 MPa). The casing failed, and 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 bubble up at the surface. Ultimately, nearly 168,000 gallons (636 m^3) of fluids and approximately 2,860 tons (2,595 metric tons) of contaminated soil were removed from the site (Jacob, 2011). Sampling of two monitoring wells in the drinking water aquifer identified brine contamination that was consistent with mixing of local ground water with brine from Madison Group formations, which the well had penetrated (U.S. EPA, 2015j). Tert-butyl alcohol (TBA) was also found in the two wells with brine contamination. The TBA was consistent with degradation of tert-butyl hydroperoxide, a component of the fracturing fluid used in the Franchuk well. The rupture (blowout) was the only source consistent with findings of high brine and TBA concentrations in the two wells.[1] For additional information about impacts at the Killdeer site, see Text Box 5-12 in Section 5.5 and Section 6.3.2.2.

Inadequate casing or cement can respond poorly when blowout preventers activate. 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 7.7.3.2.

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. Several studies have evaluated the components of a well that can affect well performance and integrity. Ingraffea et al. (2014) conducted a study of well integrity in Pennsylvania production wells to assess overall trends in well integrity. This study identified a significant increase in well integrity problems from 2009 to 2011 rising to 5% to 6% of all wells, followed by a decrease beginning in 2012 to about 2% of all wells, a reduction of approximately 100

[1] A well blowout is the uncontrolled flow of fluids out of a well. 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.

violations among 3,000 wells. The rise in well integrity problems between 2009 and 2011 coincided with an increase in the number of wells in unconventional reservoirs.

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 6-2 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." Seven of these clusters were stripped of atmospheric gases (Ar^{36} and Ne^{20}) and were 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. Possible explanations for the rapid migration include transport up the well and through a leaky casing (Pathway 1 in Figure 6-3) or along uncemented or poorly cemented intervals from shallower depths (Pathways 2 through 5 in Figure 6-3). 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 6-2. Stray Gas Migration.

Stray gas refers to the phenomenon of natural gas (primarily methane) migrating into shallow drinking water resources, into water wells, or to the surface (e.g., cellars, streams, or springs). Stray gas in the wellhead of a production well is an indicator of an active wellbore pathway. Methane is not a regulated drinking water contaminant, but it can initiate chemical and biological reactions that release or mobilize other contaminants, and gas can accumulate to explosive levels when allowed to exsolve (degas) from ground water in closed environments. Stray gas may originate from conventional and unconventional natural gas reservoirs, as well as from coal mines, landfills, leaking gas wells, leaking gas pipelines, and buried organic matter (Baldassare, 2011).

Detectable levels of dissolved hydrocarbons (generally methane and/or ethane) exist in most oxygen-poor aquifers, even in the absence of human activity (Gorody, 2012). Pre-drilling studies show that low levels of methane are frequently found in water wells in northern Pennsylvania and New York (Kappel, 2013; Kappel and Nystrom, 2012); one USGS study detected methane in 80% of sampled wells in Pike County, Pennsylvania (Senior, 2014). The origin of methane in ground water 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). Occurrence of thermogenic methane in shallower formations depends upon the existence of a hydrocarbon source and pathways by which the gas can migrate. Interactions between hydrocarbon production and natural systems must also be considered. For example, Brantley et al. (2014) describe how northern Pennsylvania's glacial history may help explain why stray gas is more common there than in the southern part of the state.

Stray gas migration can be a technically complex phenomenon, in part because there are many potential routes for migration. The lack of detailed monitoring data, including a lack of baseline measurements prior to hydrocarbon production, often further complicates stray gas research. 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).

However, determining the source of methane does not necessarily establish the migration pathway. Well casing and cementing issues may be an important source of stray gas problems (Jackson et al., 2013b); however, other potential subsurface pathways are also discussed in the literature. Multiple researchers (e.g., Jackson et al., 2013b; Molofsky et al., 2013; Révész et al., 2012; Osborn et al., 2011) have described biogenic and/or thermogenic methane in ground water supplies in Marcellus gas production areas, although the pathways of migration are generally not apparent. The Osborn et al. (2011) study found that thermogenic methane concentrations in well water increased with proximity to Marcellus Shale production sites, while Molofsky et al. (2013) found the presence of gas to be more closely correlated with topography and elevation. Similarly, Siegel et al. (In Press) found no correlation between methane in ground water and proximity to production wells.

The EPA conducted case studies that included investigating stray gas in northeastern Pennsylvania and the Raton Basin of Colorado. In northeastern Pennsylvania, many drinking water wells within the study area were found to have elevated methane concentrations. For some of the wells, the EPA concluded that the methane (both thermogenic and biogenic) was naturally occurring background gas not attributable to gas exploration activities. In others, it appeared that non-background 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, 2015o). The Raton Basin case study examined the Little Creek Field, where potentially explosive quantities of methane were vented into a number of drinking water wells in 2007. The methane was found to be primarily thermogenic in origin, modified by biologic oxidation (U.S. EPA, 2015l). 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 ground water (U.S. EPA, 2015l).

While the sources of methane in the two studies could be determined with varying degrees of certainty, attempts to definitively identify the pathways of migration have been inconclusive. 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, 2014i). The Pennsylvania

Department of Environmental Protection (PA DEP) cited at least two operators for failure to prevent gas migration at a number of 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). A separate study (Ingraffea et al., 2014) showed that wells in this area had higher incidences of well integrity problems relative to wells in other parts of Pennsylvania. In the Raton Basin, the source of methane was identified as the Vermejo coalbeds. Based on modeling of the Raton Basin study area, the migration could be explained either by migration along natural rock features in the area or by migration caused by fracturing around the wellbore (U.S. EPA, 2015l). Because the gas production wells were shut in shortly after the incident began, the wells could not be inspected to determine whether an 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. In order to more conclusively determine sources and migration pathways, studies in which data are collected on well integrity and ground water methane concentrations both before and after hydraulic fracturing operations, in addition to the kinds of data summarized above, would be needed.

6.2.2.2. Pathways Related to Cement

Fluid movement may result from inadequate well design or construction (e.g., cement loss or other problems that arise in cementing of unconventional 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.[2,3] The well cement must be able to withstand the subsurface conditions and the stresses encountered during hydraulic fracturing operations. In this section, we present indicators that pathways within the cement are present or allowing fluid movement.

Uncemented zones can allow fluids or brines to move into drinking water resources. An improper cement job can fail to maintain zonal isolation in several ways. The first is by poor cement placement. 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 along the entire uncemented length of the wellbore, unless the wellbore sloughs in around the casing.

Because of its low density, gas will migrate up the wellbore if an uncemented wellbore is exposed to a gas-containing formation. Gas may then be able to enter other formations (including drinking

[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.

[2] External MITs, such as temperature logs, noise logs, oxygen activation logs, and radioactive tracer logs, can indicate improper cementing or degradation of the cement.

[3] Microannuli are very small channels that form in the cement and that may serve as pathways for fluid migration to drinking water resources.

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). The rate at which the gas can move will depend on the difference in pressure between the annulus and the formation (Wojtanowicz, 2008). Harrison (1985) also demonstrated that such uncemented annuli could result in the migration of gas into overlying formations open to the annulus.

In several cases, poor or failed cement has been linked to stray gas migration (see Text Box 6-2). 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) (see Section 6.2.2.1) using isotopic data, four clusters of gas contamination were linked to cement issues. 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. In a study in Utah, Heilweil et al. (2013) used a stream-based methane monitoring method to identify a case of potential gas migration near a well with defective casing or cement.

Cementing of the surface casing is the primary aspect of well construction that protects 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, which was found to be fully cemented in 93% of wells, extended below the base (i.e., the bottom, deepest, or lowermost part) of the protected ground water resource reported by well operators in an estimated 55% of wells (12,600 wells).[1] In an additional 28% of wells (6,400 wells), the operator-reported protected ground water resources were fully covered by the next cemented casing string. A portion of the annular space between casing and the operator-reported protected ground water resources was uncemented in at least 3% of wells (600 wells) (U.S. EPA, 2015o).[2] Improper placement of cement can lead to cement integrity problems. For example, an improper cement job can be the result of loss of cement during placement into a formation with 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

[1] In the in the Well File Review, protected ground water resources were reported by well operators. For most wells represented in the Well File Review, protected ground water resources were identified by the well operators from state or federal authorization documents. Other data sources used by well operators included aquifer maps, data from offset production wells, open hole log interpretations done by operators, operator experience, online databases, and references to a general requirement by the oil and gas agency.

[2] 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 ground water 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 ground water resource.

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 6-3 shows a variety of pathways for fluid migration that are possible from failed cement jobs.

One example of how cement problems associated with hydraulic fracturing contributed to a contamination incident occurred in Bainbridge, Ohio. This incident was particularly 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 (1,189 m) below ground surface (bgs) with the producing formation located between 3,600 and 3,900 ft (1,097 and 1,189 m) bgs. Overlying the producing formation were several uneconomic formations that contained 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 (213–244 m) above the producing formation to seal off these areas. During cementing, however, the spacer fluid failed to return to the surface, indicating lost cement, and the cement did not reach the intended height.[2] Despite the lack of sufficient cement, the operator proceeded with hydraulic fracturing.

During the fracturing operation, about 840 gallons (3.2 m^3) 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. About a month later, there was an explosion in a nearby house where methane had entered from an abandoned and unplugged drinking water well that was 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.

Contamination at Bainbridge was the result of inadequate cement. The ODNR determined that failure to cement the over-pressured gas formations, proceeding with the fracturing operation without verifying there was 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 (1,109 m) bgs, leaving the uneconomic gas-producing formations and a portion of the production zone uncemented. Hydraulic fracturing fluids flowing out of the annulus provided an indication that the fracturing had created a path from the producing formation to the well annulus. This pathway may have allowed gas from the producing formation along with gas from the uncemented formation to enter the annulus. 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.

[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.

While limited literature is available on construction flaws in wells that have been used in hydraulic fracturing operations, 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 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 well 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 well integrity problems, including those related to cement. The results of these studies are summarized in Table 6-1. While all of the studies shown in the table used the same database, their results vary, not only because of the different time frames, but also because they used different definitions of what violations constituted an 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 well integrity, while Vidic et al. (2013) looked only at well integrity violations that resulted 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.

Table 6-1. Results of studies of PA DEP violations data that examined well failure rates.

Study	Violations investigated	Data timeframe	Key findings[a]

Study	Violations investigated	Data timeframe	Key findings[a]
Considine et al. (2012)	Violations resulting in environmental damage (3,533 wells studied)	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 wells studied)	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 wells studied)	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)	Failure of cement/casing that allowed fluid to leak out (6,466 wells studied)	2008–2013	Approximately 3.4% of wells received this type of violation.
Olawoyin et al. (2013)	All violations (2,001 wells studied)	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%.

[a] Note: While all of these studies used the same database, their results vary because they studied different time frames and used different definitions of what violations constituted an 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 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 used for hydraulic fracturing; they assumed that unconventional wells were hydraulically fractured and conventional wells were not.

Violation rates resulting in environmental pollution among all 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. Of 845 events that caused environmental contamination, 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).

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, well integrity, and formation permeability; however, 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 approximately 20 unconventional gas wells impacted water supplies between 2008 and 2012; this equates to 0.1% to 1% of the 6,061 wells spudded between 2008 and 2012 (it is unclear exactly how many PDLs are linked to an individual well). While these oil and gas wells were linked to contamination of wells and springs, the 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). We did not perform a full and independent review of the PDLs for this assessment.

While the studies discussed above present possible explanations for higher violation incidences in hydraulically fractured wells, it should be noted that other explanations that are 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 integrity issues. The observation by Ingraffea et al. (2014) that wells drilled in unconventional reservoirs 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 integrity issues.

Thermal and cyclic stresses caused by intermittent operation also may 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 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) flowback water, can lead to contraction of the well materials (both casing and cement), which introduces additional stresses. Similar temperature changes may occur when

[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.

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. Microannuli formed by this debonding can be conduits 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 (0.3 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 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).[2] While a small area of debonding may not lead to fluid migration, the microannuli in the cement that result from the debonding can serve as initiation points for fracture propagation if re-pressurized gas enters the microannulus (Dusseault et al., 2000).

The Council of Canadian Academies (2014) found that the repetitive pressure surges that occur during the fracturing process would make maintaining an intact cement seal more of a challenge in wells that are hydraulically fractured. Wang and Dahi Taleghani (2014) performed a modeling study that showed 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 cyclical pressure stresses caused by drilling. Theoretically, such cyclical pressure events could also be experienced during multiple stage 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 that can decrease cement susceptibility to specific chemical components are available.

[1] Microannuli can also form due to an inadequate cement job, e.g., poor mud removal or improper cement placement rate.
[2] 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.

6.2.2.3. Sustained Casing Pressure

An example of how the issues related to casing and cement discussed in the preceding sections can work together and be difficult to differentiate can be seen in the case of sustained casing pressure.[1] Sustained casing pressure 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 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.

Sustained casing pressure occurs more frequently in older wells and horizontal or deviated wells. One study found that sustained casing pressure becomes worse 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 integrity problems. Watson and Bachu (2009) found that a higher portion of deviated wells had sustained casing pressure compared to vertical wells. Increased pressures, cyclic stresses (Syed and Cutler, 2010), and difficulty in cementing horizontal wells (Sabins, 1990) also may lead to increased instances of sustained casing pressure in wells where hydraulic fracturing occurs (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 liquids 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 ground water. Over-pressurization of the annulus can be avoided by venting the annulus to the atmosphere.

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, hydrocarbon and isotope concentrations were used to investigate stray gas migration into domestic drinking water (U.S. EPA,

[1] 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 that is actively being used. It is possible to have pressure in more than one of the annuli.

2014i). While the composition of the gas in the water wells was consistent with that of the gas found in nearby gas wells with high 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 casing annulus pressures. In another example in Alberta, Canada, 14% of wells drilled since 1971 have shown serious sustained casing flow, defined as more than 10,594 ft^3 (300 m^3)/day at pressures higher than 0.48 psi/ft (11 kPa/m) times the surface casing depth (Jackson and Dussealt, 2014). Another study in the same area found gas in nearby drinking water wells had a composition that was consistent with biogenic methane mixing with methane from nearby coalbed methane and deeper natural gas fields (Tilley and Muehlenbachs, 2012).

Adequate well design, detection (i.e., through annulus pressure monitoring), and repair of sustained casing pressure reduce the potential for fluid movement. Watson and Bachu (2009) found that regulations that required monitoring and repair of sustained casing vent flow or sustained casing pressure had a positive effect on lowering leak rates. The authors also found that wells initially designed for injection experienced sustained casing pressure less often than those that were retrofitted (Watson and Bachu, 2009).

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. 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, four pressured gas zones were encountered during well drilling and there was a lost cement incident, which resulted in the cement top being more than 4,000 ft (1,219 m) lower than originally intended. Due to high measured bradenhead pressure (661 psi, or 4.6 MPa), cement remediation efforts were implemented (Crescent, 2011; COGCC, 2004). 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-containing formation and to monitor casing pressures after cementing.

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 downhole communication problems (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]

[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.

6.3. Fluid Migration Associated with Induced Fractures within Subsurface Formations

In this section, we discuss potential pathways for fluid movement associated with induced fractures and subsurface geologic formations (outside of the well system described in Section 6.2). We examine 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.[1]

Fluid movement requires both a physical conduit (e.g., the permeable matrix pore volume or a fracture in the rock) and a driving force.[2] In subsurface rock formations, fluid movement is driven by the existence of a hydraulic gradient depending on elevation and pressure, which is also influenced by fluid density, composition, and temperature (Pinder and Celia, 2006). Pressure differentials in the reservoir and density-driven fluid buoyancy are the key forces governing fluid migration during and after hydraulic fracturing operations. Pressure differentials depend upon the initial conditions within these formations and are directly influenced by pressures that are created by injection or production regimes. Buoyancy depends on density differences among and between gases and liquids, and it causes fluid migration when and where these density differences exist along with a pathway (Pinder and Gray, 2008).

As hydraulic fracturing takes place, injected fluids leaving the well create fractures within the production zone and enter the formation through the newly created fractures. Unintended fluid migration may 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; or via fractures that intersect offset wells or other artificial structures (Jackson et al., 2013c). 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 that are injected into the well (including leakoff) and formation fluids (including brine or natural gas).[3]

[1] A subsurface formation (also referred to as a "formation" throughout this section) is a mappable body of rock of distinctive rock type(s), including the rock's pore volume (i.e., the void space within a formation that fluid flow can occur, as opposed to the bulk volume which includes both pore and solid phase volume), with a unique stratigraphic position.
[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.
[3] Leakoff is the fraction of the injected fluid that infiltrates into the formation and is not recovered during production (Economides et al., 2007).

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 within the reservoir prior to any production, when 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).
2. During the production period, after fracturing is completed and pressure in the fractures is reduced, and hydrocarbons (along with produced water) flow from the reservoir into the well.

Note that these two time periods vary in duration. As described in Chapter 2, 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 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 that affect 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 injected 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 flowback and 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. It depends on the geomechanical characteristics of rock formations, fluid properties, pore pressures, and subsurface stress fields. As shown in Figure 6-4, fracture formation is controlled by the three *in situ* principal compressive stresses: the vertical stress (S_V), the maximum horizontal stress (S_H), and the minimum horizontal stress (S_h). During hydraulic fracturing, pressurized fluid injection creates high pore pressures around the well. When the pressure exceeds the local least principal stress and the tensile strength of the rock, failure results and fractures form (Zoback, 2010; Fjaer et al., 2008).

Fractures propagate (increase in length) in the direction of the maximum principal stress, which is perpendicular to the direction of the least principal stress. 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, the local least principal stress is the minimum horizontal stress (S_h), and the principal fracture orientation is expected to be vertical. This is the scenario illustrated in Figure 6-4. 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 reservoirs, Fisher and Warpinski (2012) found that fractures at approximately 4,000 ft (1,220 m) below the surface or deeper are primarily vertical (see below for more information on tiltmeters). Between approximately 4,000 and 2,000 ft (1,220 and 610 m), fracture complexity increases, and fractures at approximately 2,000 ft (610 m) or shallower are primarily horizontal (Fisher and Warpinski, 2012).[1] Horizontal fracturing can also occur in deeper 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).

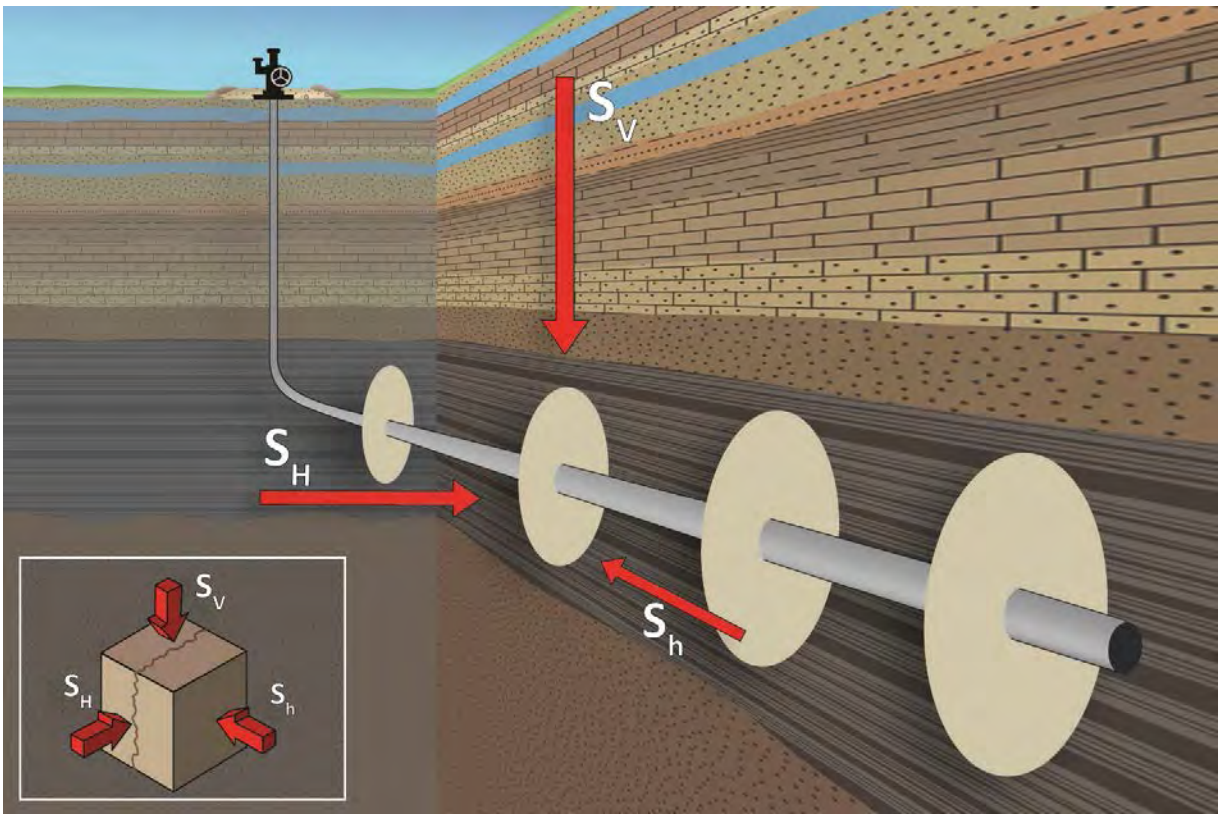

Figure 6-4. Hydraulic fracture planes (represented as ovals), with respect to the principal subsurface compressive stresses: S_V (the vertical stress), S_H (the maximum horizontal stress), and S_h (the minimum horizontal stress).

At depths greater than approximately 2,000 ft (610 m), the principal fracture orientation is expected to be vertical, as fractures propagate in the direction of S_H.

[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.

In addition to the principal subsurface stresses, other geomechanical and reservoir characteristics and operational factors affect fracture creation, geometry, and propagation.[1] These include initial reservoir pressure and saturation, injected fluid pressure or injection rate, geomechanical rock characteristics, reservoir heterogeneity, tensile strength, fluid type within fractures, and reservoir permeabilities (Kim and Moridis, 2015). Fracture creation is a complex process that involves interactions between multiple properties. For example, as described by Daneshy (2009), fracture height depends on a combination of parameters and processes including the material properties of geologic formations, pore pressures, stress differences in adjacent formations, shear failure (slippage) at the fracture tip, and the reorientation of the fracture as it crosses an interface between formations. Injection rates, the initial water saturation of the formation, and the type of fluid injected also have effects on fracture creation and propagation (Kim and Moridis, 2015, 2013).

Numerical modeling techniques have been developed to describe fracture creation and propagation and to provide a better understanding of this complex process (Kim and Moridis, 2013). 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 types of advanced models are: permeability, porosity, Young's modulus, Poisson's ratio, and tensile strength, as well as heterogeneities associated with these parameters.[2] Some investigations using these models 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 leads to greater leakoff. These findings demonstrate that elevated pore pressure can cause shear failure, thus further affecting matrix permeability, flow regimes, and leakoff (Daneshy, 2009). Computational investigations have also indicated that slower injection rates can increase the amount of leakoff (Kim and Moridis, 2013).

In addition to their use in research settings, analytical and numerical modeling approaches are used by oil and gas companies 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. The industry models range from simpler (typically two-dimensional) theoretical models to computationally more complicated and accurate three-dimensional models.

In addition to computational approaches, monitoring of hydraulic fracturing operations can provide insights into fracture development. Monitoring techniques involve both operational monitoring methods and "external" methods that are not directly related to the production operation. Operational monitoring refers to the monitoring of parameters including pressure, flow rate, fluid density, and additive concentrations using surface equipment and/or downhole sensors (Eberhard, 2011). This monitoring is conducted to ensure that the operation is proceeding as planned and to

[1] Fracture geometry refers to characteristics of the fracture such as height and aperture (width).
[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.

determine if operational parameters need to be adjusted. Interpretation of pressure data can be used to better understand fracture behavior (e.g., Kim and Wang, 2014). Anomalies in operational monitoring data can also indicate whether an unexpected event has occurred, such as communication with another well (see Section 6.3.2.3).

The volume of fluid injected is typically monitored 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 the growth of the vertical fractures, and additional information is needed to accurately predict the extent of fracture growth.

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, or caliper logs (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 one or more 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). Tiltmeters, which measure extremely small deformations in the earth, can be used to determine the direction and volume of the fractures and, within certain distances from the well, to estimate their dimensions (Lecampion et al., 2005).

6.3.2. Migration of Fluids through Pathways Related to Fractures/Formations

As noted 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 fluid movement. The following subsections describe and evaluate potential pathways for the migration of fracturing fluids, hydrocarbons, or other formation fluids from producing formations to drinking water resources. They also present cases where the existence of these pathways has been documented. As described above, potential subsurface migration pathways for fluid flow out of the production formation are categorized as follows: (1) flow of fluids into the production zone via induced fractures and out of the production zone via flow through the formation, (2) fracture overgrowth out of the production zone, (3) migration via fractures intersecting offset wells and

[1] Typical microseismic events associated with hydraulic fracturing have a magnitude on the order of -2.5 (negative two and half) (Warpinski, 2009).

other artificial structures, and (4) migration via fractures intersecting other geologic features. 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.

In many cases (depending on fracture depth, height, and direction), the distance between the producing formation and the drinking water resource is one of the most important factors affecting the possibility of fluid migration between these formations (Reagan et al., 2015; Jackson et al., 2013c). This distance varies substantially among shale gas plays, coalbed methane plays, and other areas where hydraulic fracturing takes place in the United States (see Table 6-2). 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 mile (1.6 km) or greater. This is reflected in the Well File Review, which found that the largest proportion of wells used for hydraulic fracturing—an estimated 6,200 wells (27%)—had 5,000 to 5,999 ft (1,524 to 1,828 m) of measured distance along the wellbore between the induced fractures and the reported base of protected ground water resources (U.S. EPA, 2015o).[1] However, as shown in Table 6-2, operations in the Antrim and the New Albany plays take place at relatively shallower depths, with distances of 100 to 1,900 ft (30 to 579 m) between the producing formation and the base of drinking water resources. The Well File Review indicated that 20% of wells used for hydraulic fracturing (an estimated 4,600 wells) were located in areas with less than 2,000 ft (610 m) between the fractures and the base of protected ground water resources (U.S. EPA, 2015o). In coalbed methane plays, which are typically shallower than shale gas plays, these separation distances can be even smaller. For example, 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 (30 m) (Watts, 2006).

Some hydraulic fracturing operations are conducted within formations that contain drinking water resources (see Table 6-2). 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 (WYOGCC, 2014; Wright et al., 2012). Vertical gas wells in this area target the lower Eocene Wind River Formation and the underlying Paleocene 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. Hydraulic fracturing in rock formations that meet a state or federal definition of an underground source of drinking water is also known to take place in coalbed methane operations in the Raton Basin (U.S. EPA, 2015l), in the Powder River Basin of Montana and Wyoming (as described in Chapter 7), and in several other coalbed methane plays. In one field in Alberta, Canada, there is evidence that fracturing in the same formation as a drinking water resource (in combination with well integrity

[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.

problems; see Section 6.2.2.2) led to gas migration into water wells (Tilley and Muehlenbachs, 2012). However, no information is available on other specific incidents of this type.

Table 6-2. 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 (2004). See Figures 2-2 and 2-4 in Chapter 2 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])
Shale plays			
Antrim	600 to 2,200 [183 to 671]	70 to 120 [21 to 37]	300 to 1,900 [91 to 579]
Barnett	6,500 to 8,500 [1,981 to 2,591]	100 to 600 [30 to 183]	5,300 to 7,300 [1,615 to 2,225]
Eagle Ford	4,000 to 12,000 [1,219 to 3,658]	250 [76]	2,800 to 10,800 [853 to 3,292]
Fayetteville	1,000 to 7,000 [305 to 2,134]	20 to 200 [6 to 61]	500 to 6,500 [152 to 1,981]
Haynesville-Bossier	10,500 to 13,500 [3,200 to 4,115]	200 to 300 [61 to 91]	10,100 to 13,100 [3,078 to 3,993]
Marcellus	4,000 to 8,500 [1,219 to 2,591]	50 to 200 [15 to 61]	2,125 to 7,650 [648 to 2,332]
New Albany	500 to 2,000 [152 to 610]	50 to 100 [15 to 30]	100 to 1,600 [30 to 488]
Woodford	6,000 to 11,000 [1,829 to 3,353]	120 to 220 [37 to 67]	5,600 to 10,600 [1,707 to 3,231]
Coalbed methane basins			
Black Warrior (Upper Pottsville)	0 to 3,500 [0 to 1,067]	< 1 to > 70 [< 1 to > 21]	As little as zero[b]
Powder River (Fort Union)	450 to >6,500 [137 to 1,981]	75 [23]	As little as zero[b]
Raton (Vermejo and Raton)	< 500 to > 4,100 [< 152 to > 1,250]	10 to >140 [3 to >43]	As little as zero[b]
San Juan (Fruitland)	550 to 4,000 [168 to 1,219]	20 to 80 [6 to 24]	As little as zero[b]

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])

[a] For coalbed methane, values are given for the specific coal units noted in parentheses.
[b] Formation fluids in producing formations meet the definition of drinking water in at least some areas of the basin.

The overall frequency of occurrence of hydraulic fracturing in aquifers that meet the definition of drinking water resources across the United States is unknown. 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% 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 ground water resources reported by well operators (U.S. EPA, 2015o).[1] An analysis of produced water composition data maintained by the U.S. Geological Survey (USGS) provides insight into the geographic distribution of this practice. The USGS produced water database contains results from analyses of samples of produced water 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 continental United States.[2] Just over 5,000 of these samples, which were obtained from wells located in 37 states, reported total dissolved solids (TDS) concentrations. Because the database does not track whether samples were from wells that were hydraulically fractured, we 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. This yielded 1,650 samples from wells located in Alabama, Colorado, North Dakota, Utah, and Wyoming.[3,4] The TDS concentrations among these samples ranged from approximately 90 mg/L to 300,000 mg/L. Samples from approximately 1,200 wells in Alabama, Colorado, Utah, and Wyoming reported TDS concentrations at or below 10,000 mg/L. This analysis, in conjunction with the result from the Well File Review, suggests that, while the overall frequency of occurrence may be low, the activity may be concentrated in some areas of the country.

[1] The 95% confidence interval reported in the Well File Review indicates that this phenomenon could have occurred in as few as 0.1% of the wells or in as many as 3% of the wells.
[2] We 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.
[3] See Chapter 2, Text Box 2-1, which describes how commercial hydraulic fracturing began in the late 1940s.
[4] For this analysis, we 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, we 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 EPA using the assumptions described in Section 2.3.1. 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.

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 flow of injected fluids (or displacement of formation fluids due to injection) through the formation matrix during or after a hydraulic fracturing treatment. 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., 2013c). However, there is limited information available on the fate of injected fluids that are not recovered during production (i.e., leakoff) or displaced formation fluids for cases where hydraulic fracturing takes place within or close to drinking water resources.

Leakoff into shale gas formations may be as high as 90% or more of the injected volume (see Section 7.2 and Table 7-2). The actual amount of leakoff depends on the amount of injected fluid, the hydraulic properties of the reservoir (e.g., permeability), 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] However, despite the potentially large volume of fluid that may be lost into the formation, the flow of this fluid is generally 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).[3] It has been suggested that these processes can sequester the fluids in the producing formations permanently or for geologic time scales (Engelder, 2012; Byrnes, 2011).

A limited number of studies in the literature have evaluated a combination of certain conditions that can facilitate migration of fluids despite these processes. Myers (2012b) suggests that migration of injected and/or formation fluids into the overburden may be possible in cases where there is a significant vertical hydraulic gradient, sufficient permeability, density-driven buoyancy, and the displacement of formation brines by large volumes of injected fluid. Flewelling and Sharma (2014) note that, for migration to occur, an upward hydraulic gradient would be necessary, particularly for brine that is denser than the ground water in the overlying formations; in the case of natural gas, though, buoyancy would provide an upward flux A limited number of studies in the literature have evaluated a combination of certain conditions that can facilitate migration of fluids despite these processes. Myers (2012b) suggests that migration of injected and/or formation fluids into the overburden may be possible in cases where there is a significant vertical hydraulic gradient, sufficient permeability, density-driven buoyancy, and the displacement of formation

[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).

brines by large volumes of injected fluid. Flewelling and Sharma (2014) note that for migration to occur, an upward hydraulic gradient would be necessary, particularly for brine that is denser than the ground water in the overlying formations; in the case of natural gas, though, buoyancy would provide an upward flux (Vengosh et al., 2014). Some natural conditions could create this upward hydraulic gradient in the absence of any effects from hydraulic fracturing (Flewelling and Sharma, 2014). 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—corresponding 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). Furthermore, fracturing fluid would likely be sequestered in the immediate vicinity of the fracture network due to capillary tension (Engelder, 2012).

Over-pressurization of producing formations due to the injection of large amounts of fluid during hydraulic fracturing may support the upward hydraulic gradient for fluid migration (Myers, 2012b). Myers' modeling results suggest that significant pressure buildup that occurs at the location of fluid injection may not return to pre-hydraulic fracturing levels for up to a year. However, these findings have been disputed in the literature due to certain suggested limitations of the original study (e.g., extensive simplification of the model, lack of accurate characterization of regional flow, misrepresentation of saturation conditions in shale formations), and they have been found to be physically implausible given the hydrogeologic characteristics of actual sedimentary basins (Cohen et al., 2013; Flewelling et al., 2013; Vidic et al., 2013; Saiers and Barth, 2012). Some researchers have also suggested that pressure perturbations due to hydraulic fracturing operations are localized to the immediate vicinity of the fractures, due to the very low permeabilities of shale formations (Flewelling and Sharma, 2014). However, there are emerging studies indicating that pressure impacts of hydraulic fracturing operations may extend farther than the immediate vicinity and may create risk of induced seismicity (Skoumal et al., 2015). Following hydraulic fracturing operations, a large-scale depressurization would be expected over the longer term due to hydrocarbon production, which may counteract any short-term localized pressure effects of hydraulic fracturing during production and cause fluids to flow primarily toward the fracture network (Flewelling and Sharma, 2014).

In responses to these critiques, Myers (2013, 2012a) states that they do not prove his original hypothesis or findings wrong, but instead highlight the need for complex three-dimensional modeling and detailed data collection for improving the understanding of the process and risks to drinking water resources. Myers (2013, 2012a) argues that, given the large volume of hydraulic fracturing operations in formations such as the Marcellus, these formations would have to hold very large volumes of water that would be imbibed into the shale. Furthermore, he notes that migration of these fluids into overlying formations may be facilitated by existing fractures or out-of-zone fracturing (as discussed in the following sections).

6.3.2.2. Fracture Overgrowth out of the Production Zone

Fractures that extend out of the intended production zone into another formation or an unintended zone within the same formation could provide a potential fluid migration pathway into drinking

water resources (Jackson et al., 2013c). This migration could occur either through the fractures themselves or in connection with other permeable subsurface features or formations (see Figure 6-5). 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 potential 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).

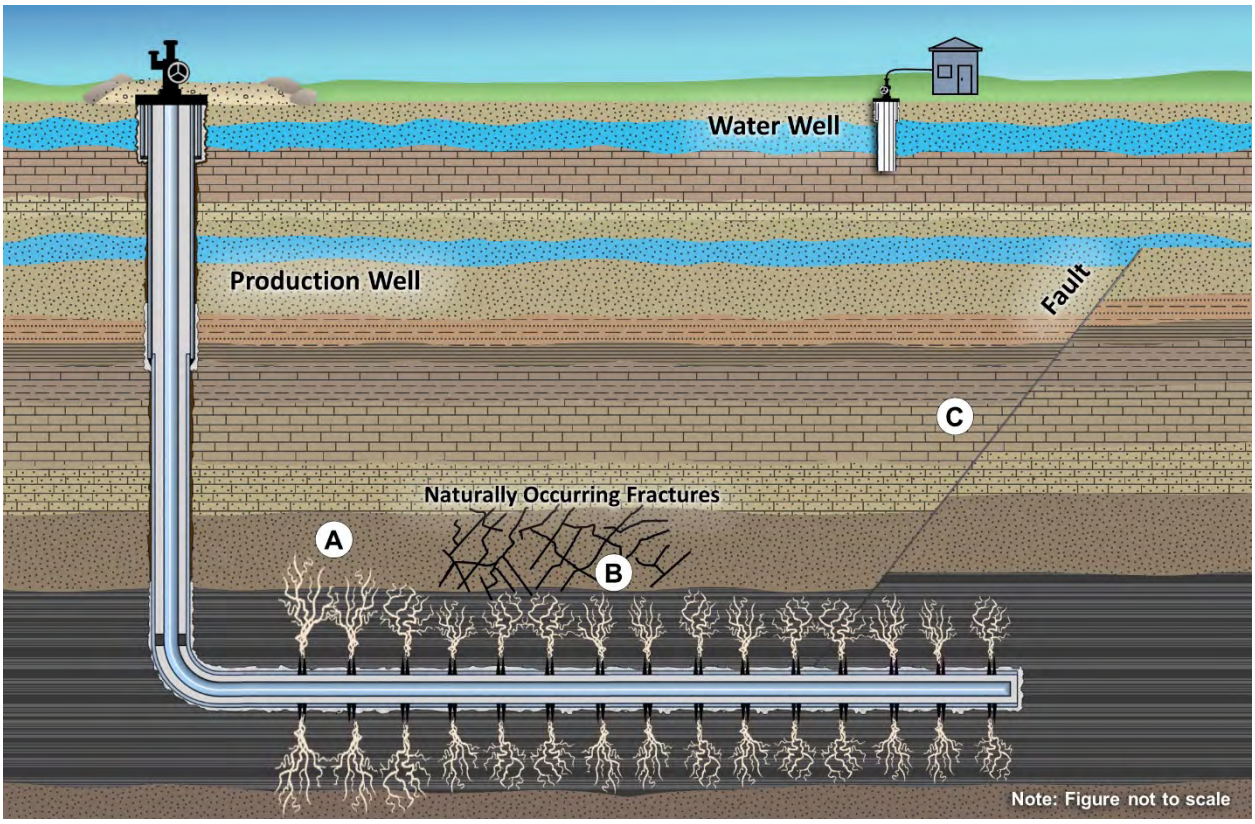

Figure 6-5. Conceptualized depiction of potential pathways for fluid movement out of the production zone: (a) induced fracture overgrowth into over- or underlying formations; (b) induced fractures intersecting natural fractures; and (c) induced fractures intersecting a transmissive fault.

Thickness and depth of production formation are important site specific factors for each operation.

The fracture's geometry (see 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 and microdeformation field monitoring techniques (Fisher and Warpinski, 2012). These data indicate typical fracture heights extending from tens to hundreds of feet. 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 for at least 1,500 ft (477 m), while the maximum thickness of the formation is generally 350 ft (107 m) or less (MCOR, 2012). However, the majority of fractures 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 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 (305 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 caused by hydraulic fracturing (Hammack et al., 2014). At three of the six wells, fractures extending between 1,000 and 1,900 ft (305 and 579 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 that is sometimes referred to as an upper barrier to hydraulic fracture growth. However, all microseismic events were at least 5,000 ft (1,524 m) below drinking water aquifers, as the Marcellus Shale is one of the deepest target formations (see Table 6-2), and no impacts to drinking water resources or another local gas-producing interval were identified. See Text Box 6-3 for more information on the Greene County site.

Similarly, in Dunn County, North Dakota, there is evidence of out-of-zone fracturing in the Bakken Shale (U.S. EPA, 2015j). At the Killdeer site (see Section 6.2.2.1 and Chapter 5, Text Box 5-12), 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. Industry experience also indicates that out-of-zone fracturing may be fairly common in the Bakken and that produced water from many Bakken wells has Madison Group chemical signatures (Arkadakskiy and Rostron, 2013b, 2012b; Peterman et al., 2012).

Text Box 6-3. 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 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 vertical gas wells completed in Upper Devonian/Lower Mississippian zones 3,800 to 6,100 ft (1,158 to 1,859 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 will be necessary to confirm that no impacts to overlying zones have occurred (Zhang et al., 2014a).

Extreme vertical fracture growth 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 these thief zones may prevent fractures from reaching shallower formations or growing to extreme vertical lengths, it is important to note that they do allow fluids to migrate out of the production zone into these receiving formations, which could 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 the fractures are unlikely to extend into drinking water resources (Kim and Moridis, 2015).

Modeling studies have identified other factors that 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). Modeling and monitoring studies generally agree that physical constraints on fracture propagation will prevent induced fractures from extending from deep zones directly into drinking water resources (Kim and Moridis, 2015; Flewelling et al., 2013; Fisher and Warpinski, 2012).

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 ground water unit. Migration was assessed immediately after hydraulic fracturing and for up to a 2-year time period during the production stage. The potential migration pathway was assumed to be a permeable fracture or fault connecting the producing formation to the shallower ground water unit. Such a pathway may be either entirely hydraulically induced (due to fracture overgrowth in a case where the separation distance is limited, as discussed below), or may be a smaller induced fracture connecting to a natural, permeable fault or fracture (as discussed in Section 6.3.2.4). For the purposes of this study, the pathway was assumed to be pre-existing, and Reagan et al. (2015) did not model the fracturing process itself.

The subsurface system evaluated in the modeling investigation included a horizontal well used for hydraulic fracturing and gas production, the connecting fracture or fault between the producing formation and the aquifer, and a shallow vertical water well in the aquifer (see Figure 6-5). The parameters and scenarios used in the study are shown in Table 6-3; 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. Over-pressurization during hydraulic fracturing may create an additional driving force for upward migration. Results of this investigation, which represents a typical production period, indicate a generally downward water flow within the connecting fracture (from the aquifer through the connecting fracture into the hydraulically induced fractures in the production zone) and some upward migration of gas (Reagan et al., 2015). In certain cases, gas breakthrough (i.e., 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, driving the fluid migration toward the production well, was occurring in the reservoir. Simulations including a producing gas well showed only a few instances of breakthrough, while simulations without gas production tended to result in breakthrough; these 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 available for migration in hydraulically induced fractures prior to production.

Table 6-3. 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 6-5, Figure 6-6, and Figure 6-7 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
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)

Based on the results of the Reagan et al. (2015) 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. In contrast, Reagan et al. (2015) found 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 producing gas well, the gas may 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 for 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 amount of migrating gas depended upon the permeability of the connecting feature: the higher the permeability, the larger the amount. The 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 their assessment.

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 injected fluids or displaced subsurface fluids move through newly created fractures into an offset well or its fracture network, resulting in well communication (Jackson et al., 2013c). This may be a concern, particularly in shallower formations where the local least principal stress is vertical (resulting in more horizontal fracture propagation) and where there are shallow drinking water wells in the same formation.

The offset well can be an abandoned, inactive, or active well; if the well has also been used for hydraulic fracturing, the fracture networks of the two wells might intersect. The situation where hydraulic fractures unintentionally propagate into other existing, producing 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). Figure 6-6 provides a schematic to illustrate fractures that intercept an offset well, and Figure 6-7 depicts how the fracture networks of two wells can intersect.

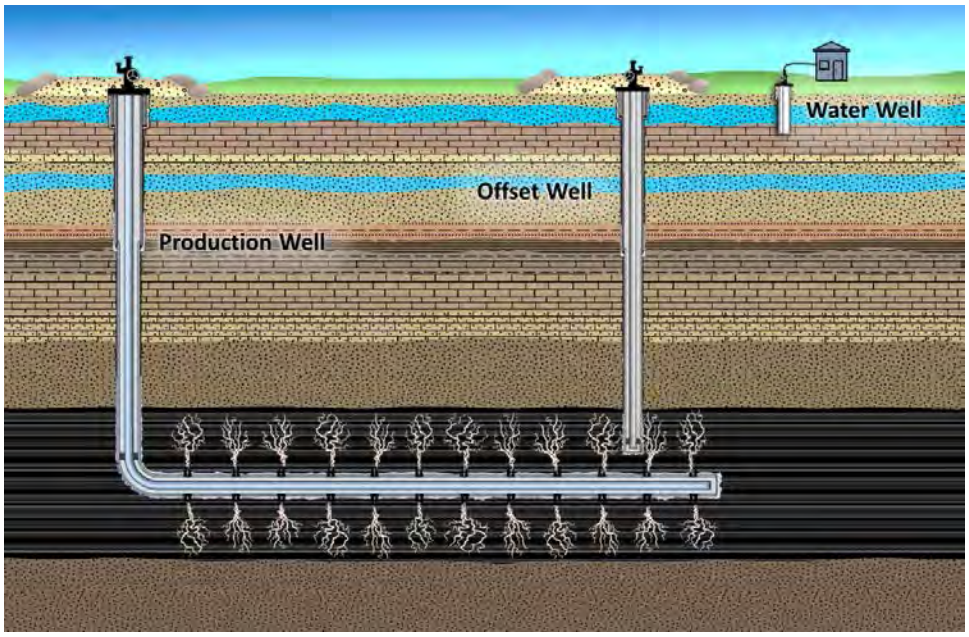

Figure 6-6. Induced fractures intersecting an offset well (in a production zone, as shown, or in overlying formations into which fracture growth may have occurred).

This image shows a conceptualized depiction of potential pathways for fluid movement out of the production zone (not to scale).

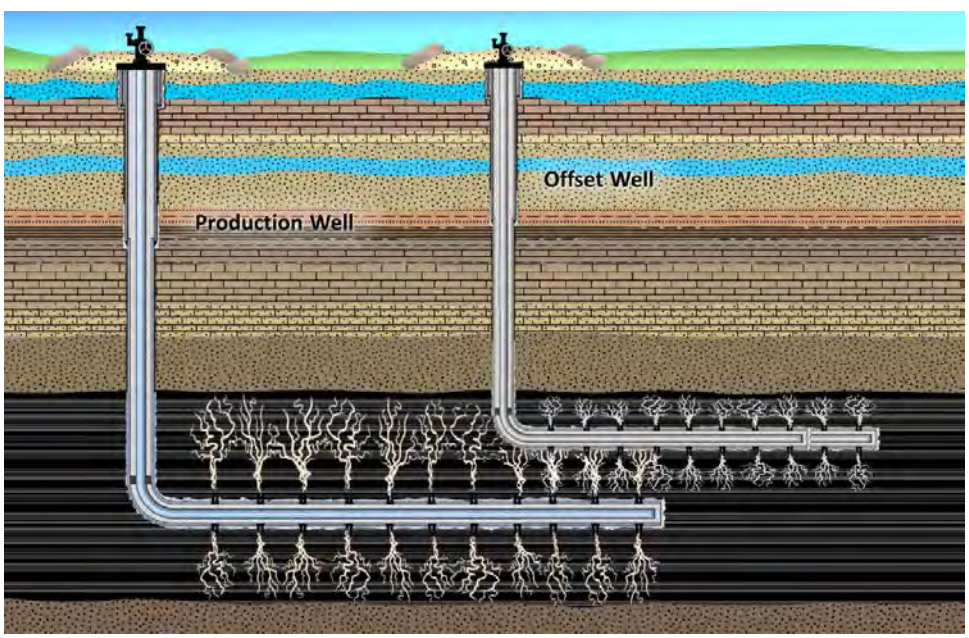

Figure 6-7. Well communication (a frac hit) via induced fractures intersecting another well or its fracture network.

This image shows a conceptualized depiction of potential pathways for fluid movement out of the production zone (not to scale).

Instances of well communication have been known to occur and are described in 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 (Vaidyanathan, 2014). In some cases, well communication incidents have led to documented production and/or environmental problems. A study from the Barnett Shale noted two cases of well communication, one with a well 1,100 ft (335 m) away and the other with a well 2,500 ft (762 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. The EPA (2015n) recorded 10 incidents in which fluid spills were attributed to well communication events (see Chapter 7 for more information).[1] The subsurface effects of frac hits have not been extensively studied, but these cases demonstrate the possibility of fluid migration via communication with other wells and/or their fracture networks. More generally, well communication events may indicate fracture behavior that was not intended by the treatment design.

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 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 (2,414 m), measured 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.[2]

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, 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 (305 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

[1] Line numbers 163, 236, 265, 271, 286, 287, 375, 376, 377, and 380 in Appendix B of U.S. EPA (2015n).
[2] The numbers of wells cited in the study reflect separate analyses, and the numbers cited are not additive.

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 (1,219 m) apart, but rose to nearly 50% in wells less than 1,000 ft (305 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.

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 (see Table 6-2), hydraulic fracturing treatments tend to enter portions of the reservoir that have already been fractured as 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 may 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 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 may occur during a well communication event. However, if the offset well is not able to withstand the pressure of the fracturing fluid, well components may fail, allowing fluid to migrate out of the well. The highest pressures most wells will face during their life spans occur during fracturing. 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 may 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, 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 (see Text Box 6-4) 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 any formations that are uncemented along the wellbore.

Text Box 6-4. Well Communication at a Horizontal Well near Innisfail, Alberta, Canada.

In most cases, well communication during fracturing may only result in a pressure surge accompanied by a drop in gas production and additional flow of produced water or 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 an estimated 19,816 gallons (75 m^3) of fracturing fluid, brine, gas, 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. 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 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.

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. 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 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 natural gas migration had been caused by well communication events with old, abandoned wells (PA DEP,

2009b). The Interstate Oil and Gas Compact Commission (IOGCC, 2008) estimates that over 1 million wells may have been drilled in the United States prior to a formal regulatory system, and the status and location of many of these wells are unknown. Various state programs exist to plug identified orphaned wells, but they face the challenge of identifying and addressing a large number of wells.[1] For example, 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 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).

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 ground water unit (see Section 6.3.2.2). In 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.) More specifically, this analysis was designed to assess transport through deteriorating cement between the subsurface formations and the outermost casing, through voids resulting from incomplete cement coverage, through breached tubing, or in simpler well installations without multiple casings. 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 the previous section, the study investigated the effect of multiple well- and formation-related variables on potential fluid migration (see Table 6-3).

Based on the simulation results, an offset well pathway may have a greater potential for gas release from the production zone into a shallower ground water unit than the fault/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; the offset well pathway may have a significantly lower pore volume compared to the fault/fracture pathway, which reduces possible gas storage in the connecting feature and increases the speed of buoyancy-dependent migration. However, as with the fault/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. Therefore, any incidents of gas breakthrough observed in this study were found to be limited in both duration and magnitude.

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 fault/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

[1] An orphaned well is an inactive oil or gas well with no known (or financially solvent) owner.

available for upward migration and creating a pressure gradient toward the production well. Only scenarios without the mitigating feature of gas production result in any 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 gas well is operating. The producing formation and aquifer permeabilities appear not to be significant factors for upward gas migration via this pathway. In addition, Reagan et al. (2015) found the permeability of the connecting offset well to be one of the main factors affecting the migration of gas to the aquifer and the water well. Very low permeabilities (less than 1 mD) lead to no migration of gas into the aquifer regardless of the vertical separation distance, whereas larger permeabilities present a greater potential for gas breakthrough.

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 28,000 abandoned mines in the United States and is adding new mines to its inventory every year (BLM, 2013a). 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, 2015o). The analysis suggests that emplacing cement within such zones may 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 fault or fracture zones in conjunction with hydraulic fracturing has been recognized as a potential contamination hazard for several decades (Harrison, 1983). 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 natural "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 may allow for more significant flow pathways for migration of fluids out of the production zone (Jackson et al., 2013c; Myers, 2012a). Figure 6-4 illustrates the concept of induced fractures intersecting with natural faults or fractures extending out of the target reservoir.

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., Weng et al., 2011; Dahi Taleghani and Olson, 2009; Vulgamore et al., 2007). Small natural fractures, known as "microfractures," could affect fluid flow patterns near the induced fractures by increasing the effective contact area. Conversely, the natural microfractures could act as capillary traps for the fracturing fluid during treatment (contributing to fluid leakoff) and potentially hinder hydrocarbon flow due to lower gas relative permeabilities (Dahi Taleghani et al., 2013). Rutledge and Phillips (2003) suggested that, for a hydraulic fracturing operation in East Texas, pressurizing existing fractures (rather than creating new hydraulic fractures) may be the primary process that controls

enhanced permeability and fracture network conductivity at the site. Ciezobka and Salehi (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. However, there is very little attention given in the literature to studying unintended fluid migration during hydraulic fracturing operations due to existing microfractures.

In some areas, larger-scale geologic features may affect potential fluid flow pathways. As discussed in Text Box 6-2, baseline measurements taken before shale gas development show evidence of thermogenic methane in some shallow aquifers, suggesting that natural subsurface pathways exist and allow for naturally occurring migration of gas over millions of years (Robertson et al., 2012). There is also evidence demonstrating that gas undergoes mixing in 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). 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 hydraulic fractures. When faults are present, relatively larger microseismic responses are seen and larger fracture growth can occur, as described below. Concentrated 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 (Ciezobka and Salehi, 2013).

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 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 can extend laterally for thousands of feet.) In the Fisher and Warpinski (2012) data set (see 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 (see Section 6.3.2.2 and Text Box 6-3). The authors suggested that clusters of microseismic events may have occurred where preexisting small faults or natural fractures were present above the Marcellus Shale. At a site in Ohio, Skoumal et al. (2015) found that hydraulic fracturing induced a rupture along a pre-existing fault approximately 0.6 miles (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 miles (1 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. Myers (2012a, 2012b) found that a highly conductive fault could result in rapid (<1 year) fluid migration from a deep shale zone to the surface (as described in Section 6.3.2.1). Other researchers reject the notion that open, permeable faults would coexist with hydrocarbon accumulation (Flewelling et al., 2013), although it is unclear whether the existence of faults in low permeability reservoirs would affect the accumulation of hydrocarbons because, under natural conditions, the flow of gas may be limited due to capillary tension. Results from another recent modeling study suggest that, under specific circumstances, interaction with a conductive fault could result in fluid migration to the surface only on longer (ca. 1,000 year) time scales (Gassiat et al., 2013). Rutqvist et al. (2013) found that, while somewhat larger microseismic events are possible in the presence of faults, repeated events and aseismic 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 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 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).

Other conditions in addition to the physical presence of a pathway would need to exist for fluid migration to a drinking water resource to occur. The modeling study conducted by (Reagan et al., 2015) 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 natural and well-based factors may increase the potential for fluid migration into drinking water resources. For example, in the Mamm Creek area of Colorado (see Section 6.2.2.2), well integrity and drilling-related problems likely acted in concert with natural fracture systems to result in a gas seep into surface water and shallow ground water (Crescent, 2011).

6.4. Synthesis

In the injection stage of hydraulic fracturing, operators inject fracturing fluids into a well under high pressure. These fluids flow through the well and into the surrounding formation, where they

increase pore pressure and create fractures in the rock, allowing hydrocarbons to flow through the fractures and up the well.

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 drinking water 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 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

Potential pathways for impacts on drinking water (i.e., the movement of hydrocarbons, formation brines, or other fracturing-related fluids into drinking water resources), may be linked to one or more components of the well and/or features of the subsurface system. If present, these potential pathways can, in combination with the high pressures under which fluids are injected and pressure changes within the subsurface, have an impact on 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 the development of one pathway within this system does not necessarily result in an impact to a drinking water resource. For example, if cracks were to form in the cement of a well, the vertical distance between the production zone and a drinking water resource (and the multiple layers of rock in between) could isolate and protect the drinking water aquifer if pressures were insufficient to allow fluid movement to the level of the drinking water resource. Conversely, if an undetected fault were present in a rock formation, intact cement within the production well could keep fluids from migrating up along the well to the fault and protect drinking water resources.

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. These higher stresses may contribute to the formation of potential pathways associated with the casing or cement that can result in the unintentional movement of fluids through the production wellbore if the well cannot withstand the stresses experienced during hydraulic fracturing operations (see Section 6.2).

Multiple barriers within the well, including casing, cement, and a completion assembly, isolate hydrocarbon-bearing formations from drinking water resources. However, inadequate construction, defects in or degradation of the casing or cement, or the absence of redundancies such as multiple layers of casing, can allow fluid movement, which can then affect the quality of drinking water resources. Ensuring proper well design and mechanical integrity—particularly proper

cement placement and quality—are important actions for preventing unintended fluid migration along the wellbore.

6.4.1.2. Fluid Movement within Subsurface Geologic Formations

Potential subsurface pathways for fluid migration 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 fractures intersecting with faults or natural fractures (see Section 6.3).

Vertical separation between the production zone where hydraulic fracturing operations occur and drinking water resources, and lateral separation between wells undergoing hydraulic fracturing and other wells can reduce the potential for fluid migration that can impact drinking water resources.

Well communication incidents or "frac hits" have been reported in New Mexico, Oklahoma, and other locations. While some operators design fracturing treatments to communicate with the fractures of another well and optimize production, unintended communication between two fracture systems can lead to spills in the offset well and is an indicator of hydraulic fracturing treatments extending beyond their planned design. Surface spills from well communication incidents have been documented in the literature, which provides evidence for occurrence of frac hits. Based on the available information, frac hits most commonly occur on multi-well pads and when wells are spaced less than 1,100 ft (335 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 an impact on drinking water resources associated with hydraulic fracturing operations in Bainbridge, Ohio. Failure to cement over-pressured formations through which the production well passed—and proceeding with the 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 (see Section 6.2.2.2).

Casings at a production well near Killdeer, North Dakota, ruptured 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 wells was the well that ruptured. There is also evidence that out-of-zone fracturing occurred at the well (see Sections 6.2.2.1 and 6.3.2.2).

There are other cases where hydraulic fracturing could be a contributing cause to impacts on drinking water resources, or where the specific mechanism that led to an impact on a drinking water resource cannot be definitively determined. For example:

- Migration of stray gas into drinking water resources involves many potential routes for migration of natural gas, including poorly constructed casing and naturally existing or

induced fractures in subsurface formations. Multiple pathways for fluid movement may be working in concert in northeastern Pennsylvania (possibly due to cement issues or sustained casing pressure) and the Raton Basin in Colorado (where fluid migration may have occurred along natural rock features or faulty well seals). 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 (see Text Box 6-2).

- 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 well stimulation, can work together to create a pathway for fluids to migrate toward drinking water resources (see Sections 6.2.2.2 and 6.3.2.4).

Additionally, some hydraulic fracturing operations involve the injection of fluids into formations where there is relatively limited vertical separation from drinking water resources. The EPA identified an estimated 4,600 wells that were located in areas with less than 2,000 ft (610 m) of vertical separation between the fractures and the base of protected ground water resources.

There are places in the subsurface where oil and gas reservoirs and drinking water resources co-exist in the same formation. Evidence we examined suggests that some hydraulic fracturing for oil and gas occurs within formations where the ground water has a salinity of less than 10,000 mg/L TDS. By definition, this results in the introduction of fracturing fluids into formations that meet the Safe Drinking Water Act (SDWA) salinity-based definition of a 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.

The practice of injecting fracturing fluids into a formation that also contains a drinking water resource directly affects the quality of that water, since it is likely some of that fluid remains in the formation following hydraulic fracturing. 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 drinking water contamination. Data limitations in most of those cases (including the unavailability of information in litigation settlements resulting in sealed documents) make it impossible to definitively assess whether or not hydraulic fracturing was a cause of the contamination in these cases.

6.4.2. Factors Affecting Frequency and Severity of Impacts

Proper cementing across oil-, gas-, or water-bearing zones prevents the movement of brines, gas, or hydraulic fracturing fluids along the well into drinking water resources. The likelihood of contamination is reduced when the well is fully cemented across these zones; however, this is not

the case in all hydraulically fractured wells, either because the cement does not extend completely through the base of the drinking water resource or the cement that is present is not of adequate quality. Fully cemented surface casing that extends through the base of drinking water resources is a key protective component of the well. Most, but not all, wells used in hydraulic fracturing operations have fully cemented surface casing.

Deviated and horizontal wells, which are increasingly being used in hydraulic fracturing operations, may exhibit more casing and cement problems compared to vertical wells. Sustained casing pressure—a buildup of pressure within the well annulus that can indicate the presence of small leaks—occurs more frequently in deviated and horizontal wells compared to vertical wells. Cement integrity problems can also arise as a result of challenges in placing cement in these wells, because they are more challenging than vertical wells to center properly.

Older wells may exhibit more integrity problems compared to newer wells, which may be an issue if older wells are hydraulically fractured or re-fractured. Degradation of the casing and cement as they age or the cumulative effects of stresses exerted on the well over time may result in changes in well integrity. Integrity problems can also be associated with the inadequate design of wells that were constructed pursuant to older, less stringent requirements. Well components that are subject to corrosive environments, high pressures, or other stressors tend to have more problems than wells without these additional stressors.

The extent of subsurface fluid migration within subsurface rock formations and the potential for the development of pathways that can adversely affect drinking water depend on site-specific characteristics. These include the physical separation between the production zone and drinking water resources, the geological and geomechanical characteristics of the formations, hydraulic fracturing operational parameters, and the physical characteristics of any connecting feature (e.g., abandoned wells, faults, and natural fractures).

As noted above, vertical separation between the production zone and drinking water resources protects drinking water. Additionally, the proximity of wells undergoing hydraulic fracturing to other wells increases the potential for the formation of pathways for fluids to move via these wells to drinking water resources. For example, if there is a deficiency in the construction of a nearby well (or degradation of the well components), that well could serve as a pathway for movement of fracturing fluids, methane, or brines that might affect a drinking water resource. If the fractures were to intersect an uncemented portion of a nearby wellbore, the fluids could migrate along that wellbore into any uncemented formations.

Fractures created during hydraulic fracturing can extend out of the target production zone. Out-of-zone fracturing could be a concern for fluid migration if the hydraulic fracturing operation is not designed to address site-specific conditions, for example if the production zone is thin and fractures propagate to unintended vertical heights, or if the production zone is not horizontally continuous and fractures extend to unintended horizontal lengths. The presence of natural faults or fractures can affect the extent of hydraulic fractures. When faults are present, relatively larger microseismic responses are seen during hydraulic fracturing, and larger fracture growth can occur than in the

absence of natural faults or fractures. However, modeling studies indicate that fluid migration from deep production zones to shallow drinking water resources along natural faults and fractures or offset wells is unlikely. These studies indicate that, in both cases, gas available for migration is limited to the amount that existed in the fractures and pore space of connecting features following hydraulic fracturing prior to production. Following the completion of a hydraulic fracturing treatment, depressurization of the production formation surrounding the fractures due to hydrocarbon production would make upward fluid migration into drinking water resources unlikely to occur.

Based on the information presented in this chapter, the increased deployment of hydraulic fracturing associated with oil and gas production activities, including techniques such as horizontal drilling and multi-well pads, may increase the likelihood that these pathways could develop. This, in turn, could lead to increased opportunities for impacts on drinking water resources.

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 can be observed and measured at the surface. Furthermore, while there is a significant amount of information available on production wells in general, there is little information that is specific to hydraulic fracturing operations and much of this data is not readily accessible, i.e., in a centralized, national database.

6.4.3.1. Limited Availability of Information Specific to Hydraulic Fracturing Operations

There is extensive information 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, based on the long history of oil and gas production activities, we know how production wells are constructed and have performed over time. Over the years, many studies have documented how these wells are constructed, how they perform, and the rates at which they experience problems that can lead to the formation of pathways for fluid movement. However, because we do not know which of these wells were hydraulically fractured, we cannot definitively determine whether the rates at which integrity problems arise (or other data pertaining to oil and gas wells in general) directly correspond 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 resources 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 meet 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, including MIT

results, 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 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.

There are also a limited number of published monitoring studies or sampling data that provide evidence to assess whether formation brines, injected 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 in the subsurface 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 2).

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.

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 integrity problems that can contribute to 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 states or 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 also no systematic collection, reporting, or publishing of empirical baseline (pre-drilling and/or pre-fracturing) and post-fracturing monitoring data 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. Ideally, data from ground water monitoring are needed to complement theories and modeling on potential pathways and fluid migration.

While some of the types of impacts described above may occur quickly (i.e., on the scale of days or weeks, as with integrity problems or well communication events), other impacts (e.g., in slow-moving, deep ground waters) may only occur or be able to be detected on much longer timescales. Given the surge in the number of modern high-pressure hydraulic fracturing operations dating from the early 2000s, evidence of any fracturing-related fluid migration affecting a drinking water

resource (as well as the information necessary to connect specific well operation practices to a drinking water impact) could take years to discover.

The limited amount of information hinders our ability to evaluate whether—or how frequently—drinking water impacts are occurring (or the potential for these impacts to occur) or to tie possible impacts to specific well construction, operation, or 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 or suspected contamination in areas where hydraulic fracturing occurs.

6.4.4. Conclusions

Fluids can migrate from the wellbore and surrounding subsurface formations due to inadequate casing or cement, and via natural and man-made faults, fractures, and offset wells or mines (see Text Box 6-5). To prevent fluid migration through the wellbore or through subsurface pathways, wells must have adequate casing and cement, and induced fractures must not intersect existing fractures or permeable zones that lead to drinking water resources. Evidence shows that the quality of drinking water resources may have been affected by hydraulic fracturing fluids escaping the wellbore and surrounding formation in certain areas, although conclusive evidence is currently limited.

Text Box 6-5. Research Questions Revisited.

How effective are current well construction practices at containing fluids—both liquids and gases—before, during, and after fracturing?

- Wells that were designed with uncemented intervals of casing across porous or permeable zones, wells in which cementing does not resist formation or operational stresses, and wells in which cementing does not meet design specifications have the potential to promote unintended subsurface fluid movement. Even in optimally designed wells, metal casings and cement can degrade over time, either as a result of aging or of exposure to stresses exerted over years of operations. See Section 6.2.2.2.
- We have limited information on the degree to which wells are designed and constructed with the multiple layers of casing that can withstand hydraulic fracturing pressures and contact with injected and produced fluids. We also are lacking information about whether wells have suitable cements that can prevent fluid movement outside the wellbore and between the production zone and drinking water resources. We also do not have information on the degree to which mechanical integrity is verified before or after hydraulic fracturing operations. See Section 6.2.2.1.

Can subsurface migration of fluids—both liquids and gases—to drinking water resources occur and what local geologic or artificial features might allow this?

- The presence of artificial penetrations, especially poorly constructed offset wells or undetected abandoned wells, mines, or other subsurface structures, provides pathways that, in the presence of a driving force, could allow for fluid movement to shallow geologic zones such as drinking water resources. See Section 6.3.2.3.

- Intersections of induced fractures with transmissive faults or naturally occurring fractures or porous/permeable rock zones can allow fluids to move out of the targeted fracture areas. However, modeling studies indicate that fluid migration from production zones to drinking water resources along natural faults and fractures is unlikely. See Section 6.3.2.4.
- Some hydraulic fracturing operations involve the injection of fluids into formations where there is relatively limited vertical separation from drinking water resources. Other hydraulic fracturing is performed within formations that meet the SDWA or state salinity-based definition of a source of drinking water, in addition to the broader definition of a drinking water resource developed for this assessment. See Section 6.3.2.

6.5. References for Chapter 6

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Chapter 7

Flowback and Produced Water

7. Flowback and Produced Water

7.1. Introduction

Water is a byproduct of oil and gas production. After hydraulic fracturing is completed, either in its entirety or for a specified stage, the operator reduces the injection pressure. Water is allowed to flow back from the well to prepare for oil or gas production. This return-flow water may contain chemicals injected as part of the hydraulic fracturing fluid, chemicals characteristic of the formation, hydrocarbons, and in-formation reaction and degradation products. Initially this water, called flowback, is mostly fracturing fluid, but as time goes on, it becomes more similar to the formation water. For formations containing saline water (brine), the salinity of the water increases as time passes, marking the increased contact time with the formation and in some cases the flow of formation water itself. This later stage water is called produced water, a term which can also refer to flowback and produced water collectively.

Flowback and produced water are stored and accumulated at the surface for eventual reuse or disposal. Typical storage facilities include open air impoundments and closed containers such as those shown in Figure 1-1. Produced water is collected and may be taken to disposal wells, recyclers, wastewater treatment plants, or in some cases the water may be left in pits to evaporate or infiltrate. Flowback and produced water leaks can occur on the well pad as a result of human error, failure of container integrity, equipment failure, communication between wells, pipeline leaks, and blowouts.[1] Above-ground piping systems can connect multiple well pads to impoundments, and piping or impoundments may leak. Much produced water is transported by truck, and pad incidents leading to spills of produced water can occur when trucks are filled. On-road accidents are also possible, some of which could release produced water loads to the environment.

Impacts to drinking water resources can occur if spilled flowback or produced water enters surface water bodies or aquifers. Environmental transport of chemical constituents depends on the characteristics of the spill, the fluid (e.g., density, as for highly saline water), the chemicals, and the environment. Attenuation processes (e.g., dilution, biodegradation of organics) in surface water and aquifers tend to reduce concentrations.

We begin this chapter with a review of definitions for flowback and produced water. We then discuss typical volumes of flowback and produced water on a per-well basis. This information is aggregated to the state and basin level in Chapter 8. The characteristics of hydraulically fractured shale, tight, and coalbed methane (CBM) formations are described. Spatial and temporal trends on composition of produced water are illustrated with examples from the literature and data compiled for this report. The processes controlling the chemical composition of produced water are described in Appendix E. The potential for impacts on drinking water resources of flowback and produced water are described based on reported spill incidents, contaminant transport principles, and field study examples. The chapter concludes with a discussion of uncertainties and knowledge

[1] For discussion of well communication, see Chapter 6.

gaps, factors that influence the severity of impacts, and a synthesis based on the EPA research questions.

7.1.1. Definitions

Multiple definitions exist for the terms flowback and produced water. These differing definitions indicate challenges in determining the distinctions between the two terms or indicate that different usage of the terms routinely occurs among various industry, private, and public groups. However, the majority of produced water definitions are fundamentally similar. The following definition is used in this report: water that flows from oil or gas wells.

This definition is similar to the definition used by the American Petroleum Institute (API): "Produced water is any of the many types of water produced from oil and gas wells" (API, 2010b); the definition used by the Department of Energy (DOE): "Produced water is water trapped in underground formations that is brought to the surface along with oil or gas" (DOE, 2004), and a similar definition used by the American Water Works Association (AWWA): "Produced water is the combination of flowback and formation water that returns to the surface along with the oil and natural gas" (AWWA, 2013). Produced water can variously refer to formation water, a mixture of spent hydraulic fracturing fluid and formation water or returned hydraulic fracturing fluid. Thus the term produced water is used when a distinction between fracturing fluid and formation water is not necessary.

In general, the term flowback refers either to fluids predominantly containing hydraulic fracturing fluid that returns to the surface or to a process used to prepare the well for production. Because formation water can contact and mix with injection fluids, the distinction between returning hydraulic fracturing fluid and formation water is not clear. In the early stages of operation, however, a higher concentration of chemical additives is expected and later, water that is typical of the formation (Stewart, 2013a). In most cases, a precise distinction between these waters is not determined during operations.

Various definitions have been used for the term flowback. The American Petroleum Institute defined flowback as "the fracture fluids that return to the surface after a hydraulic fracture is completed," (API, 2010b) and the American Water Works Association used "fracturing fluids that return to the surface through the wellbore after hydraulic fracturing is complete" (AWWA, 2013). Other definitions include production of hydrocarbons from the well (Barbot et al., 2013; U.S. EPA, 2012f), or a time period (USGS, 2014f; Haluszczak et al., 2013; Warner et al., 2013b; Hayes and Severin, 2012a; Hayes, 2009). As mentioned above, flowback can also be defined as a process used to stimulate the well for production by allowing excess liquids and proppant to return to the surface. Because we use existing literature in our review, we do not introduce a preferred definition of flowback, but rather we mention the assumptions used by the author(s) we discuss.

7.1. Volume of Hydraulic Fracturing Flowback and Produced Water

The characteristics and volume of flowback and produced water vary by well, formation, and time. 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.

The amount of flowback from a well varies and depends on several types of factors, including: production, formation, and operational. Production factors include the amount of fluid injected, type of hydrocarbon produced (gas or liquid), and location within the formation. Formation factors include the formation pressure, interaction between the formation and injected fluid (capillary forces) and reactions within the reservoir. Operational factors include loss of mechanical integrity and subsurface communication between wells (U.S. GAO, 2012; Byrnes, 2011; DOE, 2011a; GWPC and ALL Consulting, 2009; Reynolds and Kiker, 2003). The latter two factors might be indicated by an unexpected increase in water production (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. Second is an unforced imbibition following stimulation where the fluid redistributes within the reservoir rock, due to capillary forces, when the well is shut-in. The last phase consists of flow out of the formation when the well is opened and pressure reduced in the borehole and fractures. The purpose of this phase is to recover as much of the injected fluid as possible (Byrnes, 2011) in order to reduce high water saturations at the fracture face and eventually allow higher 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 effective permeability of the reservoir, capillary pressure properties of the reservoir rock, the pressure near the fracture faces, and whether the well is flowing or shut in.[1] The well can be shut in for varying time periods depending on operator scheduling, surface facility construction or hookup, or other reasons.

7.1.1. Flowback of Injected Hydraulic Fracturing Fluid

Generally, the fluid that initially returns to the surface has been attributed to a mixture of the injected fracturing fluid, its transformation products, and the natural formation water. In some cases, as shown below, 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 an adjacent formation (Arkadakskiy and Rostron, 2013a). Several authors used geochemical analyses to postulate mixing between formation water and injected fluid in the Marcellus Shale (Engle and Rowan, 2014; Barbot et al., 2013; Haluszczak et al., 2013); Rowan et al., 2015). These possible explanations are summarized in a following section (see Section 7.6.4). Salinity increases in flowback from highly saline formations, so it is not possible to specify precisely the amount of injected fluids that return in the flowback (GWPC and ALL Consulting, 2009). Rather, such estimates relate the amount of produced water measured at a given time after fracturing as a percentage of the total amount of injected fluid.

Estimates vary but in composite indicate on average that between 5% and 75% (see Table 7-1, Table 7-2, and Table 7-3) of the volume of injected fracturing fluid may flow back to the surface

[1] 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.

after hydraulic fracturing is complete (U.S. EPA, 2015q; Vengosh et al., 2014; Mantell, 2013b; Vidic et al., 2013; Minnich, 2011; Xu et al., 2011). These data (see Table 7-1) illustrate that the formations differ in their water requirements for hydraulic fracturing and generation of produced water over the short term.[1] Low percentages of flowback are typical, as is the decrease of flowback volume with time as the wells enter the production phase (Gregory et al., 2011; McElreath, 2011; GWPC and ALL Consulting, 2009). Some formations produce higher volumes, as noted for the Barnett Shale in Texas (Nicot et al., 2014) and discussed below.

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 (Mantell, 2013b).

Formation	Approx. total average water use per well (million gal)	Produced water 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
Cleveland/Tonkaw	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.

[1] Flowback estimates may be based on specific time periods (e.g., the flowback during the first 10, 15, or 30 days).

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
Mid duration			
WV—Marcellus	8%	Hansen et al. (2013)	30 days
Marcellus Shale	24%	Hayes (2011, 2009)	Average from 19 wells, 90 days
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 and long-term produced water characteristics for wells in unconventional formations (U.S. EPA, 2015e).

Source: (U.S. EPA, 2015q).

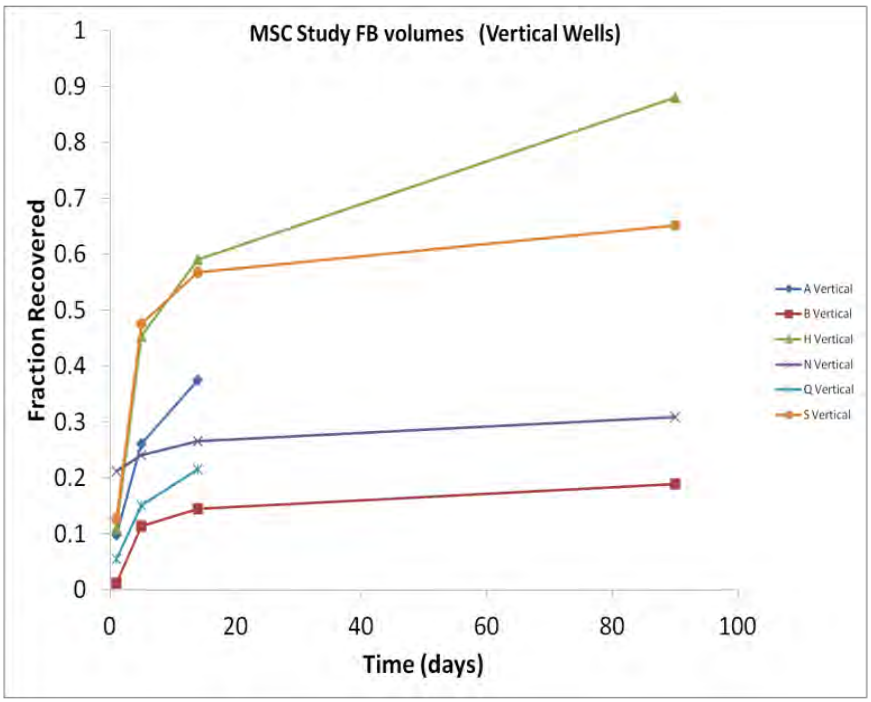
Resource type	Drill type	Fracturing fluid (million gal)			Flowback (percent of fracturing fluid returned)		
		Median	Range	Number of data points	Median	Range	Number of data points
Shale	Horizontal	4.0	0.13–15	50,053	6%	1% – 50%	6,488
	Directional	1.6	0.051–12	124	14%	4% – 31%	19
	Vertical	1.2	0.015–22	4,152	24%	7% – 75%	18
Tight	Horizontal	2.2	0.042–9.4	765	7%	7% – 60%	39
	Directional	0.60	0.056–4.0	693	6%	0% – 60%	263
	Vertical	0.31	0.019–4.0	1,287	8%	1% – 83%	48
Long-term produced water (gal/day per well)							
Shale	Horizontal	900	0–19,000	22,222			
	Directional	480	22–8,700	695			
	Vertical	380	0–4,600	12,393			
Tight	Horizontal	620	0–120,000	2,394			
	Directional	750	12–1,800	3,816			
	Vertical	570	0–4,000	21,393			

In the following subsections, we first discuss water produced during the flowback period, then longer-term produced water.

7.1.1.1. Produced Water during the Flowback Period

Data were collected from six vertical and eight horizontal wells in the Marcellus Shale of Pennsylvania and West Virginia (Hayes, 2009). The author collected samples of flowback after one,

five, and 14 days after hydraulic fracturing was completed, as well as a produced water sample 90 days after completion of the wells. Both the vertical and horizontal wells showed their largest volume of flowback between one and five days after fracturing, as shown in Figure 7-1. The wells continued to produce water, and at 90 days, samples were available from four each of the horizontal and vertical wells. The vertical wells produced on average 180 bbl/day (7,600 gal/day or 29,000 L/day) and the horizontal wells a similar 200 bbl/day (8,400 gal/day or 32,000 L/day). Results from one Marcellus Shale study were fitted to a power curve, as shown in Figure 7-2 (Ziemkiewicz et al., 2014). These and the Hayes (2009) data show decreasing flowback with time.



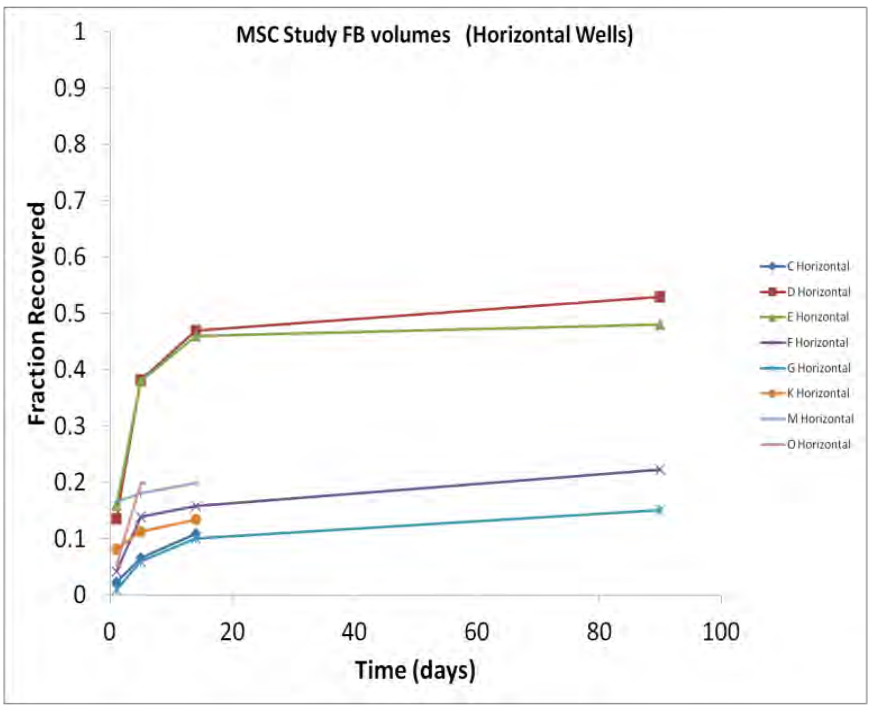


Figure 7-1. Fraction of injected hydraulic fracturing fluid recovered from six vertical (top) and eight horizontal (bottom) wells completed in the Marcellus Shale.

Data from Hayes (2009).

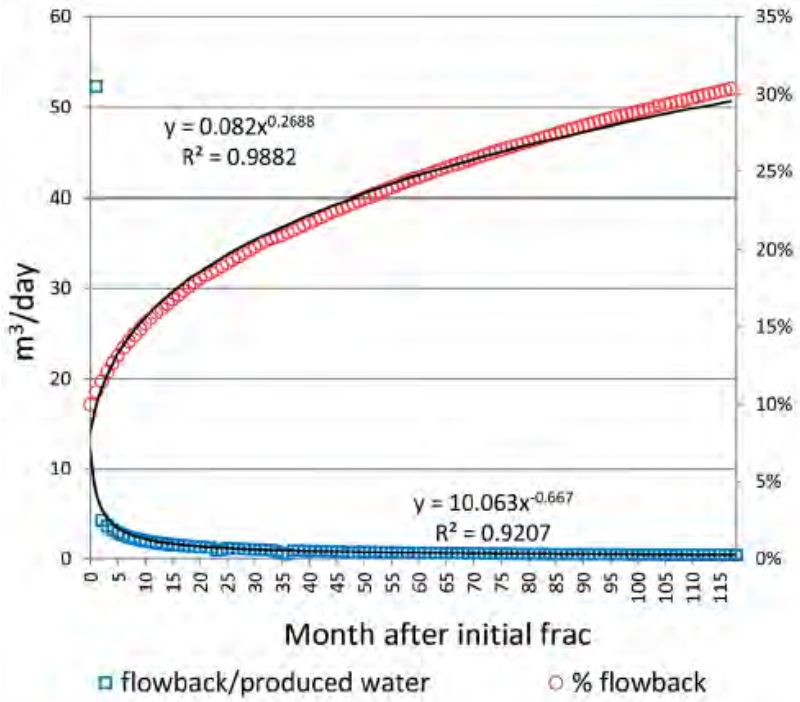


Figure 7-2. Example of flowback and produced water from the Marcellus Shale, illustrating rapid decline in water production and cumulative return of approximately 30% of the volume of injected fluid.

Source: Ziemkiewicz et al. (2014). Reprinted with permission from Ziemkiewicz, P; Quaranta, JD; Mccawley, M. (2014). Practical measures for reducing the risk of environmental contamination in shale energy production. Environmental Science: Processes & Impacts 16: 1692-1699. Reproduced by permission of The Royal Society of Chemistry. http://dx.doil.org/10.1039/C3EM00510K.

In West Virginia, water recovered at the surface within 30 days following injection or before 50% of the injected fluid volume is returned to the surface is reported as flowback. Data from 271 wells in the Marcellus Shale in West Virginia (Hansen et al., 2013) reveals the variability of recovery from wells in the same formation and that the amount of injected fluid recovered was less than 15% from over 80% of the wells (see Figure 7-3).

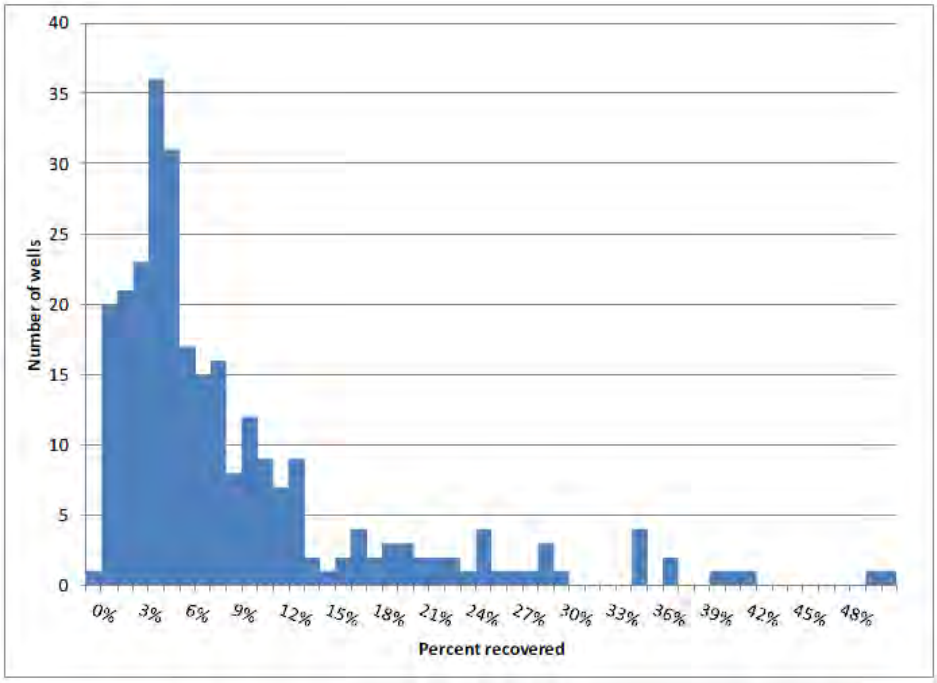


Figure 7-3. Percent of injected fluid recovered for Marcellus Shale wells in West Virginia (2010–2012).

Source: Hansen et al. (2013). One data point showing 98% recovery omitted. Reprinted with permission from Hansen, E; Mulvaney, D; Betcher, M. (2013). Water resource reporting and water footprint from Marcellus Shale development in West Virginia and Pennsylvania. Durango, CO: Earthworks Oil & Gas Accountability Project. Copyright 2013. Permission Downstream Strategies, San Jose State University, and Earthworks Oil & Gas Accountability Project.

The amount of flowback water produced by wells within the first few days of fracturing varies from formation to formation. Wells in the Mississippi Lime and Permian Basin can produce 10 million gal (37.8 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; while Haynesville wells produce less, about 350,000 gal (1.32 million L) (Mantell, 2013b).

7.1.2. Produced Water

During oil and gas production, other fluids which contain water are produced with hydrocarbons. Throughout this production phase at oil and certain wet gas production facilities, produced water is stored in tanks and pits that may contain free phase, dissolved phase, and emulsified crude oil in the produced water.[1] This crude oil can be present in the produced water container or pit, because the crude oil is not efficiently separated out by the flow-through process vessels (such as three-phase separators, heater treaters, or gun barrels) and passes through to these containers/pits. The

[1] Dry natural gas occurs in the absence of liquid hydrocarbons; wet natural gas typically contains less than 85% methane along with ethane and more complex hydrocarbons (Schlumberger, 2014).

produced water containers and pits containing oil at production facilities are typically regulated under 40 CFR part 112, produced water containers or pits may also be subject to other applicable state and or local laws, regulations and/or ordinances.

Lutz et al. (2013) evaluated data reported to the Pennsylvania Department of Environmental Protection (PA DEP) for the time period January 2000 to December 2011. The data were divided between conventional gas wells that might have been hydraulically fractured and hydraulically fractured completions in the Marcellus Shale. The conventional wells produced less drilling water, less flowback (when fractured), and less brine than the shale wells (Lutz et al., 2013; see Table 1). The average amount of produced water per well was 136,000 gal (514,000 L) for the conventional wells and 1.38 million gal (5.211 million L) for the shale wells. The produced water to gas ratio was 1.27 gal (4.8 L) water per MMBtu for the shale wells, which was 2.8 times lower than for conventional wells. Both the produced water and gas produced per well decreased over the four-year period covered by the study. In contrast, conventional oil wells tend to have increased volumes of produced water as they age, and in some cases, older wells may produce five times as much water as new wells (U.S. GAO, 2012).

From experience in several shale formations, Mantell (2013b, 2011) characterized the amount of produced water over the long term as high, moderate, or low. 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 because of formation characteristics. The most productive of these can be as high as 5,000 gal (19,000 L) per MMCF. As a specific example, a high-producing formation in the western United States was described as producing 4,200 gal (16,000 L) per MMCF 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.

Similarly, produced water from horizontal wells in the Barnett Shale decreased rapidly after the wells began producing gas (Nicot et al., 2014) (see Figure 7-4). The data show a high degree of variability, which was attributed by Nicot et al. (2014) to a few wells with exceptionally high water production. When the produced water data were presented as the percentage of injected fluid, the median exceeded 100% at around 36 months, and the 90th percentile was 350% (see Figure 7-5). This means that roughly 50% of the wells were producing more water than was used in stimulating production. Nicot et al. (2014) noted an inverse relationship between gas and water production but did not identify the source or mechanism for the excess water. Systematic breaching of the underlying karstic Ellenburger Formation was not believed likely; nor was operator efficiency or skill. A number of geologic factors that could impact water migration were identified by (DOE, 2011a) in the Barnett Shale, including fracture height, aperture size, and density, fracture mineralization, the presence of karst chimneys underlying parts of the Barnett Shale, and others, but the impact of these on water migration was undetermined.

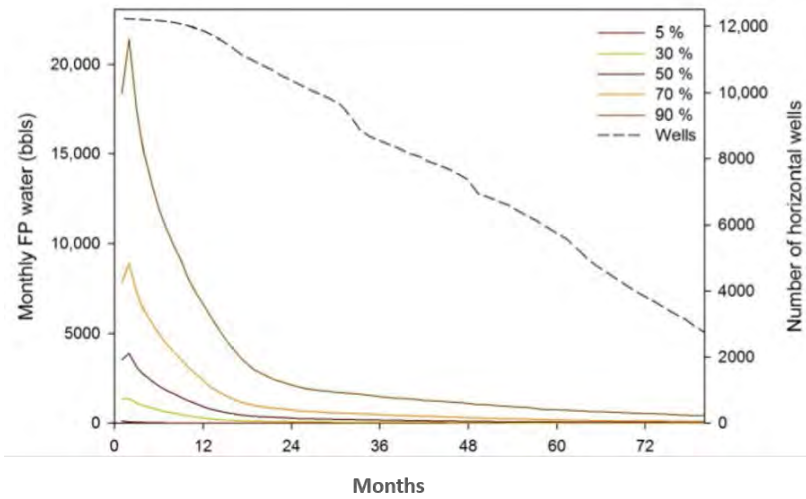


Figure 7-4. Barnett Shale monthly water-production percentiles (5th, 30th, 50th, 70th, and 90th) and number of wells with data (dashed line).

Source: Nicot et al. (2014). FP is the amount of water the flows back to the surface, commingled with water from the formation. Reprinted with permission from Nicot, JP; Scanlon, BR; Reedy, RC; Costley, RA. (2014). Source and fate of hydraulic fracturing water in the Barnett Shale: a historical perspective. Environ Sci Technol 48: 2464-2471. Copyright 2014 American Chemical Society.

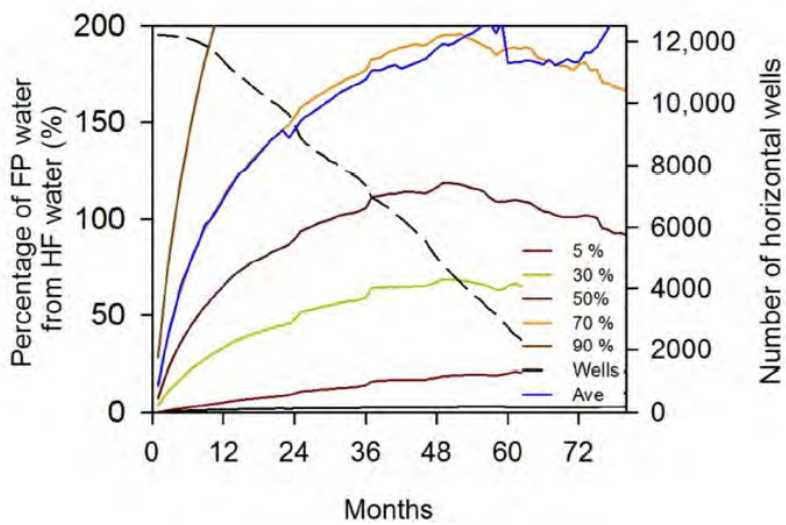


Figure 7-5. Barnett Shale production data for approximately 72 months.

Source: Nicot et al. (2014). Flowback and produced water are reported as the percentage of injected fluid. The dashed line shows the number of horizontal wells included. Data for each percentile show declining production with time, but the median production exceeds 100% of the injected fluid. FP is the amount of water the flows back to the surface, commingled with water from the formation. Reprinted with permission from Nicot, JP; Scanlon, BR; Reedy, RC; Costley, RA. (2014). Source and fate of hydraulic fracturing water in the Barnett Shale: a historical perspective. Environ Sci Technol 48: 2464-2471. Copyright 2014 American Chemical Society.

The Niobrara, Granite Wash, Eagle Ford, Haynesville, and Fayetteville Shales are relatively dry and produce between 200 and 2,000 gal (760 to 7,600 L) of produced water per MMCF (Mantell, 2013). The Utica and Marcellus Shales are viewed as drier and produce less than 200 gal (760 L) per MMCF. DOE (2011a) 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 Chapter 6). For dry formations, low shale permeability and high capillarity cause water to imbibe into the formation, where it is retained permanently (He, 2011). Engelder (2012) estimated that more than half of the fracturing fluid could be captured within the Marcellus if imbibition drove fluid just 5 cm (2 in) deep into reservoir rocks across the fracture surfaces. This estimate is in agreement with the generalized analysis presented by Byrnes (2011), who estimated depths of 5 to 15 cm (2 to 6 in).

After fracture of coalbeds, water is withdrawn to liberate gas. CBM tends to produce large volumes of water early on: more in fact, than conventional gas-bearing formations (U.S. GAO, 2012). Within producing formations, water production can vary for unknown reasons (U.S. GAO, 2012). Data show that CBM production in the Powder River Basin produces 16 times more water than in the San Juan Basin (U.S. GAO, 2012).

The EPA (2015q) reported characteristics of long-term produced water for shale and tight formations (see Table 7-3). For shale, horizontal wells produced more water (900 gal/day) than vertical wells (380 gal/day). Typically, this would be attributed to the longer length of horizontal laterals than vertical wells, but the data were not normalized to these lengths. The formation-level data used to develop Table 7-3 appear in Table E-1 of Appendix E.

The EPA (2015q) reported that a general rule of thumb is that flowback occurring in the first 30 days of production is roughly equal to the long-term produced water for unconventional formations. As a specific example, from Pennsylvania Marcellus Shale data, the EPA determined that for vertical wells in unconventional formations, 6% of water came from drilling, 35% from flowback, and 59% from long-term produced water; and for horizontal wells the corresponding numbers were 9%, 33%, and 58%. These values deviate from the rule of thumb, because the Marcellus Shale was believed to generate low levels of flowback relative to other formations (U.S. EPA, 2015q).

7.2. Flowback and Produced Water Data Sources

Unlike the evaluation of hydraulic fracturing fluid itself where the chemical composition may be disclosed, knowledge concerning flowback and produced water composition comes from measurements made on samples.

A number of factors are involved in the proper sampling and analyzing of environmental media (U.S. EPA, 2013e; ATSDR, 2005; U.S. EPA, 1992). There may be significant issues obtaining samples, because the specialized equipment used to contain high-pressure natural gas is not designed for producing environmental samples (Coleman, 2011).

To choose the correct analytical methods, it is necessary to have information on:

- Physical state of the sample.
- Identification of analytes of interest.
- Required sensitivity and quantitation limits.
- Analytical objective (i.e., unknown identification, monitoring).
- Required sample containers, preservation, and holding times.

Because some components of hydraulic fracturing fluid are proprietary chemicals, and subsurface reaction products may be unknown, prior knowledge of the identity of analytes may not be available. Consequently, studies may be limited in their ability to determine the presence of either unknown or proprietary constituents contained in flowback or produced water simply because of the lack of knowledge of the identities of the constituents.

After laboratory analysis, the results are evaluated according to quality criteria. Data may be judged to meet applicable quality criteria as determined by the analytical methods or they may be "flagged." Typically, encountered flags are non-detect, below reporting limit or diluted to meet calibration requirements or because of matrix interference (e.g., Hayes, 2009).[1] For produced water, a primary interference is from high total dissolved solids (TDS). Interferences also arise from agents which cause foaming and alter surface tension (Coleman, 2011). Diluted samples result in higher detection limits, and thus lessen ability to identify lower concentrations in samples.

Because of identified limitations in existing methods, the EPA developed new methods for some reported components of hydraulic fracturing fluids, including ethanols and glycols (U.S. EPA, 2014k), certain nonionic surfactants (DeArmond and DiGoregorio, 2013a), and acrylamide (DeArmond and DiGoregorio, 2013b).[2,3] Each of these methods are applicable to ground and surface waters, and the last (DeArmond and DiGoregorio, 2013b) to waters with TDS well above 20,000 mg/L.

Generally, analytical methods are impacted by elevated TDS and chloride concentrations, especially inorganic and wet chemistry methods (Nelson et al., 2014; U.S. EPA, 2014b; Coleman, 2011). Matrix interference impacts standard analysis (EPA Method 8015) for glycols, resulting in high detection limits (10,000 μg/L to 50,000 μg/L) (Coleman, 2011).

Produced water levels of naturally occurring radionuclides may be 1,000 to 10,000 times the levels of activity found in typical environmental water samples (U.S. EPA, 2014b). The standard EPA method (Method 900.0) for gross alpha and gross beta involves evaporation of the sample to a layer of residue and analyzing emitted alpha and beta particles. The method has several noted

[1] Matrix interference occurs when components of the sample other than the analyte of interest have an effect on a measurement (IUPAC, 2014).
[2] The compounds included were: Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, 2-Butoxyethanol and 2-Methoxyethanol.
[3] The compounds included were: C12-C16 and C18 alcohol ethoxylates, and alkylphenol ethoxylates.

limitations, including known under representation of radium 228, and applicability to drinking water samples with low levels (<500 mg/L) of TDS. As discussed below, produced water can have much higher TDS levels. Because of these limitations, the EPA (2014b) developed an updated method for the detection of gross alpha and gross beta to reduce the matrix interferences, although further improvement is possible.[1]

Due to the high ionic strength and dissolved solids concentration of flowback water from shale operations, Nelson et al. (2014) similarly found that traditional wet chemistry techniques (EPA Methods 903.0 and 904.0) inefficiently recover radium from samples, with radium-226 recovery sometimes less than 1% . This concern, which could lead to false negatives, was previously noted by Demorest and Wallace (1992). Nelson and coauthors demonstrated that an accurate assessment of flowback radium levels can be performed through nondestructive high-purity germanium gamma spectroscopy and emanation techniques. Studies reporting radium concentrations obtained directly via wet chemistry techniques or studies reporting third-party radium data via wet chemistry techniques may need to be evaluated appropriately as these techniques may underestimate the total radium loads of produced water (Nelson et al., 2014).

Data have been generated from specific produced water studies (e.g., Hayes, 2009) or compilations from various sources, such as the USGS produced water database developed in 2002 (Breit, 2002) and updated in 2014 (Blondes et al., 2014). In this database, data were compiled from a variety of sources, some of which we cite as examples below. The data that appear in this chapter and Appendix E are drawn individually from scientific literature and published reports, where necessary we have filled gaps with data from the USGS database.

7.3. Background on Formation Characteristics

Subsurface processes and resulting flowback and produced water composition vary depending upon the mineralogy, geochemistry, and structure of formation solids, as well as, residence time and other factors (Dahm et al., 2011; Blauch et al., 2009). The mineralogy and structure of formation solids are determined initially by deposition, when rock grains settle out of their transporting medium (Marshak, 2004). Generally, shale results from clays deposited in deep, oxygen-poor marine environments, and sandstone results from sand deposited in shallow marine environments (Ali et al., 2010; U.S. EPA, 2004). Coal forms when carbon-rich plant matter collects in shallow peat swamps. In the United States, coal is formed in both freshwater and marine environments (NRC, 2010). In the northern Rocky Mountains, coal formed within freshwater alluvial systems of streams, lakes, and peat swamps. In contrast are parts of the Black Warrior formation, which were deposited in brackish and marine settings (Horsey, 1981).

Variation in produced water composition follows, in part, from differences in formations which are related to geologic processes. After deposition, physical, chemical, and biological processes occur as

[1] The method developed for determining gross alpha (Th, U, and Po) by liquid scintillation is based on: manganese dioxide coprecipitation followed by group separation of thorium, uranium and polonium on TRU Resin, stripping with ammonium bioxalate, and pulse-shape discrimination liquid scintillation analysis. The average recovery was 74±11% of the known concentration of 230Th with recoveries which ranged from 57% to 104%.

sediments and are consolidated and cemented into rocks in a process called diagenesis. These processes, which can also occur in existing sedimentary rocks, are caused by increased pressure, temperature, and reaction with mineral-rich ground water (Rushing et al., 2013; Marshak, 2004). Diagenesis may either decrease or increase porosity and permeability through sediment compaction and mineral precipitation, or through grain and cement dissolution (Ali et al., 2010; Schmidt and McDonald, 1979). Temperature and pressure greatly affect the types and extent of subsurface reactions, influencing the solubility of formation solids, saturation of pore waters, and prevalence of precipitates (Rushing et al., 2013).

7.4. Flowback Composition

The composition of returning hydraulic fracturing fluid changes with increasing residence time. In this section, we present several examples from individual wells which demonstrate how concentrations approach apparently asymptotic values during the first few days or weeks after hydraulic fracturing.

7.4.1. General Characteristics

Several interacting factors that influence the composition of hydraulic fracturing flowback and produced water are recognized in the scientific literature: (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).

By design, hydraulic fracturing exposes fresh, organic- and mineral-rich surfaces. Subsurface interactions between injected hydraulic fracturing fluids, formation solids, and formation waters follow. As residence time increases, allowing in situ interactions between injected fluids, formation fluids, and formation solids, changes in the geochemical content of flowback occur such that it still largely reflects that of injected fluids, while later flowback and produced water reflect that of formation-associated fluid (Rowan et al., 2011).

7.4.2. Temporal Changes in Flowback Composition

Ionic loads, metals, naturally occurring radioactive material (NORM), and organics increase in concentration as water production continues (Barbot et al., 2013; Murali Mohan et al., 2013; Rowan et al., 2011). 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. Multiple geochemical studies confirm this trend (Barbot et al., 2013; Haluszczak et al., 2013; Chapman et al., 2012; Davis et al., 2012; Gregory et al., 2011; Blauch et al., 2009).

Concurrent precipitation of sulfates (e.g., $BaSO_4$) and carbonates (e.g., $CaCO_3$) alongside decreases in pH, alkalinity, and dissolved carbon load occur over time (Orem et al., 2014; Barbot et al., 2013; Blauch et al., 2009; Brinck and Frost, 2007). Orem and colleagues showed that organics within CBM produced waters also decrease over time, possibly due to the exhausting of coal-associated waters through formation pumping (Orem et al., 2007). Decreases in microbial abundance and diversity also occur over time after hydraulic fracturing (Murali Mohan et al., 2013; Davis et al., 2012).

The primary dissolution of native and emplaced salts within the formation and the mobilization of in situ brines constitute the major subsurface processes that control TDS levels in flowback and produced water (Dresel and Rose, 2010; Blauch et al., 2009).[1] Leaching of organics appears to be a result of injected and formation fluids associating with shale and coal strata (Orem et al., 2014).

7.4.3. Total Dissolved Solids Enrichment

To varying degrees, produced water is enriched in dissolved solids, and the enrichment is dependent upon residence time (Rowan et al., 2011). As an example, TDS concentrations increased until a limit was reached in flowback and produced water samples from four Marcellus Shale gas wells in three southwestern Pennsylvanian counties (Chapman et al., 2012) (see Figure 7-6). As is shown in Figure 7-7, TDS in flowback from both Westmoreland County wells became consistent with TDS concentrations cited for typical seawater (35,000 mg/L) within three days, and became consistent with TDS cited for brines (greater than 50,000 mg/L) within five days (Chapman et al., 2012). TDS concentrations during production exceeded 188,000 mg/L for one well in Greene County. Chapman et al.'s findings are further substantiated by Hayes and colleagues' earlier report of produced water TDS concentrations in 19 Marcellus Shale wells in Pennsylvania and West Virginia (Hayes, 2009). From an initial injected median value of less than 1,000 mg/L, TDS concentrations increased to a median value exceeding 200,000 mg/L within 90 days (Hayes, 2009). In the Marcellus Shale, the cation portion of TDS is typically dominated by sodium and calcium, whereas the anion portion is dominated by chloride (Chapman et al., 2012; Blauch et al., 2009). In section 7.6.4, we note that there is disagreement over whether increased salinity in Marcellus Shale produced water is due to dissolution of salts or mixing of formation water with hydraulic fracturing fluid.

[1] Native salts are formed inside the rock matrix, and can include evaporite minerals such as halite (NaCl), polyhalite ($K_2Ca_2Mg(SO_4)^4 \bullet 2H_2O$), celestite ($SrSO_4$), anhydrite ($CaSO_4$), kieserite ($MgSO_4 \bullet H_2O$), or sylvite (KCl) (Blauch et al., 2009). Hydrologic intrusion emplaces salts within formation pores and fractures (Blauch et al., 2009).

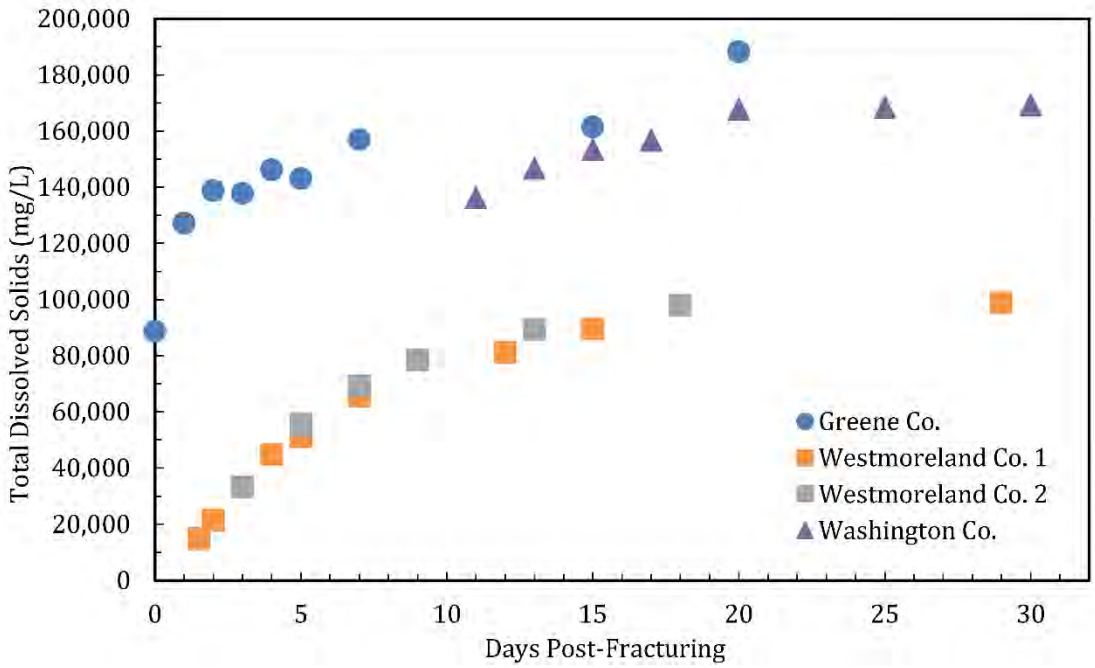


Figure 7-6. TDS concentrations measured through time for injected fluid (at 0 days), flowback, and produced water samples from four Marcellus Shale gas wells in three southwestern Pennsylvanian counties.

Data from Chapman et al. (2012).

7.4.4. Radionuclide Enrichment

Injected fluids used in hydraulic fracturing typically do not contain radioactive material (Rowan et al., 2011).[1] Shales and sandstones, however, are naturally enriched in various radionuclides, as described below (Sturchio et al., 2001). Radium in pore waters or adsorbed onto clay particles and grain coatings can dissolve and return within flowback (Langmuir and Riese, 1985). Where data are available, radium and TDS produced water concentrations are positively correlated with time passed since hydraulic fracturing (Rowan et al., 2011; Fisher, 1998). Radium remains adsorbed to mineral surfaces in low saline environments, and then desorbs with increased salinity into solution (Sturchio et al., 2001). Over the course of 20 days, Marcellus Shale produced waters from a gas well were enriched almost fourfold in radium and from another gas well were enriched over twofold in TDS concentrations as residence time increased (Chapman et al., 2012; Rowan et al., 2011) (see Figure 7-7).

[1] Recycling produced water may introduce radioactive material into hydraulic fracturing fluid. See section 8.4.3 and PA DEP (2015b).

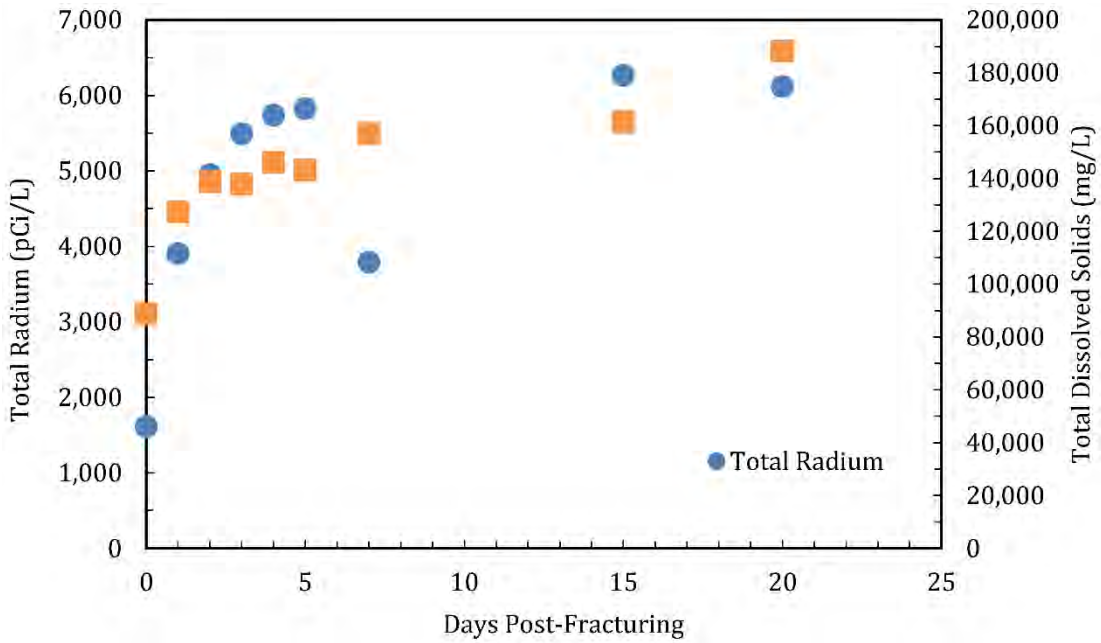


Figure 7-7. Total radium and TDS concentrations measured through time for injected (day 0), flowback, and produced water samples from mutually exclusive Greene County, PA, Marcellus Shale gas wells.

Data from Rowan et al. (2011) and Chapman et al. (2012).

7.4.5. Leaching and Biotransformation of Naturally Occurring Organic Compounds

Many organics are known to leach naturally into formation water through association with shale, sandstone, and coal strata (Benko and Drewes, 2008; Orem et al., 2007). Orem et al. (2014) show that formation and produced waters from shale plays that were not impacted by production chemicals contain an array of organic compound classes associated with the formation. When unconventional formations are hydraulically fractured, additional organics from the freshly fractured hydrocarbon-bearing formation and the chemical additives contribute to a large increase in flowback and produced water organic loads (Orem et al., 2014).

The nature of the in-situ hydrocarbons reflects the formation's thermal maturity and heavily influences the organic content of the produced water.[1] The Marcellus Shale is largely considered a mature formation and therefore consists of wet and dry gas (Barbot et al., 2013; Repetski et al., 2008). Conversely, the Utica Shale is less thermally mature; available hydrocarbon resources consist of oil, condensate, and gas (Repetski et al., 2008). Additionally, some coals within the eastern and west-central regions of the San Juan Basin produce little to no water during production, due to the regional thermal maturity, hydrostratigraphy, and in situ trapping mechanisms (New Mexico Bureau of Mines and Mineral Resources, 1994).

[1] With increasing subsurface temperature after burial, petroleum source material (kerogen) produces hydrocarbons in a sequence from methane (immature), to oil (more mature), to gas (mature). Gas is produced by thermal cracking of oil (PA DCNR, 2015).

Dissolved organic carbon (DOC) concentrations decrease from hydraulic fracturing through flowback in shales and coalbeds (Murali Mohan et al., 2013; Orem et al., 2007). DOC sorption, dilution with injected or formation water, biochemical reactions, and microbial transformation (i.e., biotransformation in the form of degradation or uptake) may all cause decreased concentrations of DOC during flowback. Organic chemical additives injected during hydraulic fracturing offer a novel carbon and energy source for biotic and abiotic reactions at depth. Injected organics include many sugar-based polymer formulations, most notably of galactose and mannose (i.e., guar gum used as a gelling agent); hydrocarbon distillates used in crosslinkers, friction reducers, and gelling agents; and ethyl and ether glycol formulations used in non-emulsifiers, crosslinkers, friction reducers, and gelling agents. (Wuchter et al., 2013; Arthur et al., 2009b; Hayes, 2009).

DOC and chloride concentrations exhibit strongly correlated inverse temporal trends (Barbot et al., 2013; Chapman et al., 2012) for flowback and produced water samples obtained from three Marcellus Shale wells from the same well pad in Greene County, Pennsylvania (Cluff et al., 2014), as shown in Figure 7-8. Chloride concentrations increased five- to six-fold as a function of residence time (i.e., cumulative volumes of produced water). These chloride concentrations followed an increasing linear trend during the first two weeks of flowback (see Figure 7-8a, inset) then began to approach asymptotic levels later in production, indicating that injected fluids had acquired a brine signature as a result of subsurface mixing, fluid-solid interactions, and mineral dissolution processes.

DOC concentrations exhibit an inverse trend and decreased through flowback and production (Figure 7-8b) (Cluff et al., 2014). DOC levels decreased approximately twofold between injected fluid and initial flowback samples (Figure 7-8b, inset). DOC concentrations decreased by 11-fold over the study's time frame (nearly 11 months) and leveled off several months after hydraulic fracturing, presumably as a result of in situ attenuation processes (Cluff et al., 2014).

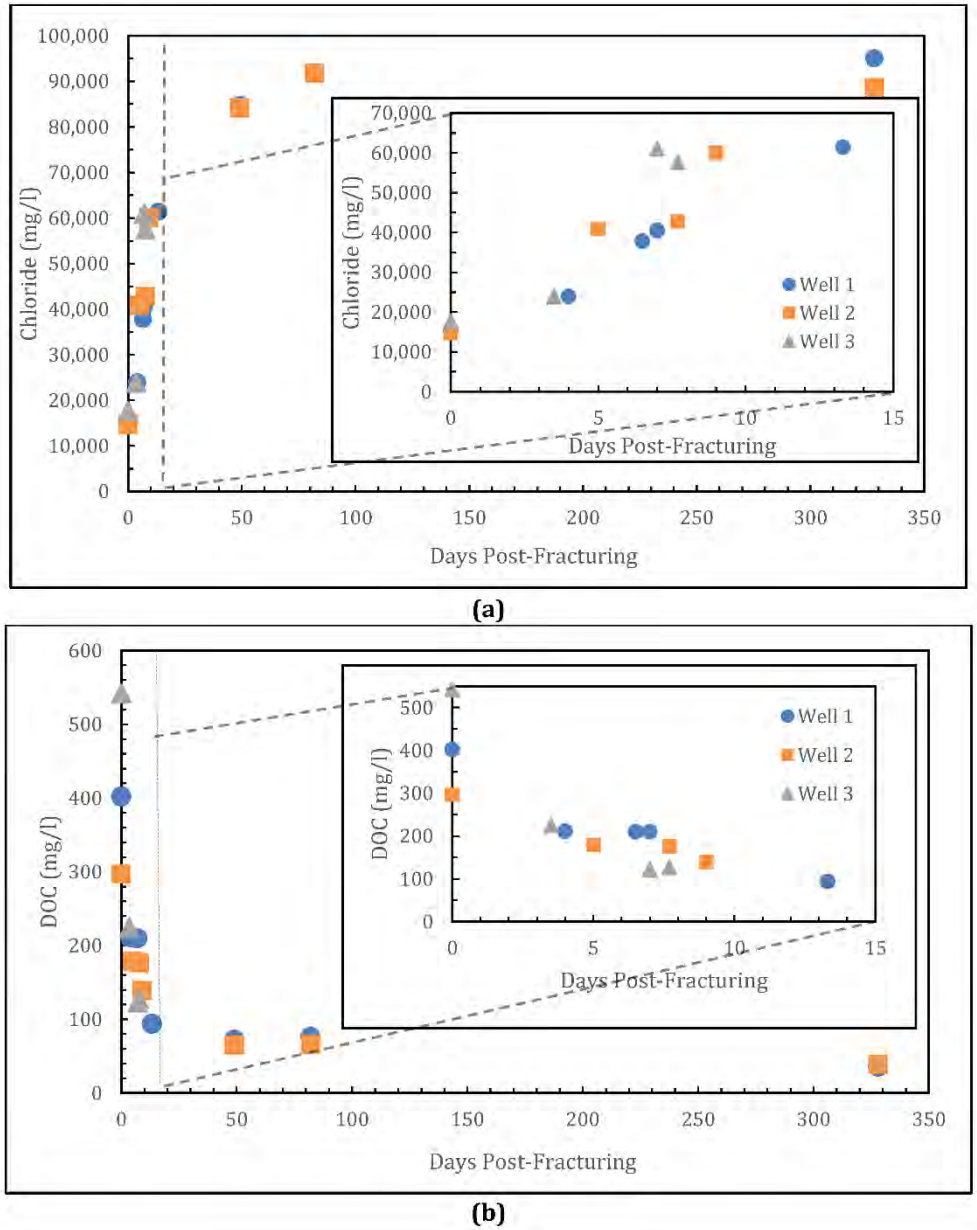


Figure 7-8. (a) Chloride (Cl) and (b) DOC concentrations measured through time for injected (day 0), flowback, and produced water samples obtained from three Marcellus Shale gas wells from a single well pad in Greene County, PA used for hydraulic fracturing.

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.

Orem et al. (2014) conducted a temporal study of two coalbed wells over the course of one year. Their results suggest that organic compound concentrations decrease over time. This trend may be due to pumping of water to the surface, which may exhaust coal-associated produced water. Subsequent produced water would not be associated with the coal. This suggests that the early produced water would contain the highest organic load (Orem et al., 2014).

As noted above, most literature addresses general organic parameters such as bulk total organic carbon (TOC) or DOC instead of individual organic compounds (Sirivedhin and Dallbauman, 2004). Emphasis on the prevalence of bulk organics as opposed to unique organics is due largely to the lack of analytical standards for many compounds and also a lack of knowledge regarding the types of organics to test in produced water samples (Schlegel et al., 2013; Strong et al., 2013).

7.5. Produced Water Composition

In this section, we discuss the characteristics of aggregated produced water data without regard for temporal changes. Similarities between conventional and unconventional produced water are noted and the variability between formation types is described. As we discuss below, produced water may contain a range of constituents, but in widely varying amounts. Generally, these may include:

- Salts, including those composed from chloride, bromide, sulfate, sodium, magnesium and calcium.
- Metals including barium, manganese, iron, and strontium.
- Dissolved organics including BTEX and oil and grease.
- Radioactive materials including radium (radium-226 and radium-228).
- Hydraulic fracturing chemicals and their transformation products.

We discuss these groups of chemicals and then conclude by discussing variability within formation types and within production zones.

7.5.1. Similarity of Produced Water from Conventional and Unconventional Formations

Unconventional produced water is reported to be similar to conventional produced waters 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 salinity varies in shales and tight formations, produced water is typically characterized as saline (Lee and Neff, 2011; Blauch et al., 2009). Produced water is also enriched in major anions (e.g., chloride, bicarbonate, sulfate), cations (e.g., sodium, calcium, magnesium), metals (e.g., barium, strontium), naturally occurring radionuclides (e.g., radium-226 and radium-228) (Chapman et al., 2012; Rowan et al., 2011), and organics (e.g., hydrocarbons) (Orem et al., 2007; Sirivedhin and Dallbauman, 2004).

7.5.2. Variability in Produced Water Composition Among Unconventional Formation Types

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 7-4, Alley et al. (2011) found that of the constituents of interest common to all three types of unconventional produced water (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).

Table 7-4. Compiled minimum and maximum concentrations for various geochemical constituents in unconventional shale gas, tight gas, and CBM produced water (Alley et al., 2011).

Source: (Alley et al., 2011).

Parameter	Unit	Shale gas[a]	Tight gas[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
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

Parameter	Unit	Shale gas[a]	Tight gas[b]	CBM[c]
Bromine	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
Chlorine	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.

Shale gas produced water tends to be more acidic, as well as, enriched in strontium, barium, and bromide. CBM produced water is highly 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]

7.5.3. General Water Quality Parameters

For this assessment, the EPA identified data characterizing the content of unconventional flowback and produced water in a total of 12 shale and tight formations and CBM basins. These formations and basins span 18 states. Note that in this subsection we treat all fluids as produced. As a consequence, the variability of reported concentrations is likely higher than if the data could be standardized to a specific point on the flowback-to-produced water continuum.

For most formations, the amount of general water quality parameter data is variable (see Table E-2 of Appendix E). 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 formations and range from 213 microsiemens (µS)/cm in the Bakken Shale to 184,800 µS/cm in Devonian sandstones (see Table E-2 of Appendix E). 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.

Of the data presented in Table E-3 of Appendix E, 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 that contrast to the freshwater conditions for the western basins.

The average dissolved oxygen (DO) concentrations of CBM produced water range from 0.39-1.07 mg/L (see Table E-3 Appendix E). By comparison, well-oxygenated surface water can contain up to 10 mg/L DO at 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 could contribute to aquatic organism stress (USGS, 2010; NSTC, 2000).

7.5.4. Salinity and Inorganics

The TDS profile of unconventional produced water 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). In order of relative abundance, the following inorganic ions are typically found in highly saline conventional produced water: sodium, chloride, calcium, magnesium, potassium, sulfate, bromide, strontium, bicarbonate, and iodide (Lee and Neff, 2011). Shale and sandstone produced water 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 flowback and produced water

[1] Several 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.

(Barbot et al., 2013; Haluszczak et al., 2013; Chapman et al., 2012). Data representing shales and tight formations are presented in Table E-4 of Appendix E.

Rowan et al. (2015) acknowledge that the origin of saline water produced from the Marcellus Shale is a matter of debate. One idea is that injected fluid returns at higher salinity, because of dissolving halite and other minerals found in shale (Blauch et al., 2009). Blauch and colleagues hypothesized that salt layers bearing barium, calcium, iron, potassium, magnesium, sodium, and strontium likely dissolve and contribute to flowback and produced water salinity (Blauch et al., 2009). However, actual mixing of formation water and fracturing fluid was postulated by Haluszczak et al. (2013) from arguments based on the near-neutral pH and low levels of chloride and sulfate in the Marcellus data from Hayes (2009), as well as, the relationship between chloride and bromide. Engle and Rowan determined that water chemistry during the first 90 days of production is controlled by mixing of injected and formation waters and stimulation of bacterial sulfate reduction (Engle and Rowan, 2014; Haluszczak et al., 2013). Rowan et al. (2015) argue, based on an observed shift to isotopically heavier water, that produced water actually contains formation water.[1] Alternately, Barbot et al. (2013) concluded from analysis of Marcellus Shale produced water that mixing (with formation water) alone could not explain the observed patterns in chloride concentrations.

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. The TDS concentration of CBM produced water can be as low as 500 mg/L ranging to nearly 50,000 mg/L (Dahm et al., 2011; Benko and Drewes, 2008; Van Voast, 2003). Lower dissolved solids are expected from CBM produced water, in part, because some coals developed in fresh water environments (Bouska, 1981). 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). In other cases, as for the Black Warrior basin, TDS can be higher along with concentrations of species that contribute to TDS (See Table E-5 Appendix E), such as calcium, chloride, and sodium.

7.5.5. Metals

The metals content of unconventional produced water varies by well and site lithology, but is typically dominated by the same metals that are associated with conventional produced water. Unconventional produced water may also contain low levels of heavy metals (e.g., chromium, copper, nickel, zinc, cadmium, lead, arsenic, and mercury) (Hayes, 2009). Data illustrating metal concentrations in produced water appear in Tables E-6 and E-7 of Appendix E.

[1] The produced water becomes isotopically heavier because of increased prevalence of Oxygen-18 in the water, compared to the more prevalent Oxygen-16.

7.5.6. Naturally Occurring Radioactive Material (NORM) and Technologically Enhanced Naturally Occurring Radioactive Material (TENORM)

7.5.6.1. Formation Solids Levels of NORM

Elevated uranium levels in formation solids have been used to identify potential areas of natural gas production for decades (Fertl and Chilingar, 1988). Marine black shales are estimated to contain an average of 15–60 ppm uranium depending on depositional conditions (Fertl and Chilingar, 1988). Shales that bear 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).

7.5.6.2. Produced Water Levels of TENORM

When exposed to the environment or concentrated NORM is termed technologically-enhanced naturally-occurring radioactive material (TENORM).[1] Radioactive materials commonly present in shale and sandstone sedimentary environments include uranium, thorium, radium, and their decay products. These are present in most unconventional produced water, but particularly so in Marcellus Shale produced water (Rowan et al., 2011; Fisher, 1998). Low levels of uranium and thorium return during flowback, typically in the concentrated form of mineral phases or organic matter, due to insolubility under prevailing reducing conditions encountered within shale formations (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). Dissolved radium primarily occurs as Ra^{2+}, but it complexes with carbonate, chloride, and sulfate ions as well (Sturchio et al., 2001; Langmuir and Riese, 1985). Ra^{2+} can also substitute for various cations (e.g., Ba^{2+}, Ca^{2+}, and Sr^{2+}) during mineral precipitation, as is sometimes the case with barite or anhydrite precipitation (Rowan et al., 2011).

Data from the Marcellus Shale show that radium and TDS produced water concentrations are positively correlated (Rowan et al., 2011; Fisher, 1998). This pattern is expected for other formations because radium remains adsorbed to mineral surfaces in low salinity environments, then desorbs as solution salinity increases (Sturchio et al., 2001). Controlling for this TDS dependence, Marcellus Shale produced water contains statistically more radium than non-Marcellus Shale produced water, with a median total radium content of 2,460 picocuries per liter (pCi/L) (n = 52) compared to 1,011 pCi/L (n = 91), respectively (Rowan et al., 2011). Radium levels in Marcellus produced water are at several thousand picocuries per liter, with maximum concentrations of total radium (radium-226 and radium-228), radium-226 and radium-228 reported at approximately 18,000, 9,000, and 1,300 pCi/L, respectively (Rowan et al., 2011) (see Table E-8 in Appendix E). Data from the Pennsylvania TENORM produced water study (PA DEP,

[1] The U.S. EPA Office of Radiation (http://www.epa.gov/radiation/tenorm/) states that technologically enhanced naturally occurring radioactive material (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 would contain NORM, because they are not exposed; produced water would contain TENORM because it has been exposed to the environment.

2015) showed similar elevated levels, and consistently showed higher medians in unconventional compared to conventional formations (Table E-8 in Appendix E).

7.5.7. Organics

The organic content of produced water varies by well and lithology, but consists of certain naturally occurring and injected organic compounds. These organics may be dissolved in water or, for the case of oil production, in the form of a separate or emulsified phase. Produced water organics can contain any of the following: (1) volatile organic compounds (VOCs) such as benzene and toluene, (2) semi-volatile organic compounds (SVOCs) such as phenols; and/or (3) non-VOCs such as macromolecular natural organic matter (Orem et al., 2014; Hayes, 2009; Benko and Drewes, 2008; Orem et al., 2007; Sirivedhin and Dallbauman, 2004). Table 7-5 presents data from naturally occurring organic chemicals in produced water.

Table 7-5. Concentration ranges (mg/L) of several classes of naturally occurring organic chemicals in conventional produced water worldwide (reported in Neff, 2002).

Source: (Neff, 2002)

Chemical class	Concentration range (mg/L)
TOC	≤0.1–>11,000
Total organic acids	≤0.001–10,000
Total saturated hydrocarbons	17–30
Total benzene, toluene, ethylbenzene, and xylenes (BTEX)	0.068–578
Total PAH	0.040–3
Total steranes/triterpanes	0.140–0.175
Ketones	1–2
Total phenols (primarily C_0–C_5 phenols)	0.400–23

Several classes of naturally occurring organic chemicals are present in conventional and unconventional produced waters, with large concentration ranges (Lee and Neff, 2011). In addition to data on total organic carbon (TOC) and dissolved organic carbon (DOC) as indicators of the presence of organics, specifically identified organics include saturated hydrocarbons, BTEX, and polycyclic aromatic hydrocarbon (PAHs) (see Table E-9 of Appendix E). Data are lacking on the presence and concentration of many other types of organic chemicals that might be present in produced water, because of their use in hydraulic fracturing fluid. There are a number of reasons for this difference, some of which could be related to analytical limitations, limited focus of produced water studies, and undocumented subsurface reactions.

7.5.8. 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

flowback and produced water. These changes can result from physical processes (e.g., rock fracturing and fluid mixing) and geochemical processes (e.g., introducing novel, oxygenated fluids) 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 targeted for unconventional 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. The storage or release of these elements in newly exposed surfaces is variable and not well studied, in part due to the vast number of possible interactions occurring continuously in the environment at the rock surface (Vine and Tourtelot, 1970).

Contact with and physical mixing of hydraulic fracturing fluids with existing formation brines also influences the geochemical evolution of produced water. For instance, Marcellus Shale brines have high concentrations of bromide, calcium, chloride, magnesium, sodium, and strontium (Engle and Rowan, 2014). Hydraulic fracturing fluid contains elevated levels of DOC, alkalinity, and sulfate (Engle and Rowan, 2014). Consequently, flowback acquires a geochemical signature reflecting both injected and formation fluids. Produced water containing bothAlthough some constituents of hydraulic fracturing fluids are known to readily degrade in the environment, little is known regarding how the subsurface degradation proceeds or how the constituents interact within a complex matrix of organics (Mouser et al., In Press).

7.6. Spatial Trends

As was reported for the volume of produced water (see 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 formation (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]

[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.

High TDS (more than 200,000 ppm) is common throughout the central portion of the United States in various basins. Low TDS (<10,000 ppm) was found in the basins of the Rocky Mountains, and sometimes in Texas and California. In other areas, there was a mixture of mid-range, which in the case of Illinois was correlated to the depth of producing zones (Breit, 2002).

Data further illustrating variability within shale, tight-gas and coalbed formations at both the formation and local scales are presented and discussed in Section E-3 of Appendix E.

7.7. Spill Impacts on Drinking Water Resources

Surface spills of flowback and produced water from unconventional oil and gas production have occurred across the country and in some cases have caused impacts to drinking water resources, as described in this section. Released fluids, if not contained on-site, may flow into nearby surface waters or infiltrate into ground water 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, most of which are based on state agency spill reports. The section concludes with discussion of two cases.

7.7.1. Produced Water Management and Spill Potential

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). Faulty connections at either end of the transfer process or leaks or ruptures in the lines carrying the fluid can result in surface spills.

Recovered fluids may be transferred to surface impoundments for long-term storage and evaporation. Surface impoundments are typically uncovered earthen pits that may or may not be lined. Recovered fluids may overflow from surface impoundments 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 impoundments 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, may 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 flowback management options, these systems also present spill potential during transfer of fluids.

7.7.2. Spills of Hydraulic Fracturing Flowback and Produced Water from Unconventional Oil and Gas Production

7.7.2.1. Pipeline Leaks

In some locations, pipelines are used to transport produced water. Aggregated information on pipeline leaks from the whole country is not available. This section, rather, contains examples of incidents that have occurred. A leak was detailed in a field report from PA DEP (2009a), which described a leak from a 90-degree bend in an overland pipe carrying a mixture of flowback and freshwater between two impoundments. Along a 0.4 mi (0.6 km) length of the impacted stream, 168 fish and 6 salamanders were killed; beyond a confluence at 0.6 km with a creek no additional dead fish were found. The release was estimated at 250 bbl (11,000 gal or 40,000 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, 2009a).

In January 2015, 70,000 barrels (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 adsorbent 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 water along the creek, the Little Muddy River, and Missouri River were found to be elevated above background levels, as were samples taken from ground water recovery trenches.

More incidents from North Dakota are documented at the North Dakota Department of Health (NDDOH) Environmental Health web site (see http://www.ndhealth.gov/EHS/Spills/). For the period from November, 2012 to November 2013, NDDOH reported 552 releases of produced water which were retained within the boundaries of the production or exploration facility and 104 which were not (see http://www.ndhealth.gov/ehs/foia/spills/ChartWebPageOG_20121101_20131111.pdf).

7.7.2.2. 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. Although the target formation was the Bakken Shale, data indicated that the residual signatures of the brine were characteristic of the overlying Madison limestone formation (U.S. EPA, 2015j). Prior research into out-of-zone hydraulic fracturing of the Bakken formation indicated that a large number of hydraulically fractured wells contain water that is external to the Bakken Zone (Arkadakskiy and Rostron, 2013a; Arkadakskiy and Rostron, 2012a; Peterman et al., 2012). The Bakken wells that contained external water were found to all contain water from the Mississippian Lodgepole formation (part of the Madison Group). The average volume of external water was 34% and the external water volume ranged from 10% to 100% (Arkadakskiy and Rostron, 2013a). 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, along with an unquantified amount of gas; some of the fluids reportedly reached a nearby stream (Barnes, 2010). The blowout occurred while

the company was drilling out the plugs used to isolate one fracture stage from another. An independent investigation found that the primary cause of the incident was that the only 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 barrels per day (2,100 gal/day or 7,900 L/day and 2,940 gal/day or 11,000 L/day) of flowback and oil (Reuters, 2014). A 3-ft berm was placed around the well for containment. Frozen droplets of oil and water sprayed on a nearby frozen creek. Liquid flowing from the well was collected and trucked offsite. Multiple well communication events reported by the media have also led to flowback and produced water spills ranging from around 700 to 35,000 gal (2,600 L to 130,000 L) (Vaidyanathan, 2013a).

7.7.2.3. Leaks from Pits and Impoundments

Leaks of flowback and produced water from on-site pits and impoundments have caused releases as large as 57,000 gal (220,000 L) and have caused surface and ground water impacts (Vaidyanathan, 2013b; PBFC 2011; PADEP 2010). VOCs have been measured in groundwater near the Duncan Oil Field in New Mexico downgradient of an unlined pit storing produced water (Sumi, 2004; Eiceman, 1986). Aspects of environmental transport from unlined pits are discussed below in Section 7.8.5.

Two of the EPA's retrospective case studies found potential impacts from produced water impoundments. In the southwest Pennsylvania case study (U.S. EPA, 2015k), elevated chloride concentrations and their timing relative to historical data suggested a recent ground water impact to a private water well occurred near an impoundment. The water quality trends suggested that the chloride anomaly was related to the impoundment, but site-specific data were not available to provide definitive assessment of the causes(s) and the longevity of the impact. Evaluation of other water quality parameters did not provide clear evidence of flowback or produced water impacts.

In the Wise County, TX case study (U.S. EPA, 2015m), impacts to two water wells were attributed to brine, but the data collected for the study were not sufficient to distinguish among four possible sources, one of which was leaks from reserve pits and/or impoundments. The others were: brine migrating from underlying formations along wellbores, brine migrating from underlying formations along natural fractures, and brine migrating from a nearby brine injection well. Alternate sources for the impacts were considered, including road salting, landfill leachate, septic tanks, and animal wastes, but evaluation of data showed that these were not likely. A third well experienced similar impacts, but a landfill leachate source could not be ruled out in that case. Ricther and Kreitler (1993) reviewed sources of salinity to ground water resources by evaluating reviewing major sources, which included natural saline ground water, halite dissolution, sea-water intrusion, oil-field brine, agriculture, saline seeps and road salt. For each source Ricther and Kreitler (1993) provided a state-by-state review of the potential occurrence, which can be used as a general guide to potential sources of salt at a specific area of interest.

7.7.2.4. Data Compilation Studies

Environmental impacts from hydraulic fracturing-related fluids have been explored to a limited extent in recent scientific literature (Brantley et al., 2014; Farag and Harper, 2014; Gross et al.,

2013; Olmstead et al., 2013; Papoulias and Velasco, 2013; Vidic et al., 2013; Considine et al., 2012; Rozell and Reaven, 2012).

From an Oklahoma Corporation Commission database of almost 13,000 releases reported from 1993 to 2003, Fisher and Sublette (2005) determined that the primary origins of produced water releases were leaks from lines, tanks, wellheads, with lesser numbers of releases from surface equipment, and pits. The most common cause was overflows followed by illegal activity, storms, fire accidents and corrosion. For these types of releases, the median release volume ranged from 20 bbl (840 gal or 3,180 L) to 60 bbl (2,500 gal or 9,500 L), and the maximums from 200 bbl (8,400 gal or 31,800 L) to 2,800 bbl (118,000 gal or 445,200 L).

As noted in Text Box 5-14 of Chapter 5, U.S. EPA (2015n) characterized hydraulic fracturing-related spills. Of the spills related to hydraulic fracturing activities (457 spills), 225 (49%) were spills of flowback and produced water. These spills were characterized with respect to volumes, spilled materials, sources, causes, environmental receptors, containment, and response. Most of the produced water spills in the EPA study occurred in Colorado (48%) and Pennsylvania (21%). Flowback and produced water constitute 84% (approximately 2.0 million gal or 7.6 million L) of the total volume of hydraulic fracturing-related spills as calculated from Appendix B of U.S. EPA (2015n).[1] Flowback and produced water spills were characterized by numerous low-volume spills; half of the spills with reported volumes were less than 1,000 gal (3,800 L), and few spills exceeded 10,000 gal (38,000 L). Of the volume of spilled flowback and produced water, 16% was recovered for on-site use or disposal, 76% was reported as unrecovered, and 8% was unknown. The potential impact of the unknown and unrecovered volume on drinking water resources is unknown.

Known sources for flowback and produced water spills include storage containers (e.g., pits, impoundments, or tanks), wells or wellheads, hoses or lines, and equipment. Storage containers accounted for 58% of flowback and produced water spills. The fewest spills occurred from wells and wellheads, but these spills had the greatest spill volumes compared to all other sources.

The causes of these spills were human error (38%), equipment failure (17%), failures of container integrity (13%), miscellaneous causes (e.g., well communication, well blowout), and unknown causes. Most of the volume spilled (74%), however, came from spills caused by a failure of container integrity.

In some of the cases, spills reached environmental receptors: soil (141 spills), surface water (17 spills), and ground water (1 spill); of these spills, 13 reached both soil and surface water. Consequently 146 unique produced water spills reached environmental receptors, accounting for 65% of the 225 cases and accounting for approximately 422,000 gal (1.60 million L) of flowback and produced water. Spills with known volumes that reached a surface water body ranged from

[1] Chemicals and products, fracturing fluid, fracturing water, equipment fluids, hydrocarbons, and unknown fluids constitute the additional 16% (approximately 360,000 gal or 1.4 million L) of the total volume of hydraulic fracturing-related spills as calculated from Appendix B of U.S. EPA (2015d).

less than 170 gal (640 L) to almost 74,000 gal (280,000 L). In 30 cases, it is unknown whether a spill of flowback and produced water reached an environmental receptor of any type.

Gross et al. (2013) analyzed the Colorado Oil and Gas Conservation Commission's database for ground water BTEX concentrations linked to hydraulic fracturing-related surface spills between July 2010 and July 2011 in Weld County, CO. Only spills with an impact on ground water were included in the study. The 77 reported spills accounted for less than 0.5% of nearly 18,000 active wells. Forty-six of the 77 spills consisted of produced water and oil. Of the remaining spills, 23 consisted of only oil and 8 consisted of only produced water. Thus the results that follow include cases with no produced water spill. From these composited spills, benzene concentrations in 90% of the ground water samples exceeded 5 μg/L, the U.S. drinking water standard. Additionally, 30% of toluene, 12% of ethylbenzene, and 8% of xylene sample concentrations exceeded 1 mg/L, 0.7 mg/L and 10 mg/L, respectively (Gross et al., 2013).

Based on five spills for which volumes were reported, the average volume of a produced water spill was 294 gal (1,110 L), ranging from 42 (160 L) to 1,176 gal (4,450 L) (Gross et al., 2013). Spill areas averaged 2,120 ft^2, with an average depth of 7 ft. Tank battery systems and production facilities were the biggest volume sources of spills with ground water impacts. Equipment failure was the most common cause of spills with ground water impacts. Shallow ground water within the study area (Niobrara Shale within the Denver-Julesburg Basin) is the main source of water for residents due to limited surface water availability. Of the 77 reported spills, secondary containment was absent from 51 of them (Gross et al., 2013).

As noted from the Colorado (Gross et al., 2013) and Oklahoma (Fisher and Sublette, 2005) studies, oil releases may occur alongside produced water spills. Review of recent oil field incidents in North Dakota also shows incidents with both produced water and oil releases (http://www.ndhealth.gov/EHS/Spills/). Oil releases are characterized by a number of features including their unique hydrocarbon composition and physical properties. Impacts can include: surface runoff, infiltration into soils, formation of sheens and oil slicks on surface waters, evaporation, oxidation, biodegradation, emulsion formation, and particle deposition (U.S. EPA, 1999).

A statistical analysis of oil and gas violations in Pennsylvania found that violations regarding structurally unsound impoundments or inadequate freeboard (vertical distance from the surface water level to the overflow elevation) were the second most frequent type of violation with 439 instances in the period from 2008 to 2010 (Olawoyin et al., 2013). In a study of pits and impoundments in West Virginia, Ziemkiewicz et al. (2014) found common problems of slope stability and liner deficiencies. Construction quality control and quality assurance were often inadequate; the authors found a lack of field compaction testing, use of improper types of soil, excessive slope lengths, buried debris, and insufficient erosion control (Ziemkiewicz et al., 2014).

Brantley et al. (2014) reviewed PA DEP's online oil and gas compliance database for notices of violation issued to companies developing unconventional gas resources. Between May 2009 and April 2013, 8 spills of flowback and produced water ranging from more than 4,000 gal (15,000 L) to

more than 57,000 gal (220,000 L) reached surface water resources. The spills typically resulted in local impacts to environmental receptors and required remediation and monitoring. However, the study indicated the likelihood of a leak or spill of hydraulic fracturing-related fluids was low (less than 1%, based on 32 large spills out of more than 4,000 complete wells). Due to lack of data, specific impacts to the eight receiving surface waters were not discussed, other than noting the produced water had contacted the surface water.

The Brantley et al. (2014) analysis of the PA DEP positive determination letters written in response to water-user complaints illustrates the importance of pre-drilling sampling, as it is one criterion that allows operators to refute the presumption that drilling caused water supply impacts (see Chapter 6). The importance of this pre-drilling sampling and analysis is highlighted by naturally occurring exceedances of EPA secondary MCLs for manganese and iron in private wells in Pennsylvania (Boyer et al., 2011; Williams et al., 1998). Boyer et al. (2011) state that more than 40% of private water wells in Pennsylvania fail to meet federal drinking water standards. Boyer et al. (2011) analyzed pre-drilling samples from private water wells in northeastern and southwestern Pennsylvania and showed that 20% (of 222 wells) failed the drinking water standard for iron and 27% (of 203 wells) failed for manganese.[1] Williams et al. (1998), in their evaluation of over 200 wells in Bradford, Tioga, and Potter counties in northeastern Pennsylvania, indicate about 50% of the wells exceeded secondary MCLs for iron and manganese.[2] According to Boyer et al. (2011), higher concentrations of these constituents tend to be associated with the sodium chloride (Na-Cl) type ground water often found in valleys in zones of more restricted ground water flow (portions of aquifers with low permeability). Saline water can be found at shallow depths in these areas (Williams et al., 1998).

As an example of another set of criteria for assessing sites potentially contaminated by hydraulic fracturing activities, the EPA (2012f) developed an approach to study sites where the impacts to drinking water resources and the potential sources of the impacts are unknown, but may have been the object of water-user complaints. The approach is based on a tiered scheme where results from each tier are used to refine activities in higher tiers. The four tiers were as follows:

- Verify potential issue:
  - Evaluate existing data and information from operators, private citizens, state and local agencies, and tribes (as appropriate).
  - Conduct site visits.
  - Interview stakeholders and interested parties.
- Determine approach for detailed investigations:
  - Conduct initial sampling of water wells, taps, surface water and soils.

[1] Percentage of other parameters failing standards: 17% of 233 wells for pH, 3% of 233 wells for TDS, <1% of 226 wells for chloride, 1% of 218 wells for Barium, <1% of 177 wells for sulfate, 33% of 125 wells for coliforms, 4% of 115 wells for arsenic, 8% of 122 wells for fecal coliforms, 32% of 102 samples for turbidity.
[2] Naturally occurring constituents occasionally exceeding EPA primary MCLs in this area include barium, combined radium-226 and radium-228, and arsenic.

  - Identify potential evidence of drinking water contamination.
  - Develop conceptual site model describing possible sources and pathways of the reported or potential contamination.
  - Develop, calibrate, and test fate and transport model(s).
- Conduct detailed investigations to detect and evaluate potential sources of contamination:
  - Conduct additional sampling of soils, aquifer, surface water, and produced water pits/tanks where present.
  - Conduct additional testing, including further water testing with new monitoring points, soil gas surveys, geophysical testing, well mechanical integrity testing, and stable isotope analyses.
  - Refine conceptual site model and further test exposure scenarios.
  - Refine fate and transport model(s) based on new data.
- Determine the source(s) of any impacts to drinking water resources:
  - Develop multiple lines of evidence to determine the source(s) of impacts to drinking water resources.
  - Exclude possible sources and pathways of the reported contamination.
  - Assess uncertainties associated with conclusions regarding the source(s) of impacts.

This tiered assessment strategy provides an outline for collecting data and evaluating lines of evidence for determining whether impacts have occurred.

7.7.3. Case Studies of Potentially Impacted Sites

7.7.3.1. Flowback and Produced Water Release from an Illegal Discharge Impacts Surface and Ground Water in Lycoming County, Pennsylvania

An estimated 6,300 gal to more than 57,000 gal (24,000 to 220,000 L) of Marcellus Shale produced water was illegally discharged at XTO Energy Inc.'s Marquardt pad and flowed into the Susquehanna River watershed in November 2010 (U.S. EPA, 2013g).[1] Overland and subsurface flow of released fluids affected proximal surface water, a subsurface spring, and soil. No impacts to drinking water wells and springs within 1 mile of the release were observed at the last sampling date (17 days post-spill). However, residual, soil-associated produced water constituents could reach drinking water resources in the future through surface runoff or infiltration to the ground water (Science Applications International Corporation, 2010). The release, which occurred at XTO's Marquardt 8537H well pad in Penn Township, Lycoming County, PA, was discovered after a routine inspection by the Pennsylvania Department of Environmental Protection. Subsequent investigation

[1] Violations associated with this incident can be found at the Pennsylvania Department of Environmental Protection's Oil and Gas Compliance Report database found at http://www.portal.state.pa.us/portal/server.pt/community/oil_and_gas_compliance_report/20299 under the following inspection IDs: 1928978, 1928992, and 1929005.

revealed that flowback and produced water had been discharging into surface waters for over two months after the fluid was released from multiple tanks with open or missing valves on November 16, 2010 (U.S. EPA, 2013g).

Geochemical characterization of this produced water indicated concentrations of barium, chloride, iron, manganese, and TDS above Pennsylvania's surface water quality standards, and above the statewide health standards for medium-specific concentrations (SHS MSCs) for ground water use in residential and nonresidential settings (Science Applications International Corporation, 2010). The produced water also contained elevated levels of bromide, calcium, sodium, and strontium, which lack state surface water quality standards and SHS MSCs (Science Applications International Corporation, 2010).

Post-spill surface water delineations indicated that released fluids migrated to an unnamed stream known as Tributary 19617. The released fluids migrated approximately 1,400 ft (427 m) overland to a depression which contains a natural fracture with a hydrological connection to a spring (Schmidley and Smith, 2011). The distance from the depression to the stream is approximately 600 ft (183 m). Released fluids also drained through surface soils into ground water, which was then released in seeps to the spring and stream; elevated levels of barium, bromide, calcium, chloride, sodium, strontium, and TDS resulted (U.S. EPA, 2013g). Elevated levels of these constituents, particularly barium, bromide, and strontium, were indicative of Marcellus Shale flowback and produced water that had mixed with surface water (Brantley et al., 2014). Barium and chloride were the only dissolved constituents detected in the stream that exceeded state surface water quality standards; the remaining constituents lack established state surface water quality standards.

Results from XTO's temporal study of surface water quality confirmed impacts to the stream from produced water. Surface water quality was characterized at the confluence of the stream and spring, and at the stream's upstream and downstream segments, for 65 days post-spill (Science Applications International Corporation, 2010). Downstream barium and bromide levels were one to two orders of magnitude greater than upstream levels through this period. In addition, stream strontium levels were two to three orders of magnitude greater than upstream levels at this time. Chloride was initially detected in the stream with concentrations exceeding state water quality standards (Schmidley and Smith, 2011). Average chloride concentrations for stream samples were two orders of magnitude greater than upstream concentrations (PA DEP, 2011c). By January 2011, stream chloride concentrations had dropped below the limit established by Pennsylvania's surface water quality standards.

Delineation of chloride concentrations within on-site soil indicated soil impacts due to overland flow of flowback and produced water (Science Applications International Corporation, 2010). Five hundred tons of affected soil was consequently excavated for off-site disposal. Chloride concentrations decreased with increased distance from the spill site but remained elevated above background levels even at distances of a few thousand feet (Science Applications International Corporation, 2010). Produced water constituents that were present in soil at concentrations above background levels (i.e., barium, sodium, strontium) could be available for long-term runoff and

infiltration. For instance, the continued presence of chloride in affected soils is likely due to precipitated chloride salts in soil pores from residual produced water (Science Applications International Corporation, 2010), which may leach later. Near-term sampling (up to 17 days after the spill) found no elevated constituents indicative of runoff or infiltration of produced water when XTO sampled 14 drinking water wells and springs within one mile of the well pad. XTO was ordered to create a storm water collection system for off-site disposal of impacted storm water and to establish on-site water monitoring wells to track long-term ground water quality between the well pad and the stream (Schmidley and Smith, 2011). Other cases of illegal dumping have been reported (Caniglia, 2014; U.S. EPA, 2013g; Paterra, 2011).

7.7.3.2. Flowback Fluid Reaches Towanda Creek Due to Well Blowout in Bradford County, Pennsylvania, Causing Short-Term Impacts

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 ten thousand gallons (38,000 L) of flowback fluids 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 and ground water monitoring (SAIC and GES, 2011). In addition, the EPA, PADEP, and Chesapeake collected split samples from seven private wells within the vicinity of the blowout. The EPA requested that the Agency for Toxic Substances and Disease Registry (ATSDR) evaluate the environmental data collected from seven private wells to determine whether harmful health effects would be expected from consuming or using the well water. Data from Pre-blowout private well samples, collected approximately six months prior to drilling activity at the site, were included in the evaluation.

Between the pre- and post-blowout samples, ATSDR (2013) determined that there was factor of ten increases in some analyte concentrations (methane, barium, calcium, chloride, magnesium, manganese, potassium, and sodium) and a factor of 7 increase in iron concentration in one well (RW04) near the site. Other wells showed elevated levels of certain analytes.[1] ATSDR concluded that although the available data *suggested* that the ground water near this site is impacted by gas activities, the data for RWO4 did not conclusively indicate an impact. ATSDR (2013) concluded that further evaluation is needed to characterize any relationship between the drinking water wells and aquifers as a result of changes in site conditions. Further sampling would be required to determine current impacts, trends, and chronic exposures to ground water constituents related to natural gas activities.

[1] Elevated sodium levels were detected in 6 wells, levels in 5 of them (RW02, RW03, RW05, RW06, and RWO7) may be of concern to sensitive subpopulations; while the last (RW04) would exceed the dietary guideline for both sensitive and the general population. ATSDR judged that elevated lithium concentration in two wells (RW04 and RW06) could be a concern to individuals undergoing lithium therapy. One well (RW02) showed elevated arsenic concentrations, but these were similar in the pre- and post-blowout samples. Gross alpha radiation levels were above the EPA maximum contaminant level in one well (RW03), and ATSDR did not expect adverse health effects from drinking this water. ASTDR did not expect adverse health effects for the user of five private wells (RW01, RW03, RW05, RW06 (excepting for possible lithium impacts) and RW07).

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 feet of the unnamed tributary exhibited elevated chloride, TDS, and specific conductance, which returned to background levels in under 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).

7.7.4. Roadway Transport of Produced Water

Accidents during transportation of hydraulic fracturing produced water are a possible mechanism leading to potential impacts to drinking water. Nationwide data are not available, however, on the number of such accidents that result in impacts. An estimate of releases from truck transport of produced water could be made as follows:

$$Total\ number\ of\ truckloads = \frac{Total\ number\ of\ wells\ \times Produced\ water\ volume\ per\ well}{Produced\ water\ volume\ per\ truck}$$

Then the total distance traveled by all trucks is given by:

$$Total\ distance\ traveled = Total\ number\ of\ truckloads\ \times Distance\ per\ truck$$

The number of crashes impacting drinking water resources can be estimated from:

$$\begin{aligned} &Total\ crashes\ impacting\ drinking\ water\ resources \\ &\quad = Fraction\ of\ crashes\ releasing\ waste\ that\ impacts\ drinking\ water\ resources \\ &\quad \times Fraction\ of\ all\ crashes\ releasing\ waste\ \times Crashes\ per\ distance \end{aligned}$$

Estimates of all but one of the quantities in these calculations can be made from various literature sources, which are described in Appendix E. A key parameter is the number of crashes of trucks per distance traveled. In 2012, the U.S. Department of Transportation (DOT) estimated that the number of crashes per 100 million highway miles driven of a type of large truck was 110, which is a relatively small number. A key parameter that is unknown is the number of crashes which impact drinking water resources, so definitive estimates of impacts to drinking water resources cannot be made. Alternatively, as an upper bound on drinking water resource impacts, the number of crashes which release waste can be estimated. Based on various assumptions and scenarios presented in Appendix E, the number of crashes with releases is bounded by the low tens of events. At 20 m^3 per truckload, the volumes are low relative to the typical volume of produced water.

Several limitations are inherent in this analysis, including differing rural road accident rates and highway rates, differing produced water endpoints, 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.

7.7.5. Studies of Environmental Transport of Released Produced Water

In this subsection, we describe transport study results that illustrate how produced waters have been shown to be transported from historical disposal practices and spills. Over the history of oil production in the U.S., produced water disposal methods have evolved from land application to storage in unlined ponds to deep well injection (Whittemore, 2007), although some unlined pits continue in use where allowed by states. The changes in practice occurred because of pollution impacts: first to surface waters and aquatic biota, and then to ground water from disposal ponds. Evaluation of sites contaminated by these historic practices sheds light on the potential for transport of released produced water, as discussed below.

Impacts to ground water might occur following a spill on land. When the liquid is highly saline, its migration is affected by its high density and viscosity compared with that of fresh water. When spilled flowback or produced water flows over land, a fraction of the liquid is subject to infiltration. The fraction depends on the rate of release, surface cover (i.e., pavement, cracked pavement, vegetation, bare soil, etc.), slope of the land surface, subsurface permeability, and the moisture content in the subsurface.

The potential for impacts from produced water spills depends on the distance from the source to receptor; the distance depends on local topography. One study investigated receptor distances on a formation basis (Entrekin et al., 2011). The distance between gas wells and drainage ways was determined to average 273 m (890 ft) for the Marcellus Shale and 353 m (1160 ft) for the Fayetteville Shale (Entrekin et al., 2011). Some wells were much closer, being as close as 1 m (3.28 ft). For one location in each formation a separate analysis gave a mean estimate of 153 m (500 ft) for the Marcellus Shale and 130 m (430 ft) for the Fayetteville Shale. The average distance to public drinking water intakes was 15 km (9.32 mi). The average distance to public water supply wells was 37 km (23.0 mi) for the Marcellus Shale and 123 km (76.4 mi) for the Fayetteville Shale. As the density of gas development increases the number of gas wells located close to drainage ways and public water supply wells may also increase.

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 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 high concentrations corresponding to low stream flows. Persistent surface water chloride contamination was attributed to slow flushing and discharge of contaminated ground water.

Transport from the land surface to the water table is further characterized in general by flow through variably water-saturated media, preferential flow paths, fractures in clays, and macropores. Preferential flow paths along microscale heterogeneities are known to exist and dominate transport even after cycles of repeated drying and rewetting. The effect of flowback on transport of colloids has recently been evaluated in laboratory sand columns. The authors found that flowback increased the mobility of colloidal particles, which potentially serve as a source of aquifer contamination (Sang et al., 2014).

In another study, Otton et al. (2007) reported on 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 (Otton et al., 2007). The mechanisms proposed were lateral movement through permeable sand bodies, vertical movement along shale fractures, and possibly increased permeability from clay flocculation and shrinkage due to the presence of highly saline water (Otton et al., 2007).

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 by States et al. (2013) for the Allegheny River.

Generally, the deeper that brine 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 brine pits. Produced water from these pits penetrated 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).

Chloride impacts from produced water spills were studied through scenario modeling releases of 100 bbl (4,200 gal or 15,900 L) and 10,000 bbl (420,000 gal or 1.59 million L) (API, 2005). The scenarios included transport through a homogeneous or heterogeneous unsaturated zone using the HYDRUS-1D model (Šimunek et al., 1998) and mixing within the top portion of a shallow aquifer using a specially developed spreadsheet model. The results of the scenario modeling indicated that ground water quality is unlikely to be impaired for spills with small soil penetration depths, which correspond to spills distributed over large areas. Large spills of 100,000 bbl (4.2 million gal or 15.9 million L) over sandy unsaturated zones were found to have a high potential to impact ground water quality (API, 2005). Spills of less than 100 bbl (420 gal or 1,590 L) were not modeled and were presumed to have low impacts based on the results from the larger spills. The results were constrained by the underlying assumptions of HYDRUS-1D—that there were no preferential flow paths, including fractured systems, systems with macropores, or fine scale heterogeneities. More rapid and spatially extensive transport could occur in these settings.

7.7.6. Coalbed Methane

A CBM produced water impoundment in the Powder River Basin of Wyoming was studied for its impact on ground water (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. The subsurface sediments were found to be highly heterogeneous both physically and chemically, which increased the complexity of studying the site. Elevated concentrations of TDS, chloride, nitrate, and selenium were found at the site. For example, TDS exceeded 100,000 mg/L in one lysimeter sample, while the concentration was 2,275 mg/L in a composite CBM produced water sample (Healy et al., 2008). Most of the solutes found in the ground water mound did not originate with the CBM produced water, but rather were the consequence of dissolution of previously existing salts and minerals. The mechanisms were thought to be gypsum dissolution, cation exchange, and pyrite dissolution. Data from other sites indicated that the study site's ground water chemistry may not be typical and that the same phenomena may not occur at other sites in the basin (Healy et al., 2011).

7.7.7. Transport Properties

The identified constituents of flowback and produced water include inorganic chemicals in the form of cations and anions (including various types of metals, metalloids, and non-metals, and radioactive materials, among others) and organic chemicals, including identified compounds in various classes, and unidentified materials measured as TOC and DOC. Environmental transport of these chemicals depends on properties of the chemical and properties of the environment, and is extensively discussed in Section 5.8.3. In this section we discuss the characteristics of transport for inorganics and note that some inorganics may move with the water, while many of the others are influenced by reactions. For organic chemicals identified in produced water, we discuss EPI Suite™ estimates of the main transport parameters identified in Chapter 5, while noting the influences of salinity and temperature on these properties.

Transport of inorganic chemicals depends on the nature of ground water and vadose zone flow, and potential reactions among the inorganic chemical, solid surfaces, and geochemistry of the water. Some inorganic anions (i.e., chloride and bromide) move with their carrier liquid and are mostly impacted by physical transport mechanisms: flow of water and dispersion. In addition to the flow-related processes, transport of most inorganics is driven by three mechanisms related to partitioning to the solid phase: adsorption, absorption, and precipitation. The effects of these mechanisms depend on both chemical and environmental characteristics, including the surface reactivity, solubility, and redox sensitivity of the contaminant; and the type and abundance of reactive mineral phases, and the ground-water chemistry (U.S. EPA, 2007). Through the use of transport models, the effects of physical transport mechanisms and chemical processes are integrated. Examples of transport models for reactive metals include the Geochemist's Workbench (Bethke, 2014) and Hydrus (Šimunek et al., 1998).

Properties of organic chemicals which tend to affect the likelihood that a chemical will reach and impact drinking water resources if spilled include high chemical mobility in water, low volatility, and high persistence in water. Using the EPA chemical database EPI Suite™, we were able to obtain actual or estimated physicochemical properties for 86 of the 134 organic chemicals identified in produced water and listed in Appendix A. A portion of these, 66, are used in the chemical mixing stage (see Appendix Table C-8). EPI Suite™ results were generated for solubility, octanol water partition coefficient (K_{ow}), and the Henry's constant (see Figure 7-9). The log K_{ow} values are of the

identified organic chemicals skewed positively, indicating some of the chemicals have low mobility which may result in less extensive dissolved contaminant plumes in ground water. These compounds, however, have a higher tendency to sorb to particulate or colloidal materials and hence be transported in systems where particle transport is dominant, for example: colloid transport in ground water and sediment transport in surface water. The log Henry constant values tend to be below 0 indicating that at equilibrium the concentration in air is less than the concentration in water. This behavior is reflected in the log solubility plot, as the solubilities skew conversely toward high values.

The EPI Suite™ results are constrained by their applicability to one temperature (25 °C), and salinity (low). Temperature changes impact Henry's constant, K_{ow}, and solubility, and depend on the characteristics of the chemical and ions present (Borrirukwisitsak et al., 2012; Schwarzenbach et al., 2002). In some cases the effect changes exponentially with salinity (Schwarzenbach et al., 2002). Therefore, property values that depart from the EPI Suite™ values are expected for produced water at elevated temperature and salinity.

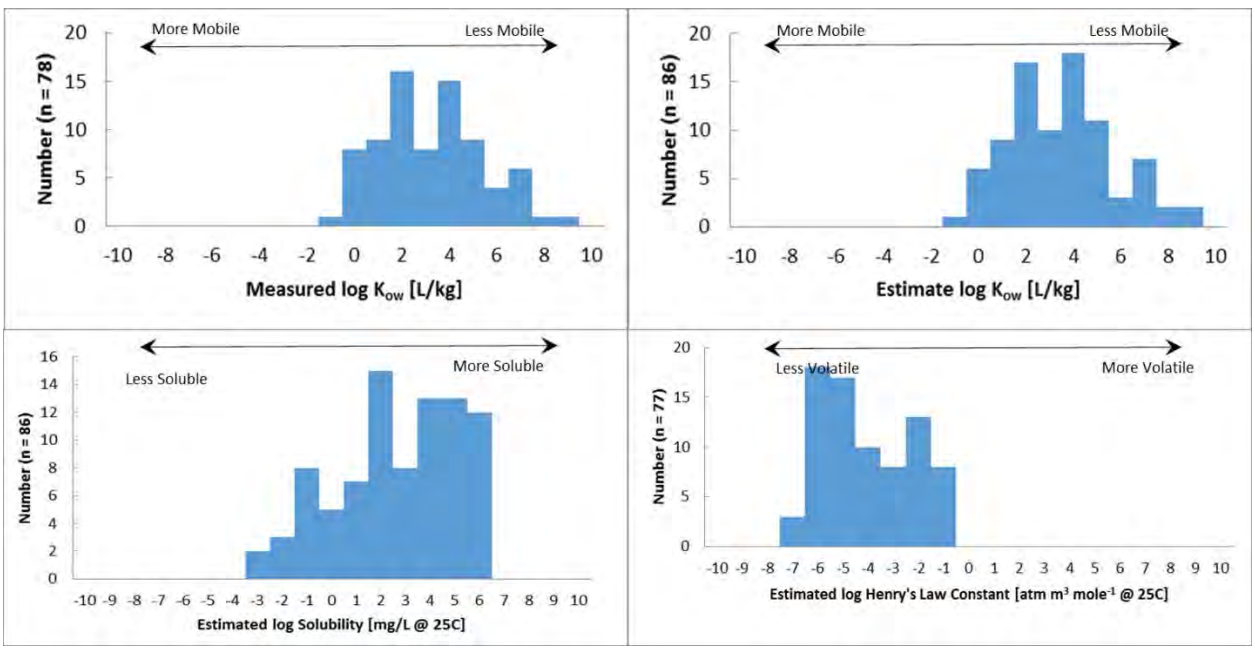


Figure 7-9. Histograms of physicochemical properties of 86 organic chemicals identified in produced water (physicochemical properties estimated by EPI Suite™).

7.8. Synthesis

After hydraulic fracturing is completed, the operator reduces injection pressure and water is allowed to flow back from the well to prepare for oil or gas production. The flowback water may contain fracturing fluid, fluid from the surrounding formation, and hydrocarbons. Initially this flowback is mostly fracturing fluid, but as time passes, the produced water becomes more similar to the water in the formation. This water is stored at the surface for eventual reuse or disposal.

Impacts to drinking water from flowback and produced water can occur if spilled flowback or produced water enters surface water bodies or aquifers.

7.8.1. Summary of Findings

The volume and composition of flowback and produced water vary geographically, both within and between different formations with time and with other site-specific factors. High initial rates of flowback decrease as time continues. The amount of fracturing fluid returned to the surface varies, and typically averages 10% to 25%. In most cases, lower flow rates of produced water continue throughout gas production.[1] In some formations (i.e., the Barnett Shale), the ultimate volume of produced water can exceed the volume of hydraulic fracturing fluid because of inflow of water.

The composition of flowback changes with time as the hydraulic fracturing fluid contacts the formation and mixes with the formation water. At the same time, reactions occur between the constituents of the fracturing fluid and the formation. 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 may 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 freshwater conditions.

Flowback and produced water spills are known to have occurred across the country. The causes identified for these spills are container and equipment failures, human error, well communication, blowouts, pipeline leaks, and illegal dumping. Spills due to trucking accidents are possible, but accident rates in the United States suggest only a small number of such releases occur.

USGS studies of impacts of produced water disposal in unlined pits document the potential for surface releases (in these cases over multiple years) that have led to ground water impacts. Contaminant plumes can be traced to high TDS water disposed of in the pits, or geochemical reaction between infiltrating low-TDS water, in the case of CBM produced water, releasing existing minerals from the unsaturated zone to ground water.

7.8.2. Factors Affecting the Frequency or Severity of Impacts

The potential of spills of flowback and produced water to affect drinking water resources depends upon the release volume, duration, and composition. Larger spills of greater duration are more likely to reach a nearby drinking water resource than are smaller spills. The composition of the spilled fluid will also impact the severity of a spill, as certain constituents are more likely to affect the quality of a drinking water resource. Low-volume and short-duration spills are less likely to cause impacts, (see Section 7.7.5).

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

[1] Note that increasing produced water flow rates are indicative of water breakthrough and declining oil production.

water threatening surface water bodies. However, infiltration through soil may lead to ground water impacts. Produced water with lower constituent concentrations may produce lesser impacts, but the USGS studies of CBM produced water impoundments described in section 7.7.5 showed impacts caused by CBM water mobilizing existing minerals. The USGS studies on historical disposal of saline produced water in unlined pits detected ground water plumes discharging into surface water bodies. The potential impact to drinking water in such cases depends on the location of drinking water wells and the size of any surface water supply reservoir.

7.8.3. Uncertainties

We first discuss data gaps in our overall knowledge of flowback and produced water; closing such gaps would enable us to better predict impacts on drinking water resources. Second, we present uncertainties that, based on site-specific conditions, also affect our ability to determine potential impacts.

7.8.3.1. General Data Gaps

Knowledge of volume and some compositional aspects of flowback and produced water are known from published sources. Most of the available data on TENORM has come from the Marcellus Shale, where these are typically high in comparison to the limited data available from other formations. Only a few studies have attempted to sample and characterize the organic fraction of flowback and produced water; some data are available for shale and CBM, but none are available for tight formations. The reported organic chemical data from flowback likely does not capture the full range of chemicals that may be present, either as original components of the hydraulic fracturing solution or transformation products generated in the subsurface.

Characterization of produced water organics is limited by several factors. Development or use of proper analytical procedures depends upon knowing the identities of injected chemicals. Because the formulation of hydraulic fracturing fluids can contain proprietary chemicals, the exact formulations are not available. In addition, subsurface transformations yield degradation products, which themselves must have appropriate analytical methods. Further difficulties are due to matrix interference from high-TDS produced water. These problems result in the need to develop new methods for analyzing both organics and inorganics in produced water.

Nationwide data on spills of flowback and 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, 2015n). Despite various studies, the total number of spills occurring in the United States, their release volumes and associated concentrations, can only be roughly estimated because of underlying data limitations.

7.8.3.2. Uncertainties at Individual Spill Sites

Spills of flowback and produced water present many uncertainties that, in combination, limit our ability to predict impacts on drinking water resources. Spills vary in volume, duration, and composition. The spilled liquid could be fracturing fluid mixed with formation water in a proportion that depends on the time that has passed since fracturing. As described in Section 7.7, spills may originate from blowouts, well communication, aboveground or underground pipeline

breaks, leaking impoundments, failed containers, human error (including illegal activities, failure to detect spills, and failure to report spills) or unknown causes. The difference between these causes affect the size and location of the spill. 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 flowback and 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 flowback and 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, or bromide from coal mine drainage), baseline sampling prior to impacts is one way to increase certainty of an impact determination. Further sampling and investigation may be used to develop the linkage between a release and a documented drinking water impact. Produced water spill response typically includes delineation of the extent of oiled soils, sheens on water surfaces, and the extent of saline water. Extensive characterization of produced water is typically not part of spill response, and therefore the chemicals, and their concentrations, potentially impacting drinking water resources are not usually known.

7.8.4. Conclusions

Flowback and produced water has the potential to affect the quality of drinking water resources if it enters into a surface or ground water body used as a drinking water resource. This can occur through spills at well pads, or during transport of flowback. 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. Flowback and produced water may contain toxic constituents and can potentially render water unpalatable or unsafe to drink. Conclusive determination of impacts to water resources depends on commitment of resources to the implementation of sampling, analysis and evaluation strategies

Text Box 7-1. Research Questions Revisited.

What is currently known about the frequency, severity, and causes of spills of flowback and produced water?

- Surface spills of flowback and produced water from unconventional oil and gas production have occurred across the country. Some produced water spills have affected drinking water resources, including a few private drinking water wells. The majority of flowback and produced water spills are under 1,000 gallons. The causes identified for these are container and equipment failures, human error, well communication, blowouts, pipeline leaks, and illegal dumping.

What is the composition of hydraulic fracturing flowback and produced water, and what factors might influence this composition?

- The composition of flowback and produced water must be determined through sampling and analysis, both of which have limitations. The former due to the ability to access through production equipment and the latter due to issues with identifying target analytes in advance of analysis and the existence of appropriate analytical methods.
- The geochemical content of water flowing back initially reflects injected fluids. After initial flowback, returning fluid geochemistry shifts to reflect the geochemistry of formation waters and formation solids.
- According to available literature and data, conventional and unconventional flowback and produced water content are often similar with respect to the occurrence and concentration of many constituents.
- The least statistical variability in produced water content is exhibited between shale gas and tight gas produced water, and the most statistical variability is exhibited between shale gas and coalbed methane produced water.
- Much produced water is generally characterized as saline (with the exception of most coalbed methane produced water) and enriched in major anions, cations, metals, naturally occurring radionuclides, and organics.
- Shale and coalbed produced water is enriched in benzene. Benzene is a constituent of concern in Marcellus Shale, Raton CBM, and San Juan CBM produced water. Shale produced water is more likely to contain elevated average total BTEX levels than other unconventional produced water.
- Typically, unconventional produced water contains low levels of heavy metals. Elevated strontium and barium levels, however, are characteristic of Marcellus Shale flowback and produced water. CBM and, in particular, shale produced water are likely to contain NORM levels of concern.
- Composition data were limited. Most of the available data on produced water content were for shale formations and CBM basins, while little data were available for sandstone formations. Additionally, the majority of data were for inorganics, and little data were available for organics. Many more organic chemicals have been reported to have been used in hydraulic fracturing fluid than have been identified in produced water. The difference may be due to analytical limitations, limited study scopes, and undocumented subsurface reactions.
- Hydraulic fracturing flowback and produced water composition is influenced by the composition of injected hydraulic fracturing fluids, the targeted geological formation and associated hydrocarbon products, the stratigraphic environment, and subsurface processes and residence time.
- Spatial variability of produced water content occurs between plays of different rock sources (e.g., coal vs. sandstone), between plays of the same rock type (e.g., Barnett Shale vs. Bakken Shale), and within formations of the same source rock (e.g., northeastern vs. southwestern Marcellus Shale).

What are the chemical and physical properties of hydraulic fracturing flowback and produced water constituents?

- The identified constituents of flowback and produced water include inorganic chemicals (cations and anions in the form of metals, metalloids, non-metals, and radioactive materials), organic chemicals and compounds, and unidentified materials measured as TOC (total organic carbon) and DOC (dissolved organic carbon). Some constituents are readily transported with water (i.e., chloride and bromide), while others depend strongly on the geochemical conditions in the receiving water body (i.e., radium and barium), and assessment of their transport is based on site-specific factors. Using the EPA chemical

database EPI Suite, we were able to obtain actual or estimated physicochemical properties for 86 (64%) of the 134 chemicals identified in produced water.

- As in the case of chemicals in hydraulic fracturing fluid, chemical properties that affect the likelihood of an organic chemical in produced water reaching and impact drinking water resources in the short-term, include: high chemical mobility in water, low volatility, and high persistence in water. In general, EPI suite results suggest that organic chemicals in produced water tend toward lower mobility in water. Consequently these chemicals could remain in soils or sediments nearby spills. Low mobility may result in smaller dissolved contaminant plumes in ground water. Although these compounds are more likely to be transported associated with sediments in surface water or small particles in ground water. Organic chemical properties vary with salinity and the effects depend on the nature of the chemical.

If spills occur, how might hydraulic fracturing flowback and produced water contaminate drinking water resources?

- Spills of flowback or produced water might impact drinking water resources if the spill or release is of sufficient volume and duration, to reach the resource at a sufficient concentration. Impacts to in-use drinking water depend on proximity to sources. Scientific literature and published reports have shown that produced water spills have impacted drinking water resources.

7.9. References for Chapter 7

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Chapter 8

Wastewater Treatment and Waste Disposal

8. Wastewater Treatment and Waste Disposal

8.1. Introduction

Hydraulic fracturing used for the development of oil and gas resources results in the production of wastewater containing a range of problematic or potentially problematic constituents (see Chapter 7) and requiring management. For the purposes of this assessment, hydraulic fracturing wastewater encompasses flowback and produced water (often referred to together as produced water) that is managed using any of a number of practices, including treatment and discharge, reuse, or injection into Class IID wells regulated under the Underground Injection Control (UIC) program under the Safe Drinking Water Act (SDWA) (see also Chapter 1).[1] In this chapter, the term "wastewater" is generally used. In limited cases where more specific information is provided about a wastewater (e.g., a source indicates that the wastewater is flowback), that information is also noted.

Although wells producing from either unconventional or conventional oil and gas reservoirs generate produced water during the course of their productive lifespan, wells conducting modern high-volume hydraulic fracturing can generate a large volume of flowback water in the period immediately after fracturing. Stakeholders reported to the U.S. Government Accountability Office that flowback volumes could be 420,000 gal to 2.52 Mgal (10,000 to 60,000 bbl or 1.59 million to 9.54 million L) per well per hydraulic fracture (U.S. GAO, 2012) (see Chapter 7.1.1 for more information on produced water volumes per well in various geologic basins and plays). This necessitates having a wastewater management strategy in place at the beginning of activities at the well. Selection of management choices may depend upon the quality and volume of the fluids, logistics, and economics.

Treatment and disposal strategies vary throughout the United States and may include underground injection, on-site or offsite treatment for reuse in subsequent hydraulic fracturing operations, reuse without treatment, or other uses. In some areas, wastewater may be applied to the land (e.g., for irrigation) or held in pits for evaporation. The large majority of wastewater generated from all oil and gas operations in the United States is disposed of via Class IID wells (Clark and Veil, 2009). As hydraulic fracturing activity matures, costs of different disposal practices may change in various regions due to factors such as regulations, available infrastructure, feasibility and cost of reuse practices, and other concerns that are difficult to anticipate and quantify at the time of this assessment.

Over the past decade, the rapid increase in modern hydraulic fracturing activities has led to the need to manage the associated wastewater. There has been a shift towards reuse in areas where

[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 produced water or flowback 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.

there are relatively few Class IID wells (e.g., the Marcellus Shale region) and indications of interest in reuse in areas where access to water for fracturing is limited (e.g., Anadarko Basin in TX and OK). 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, without regard to the level of treatment.

This chapter provides follow-on to Chapter 7, which discusses the composition and per-well volumes of produced water and the processes involved in its generation. In this chapter, discussions are included on management practices for hydraulic fracturing wastewaters, 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, issues of concern associated with wastewater constituents are also presented (Section 8.3). Management methods that are used in 2014-2015 or have been used in recent years are described (Section 8.4). Information is then presented on the types and effectiveness of treatment processes that are suitable for removal of constituents of concern in hydraulic fracturing wastewaters, either in centralized waste treatment facilities (CWTs) or on-site treatment; examples of CWTs are presented (Section 8.5 and Appendix F). With the background provided in the earlier sections of the chapter, documented and potential impacts on drinking water resources are discussed (Section 8.6), and a final synthesis discussion is then provided (Section 8.7).

This chapter makes use of background information collected by the EPA's Office of Water (OW) as part of its development of proposed effluent limitations guidelines and standards for wastewater from unconventional oil and gas resources (U.S. EPA, 2015q). These are defined by guidelines and standards as resources in low permeability formations including oil and gas shales, tight oil, and low permeability sandstones and carbonates. Coalbed methane is beyond the scope of those standards. In this chapter we consider wastewater generated by hydraulic fracturing of those unconventional oil and gas resources included in the background research done by OW in addition to wastewater generated by hydraulic fracturing in coalbed methane plays and conventional reservoirs.

8.2. Volumes of Hydraulic Fracturing Wastewater

This section of Chapter 8 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 challenges associated with the preparation and use of available estimates. (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.) Wastewater volumes most likely will vary in the future as the amount and locations of hydraulic fracturing activities change and as existing wells age and move into later phases of production. The volumes and management of

wastewater are important factors affecting the potential for wastewater to affect drinking water resources.

The volume of wastewater generated is generally tied to the volume of oil and gas production; as operators increase hydrocarbon production, there will be a corresponding increase in wastewater volumes to be managed. For example, data from the Pennsylvania Department of Environmental Protection (PA DEP) (PA DEP, 2015a) (see Figure 8-1) show trends in volumes of wastewater compared to gas produced from wells in the Marcellus Shale in Pennsylvania. Although the data show some variation, they demonstrate a general correlation between wastewater and produced gas.

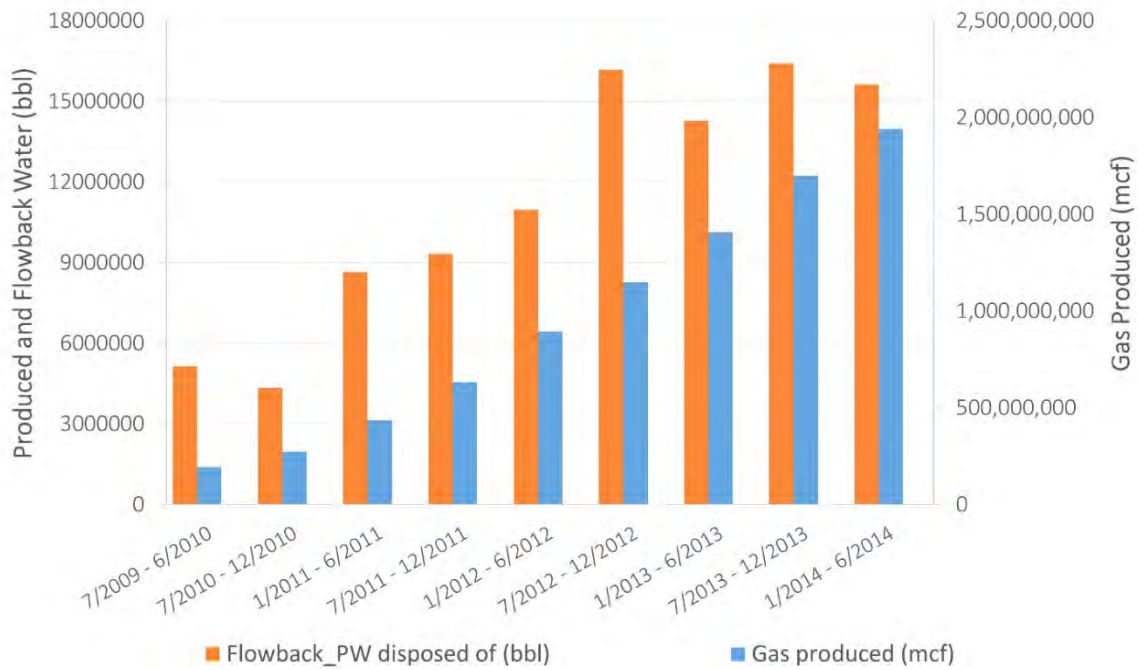

Figure 8-1. Produced and flowback water volumes and produced gas volumes from unconventional wells in Pennsylvania from July of 2009 through June of 2014.

Source: PA DEP (2015a).

Information presented in Chapter 7 highlights the initial rapid recovery of fluid in the first weeks after fracturing (see Figure 7-2), with a subsequent substantial reduction in the volume of water flowing through the well to the surface. This is followed by recovery of produced water during the longer-term productive phase of the well's life. One source 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 long-term produced water generated over a span of years, which may 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. Wells also generate some amount of drilling-fluid waste. Compared to

produced water, however, drilling wastewater can constitute a relatively small portion of the total wastewater produced (e.g., <10% in Pennsylvania during 2004-2013) (U.S. EPA, 2015q) and is not discussed further in this assessment.

In addition to variation in per-well wastewater volumes, aggregate wastewater production for an area or region will vary from year to year with hydraulic fracturing activity. For instance, the average annual volume of wastewater generated by all gas production (both shale gas and conventional) in Pennsylvania quadrupled from the 2001-2006 period to the 2008-2011 period. During the latter period, wastewater volume averaged 1.1 billion gal (26 million bbl or 4.2 billion L) per year (Wilson and Vanbriesen, 2012).

8.2.1. National Level Estimate

Clark and Veil (2009) estimated that in 2007, the approximately one million active oil and gas wells in the United States generated approximately 2.4 billion GPD (57.4 million bbl/day; 9.1 billion L/day) of wastewater; no newer comprehensive national-level estimate exists in the literature as of April 2015. Note that this estimate is not limited to wastewater from hydraulic fracturing operations. This national-level estimate is reported to represent total oil and gas wastewater (from conventional and unconventional resources, and from wells hydraulically fractured and wells not hydraulically fractured), but the authors note that it does not include the flowback water component. Although Clark and Veil (2009) conducted a state-by-state analysis, the report may have underestimated production due to significant data limitations: 1) data based on a timeframe preceding the dramatic increase in hydraulic fracturing activity seen in more recent years; 2) estimates based on data that were collected and maintained in a variety of ways, making data synthesis difficult; and 3) incomplete data (U.S. GAO, 2012).

8.2.2. Regional/State and Formation Level Estimates

The amount of wastewater generated in a given region varies widely depending upon the volume of wastewater generated per well and the number of wells in the area. The factors influencing wastewater production are discussed in Chapter 7, which also discusses differences among formations in volumes recovered during flowback and long-term water production. Table 7-2 provides rates of produced water generation for a number of formations in the United States.

At an aggregate level, wastewater volumes and geographic variability have been assessed for oil and gas production in several studies. A 2011 study by the Bureau of Land Management (BLM) (Guerra et al., 2011) states that more than 80% of oil and gas wastewater is generated in the western United States, including volumes from both conventional and unconventional resources. The BLM report notes substantial contributions from coalbed methane (CBM) wells, in particular those in the Powder River Basin (Wyoming). The authors state that Wyoming produces the second highest volume of water among the western United States. Guerra et al. (2011) also highlight the large portion of wells and wastewater associated with Texas (44% of U.S. produced water volume). 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 summarizes the findings for these western states, demonstrating the wide variability in wastewater

from state to state (likely reflecting differences in formation geology and oil and gas production activity).

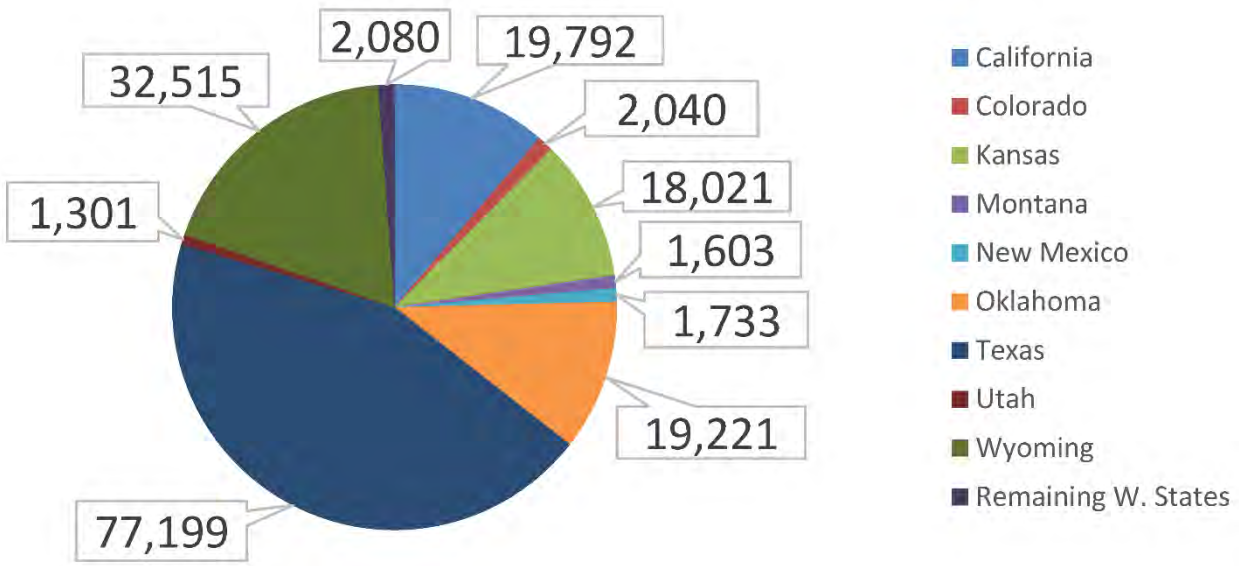

Figure 8-2. Wastewater quantities in the western United States (billions of gallons per year).

Source: Guerra et al. (2011).

Table 8-1 presents estimates of the numbers of wells and volumes of hydraulic fracturing wastewater generated in North Dakota, Ohio, Pennsylvania, Texas, and West Virginia. The data shown in this table come from publicly available state websites and databases; data for West Virginia reference a report by Hansen et al. (2013) that compiled available flowback data from West Virginia. The reported volumes have been summed by year. These states are represented in Table 8-1 because the produced water volumes were readily identifiable as associated with hydraulic fracturing activity. Differences in the years presented for the states are due to differences in data availability from the state agency databases. However, the increases in the numbers 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 2-12.

Several states with mature oil and gas industries (California, Colorado, New Mexico Utah, 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, and Wyoming) specify the producing formation along with volumes of hydrocarbons and produced water. New Mexico provides data for separate basins as well as for the entire state. 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. Appendix Table F-1 provides

estimates of wastewater volumes in these states 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 both for compiling a national estimate of hydraulic fracturing wastewater as well as comparing wastewater production among states due to dissimilar data types, presentation, and availability.

Table 8-1. Estimated volumes (millions of gallons) 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 water	-	-	-	-	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 water	-	-	-	92	340	410	350	210	Waste data from PA DEP.[c] 2nd half of 2010 and first half of 2014. Data described as unconventional as determined by formation. Separate codes are provided by PA DEP for flowback and produced water.
			Wells	-	-	-	*334*	*1,564*	*1,622*	*1,465*	*895*	
			Produced water	-	-	-	90	400	730	930	440	
			Wells	-	-	-	*1, 035*	*1,826*	*3,665*	*4,761*	*4,889*	

State	Basin	Principal Lithologies	Data Type	2000	2004	2008	2010	2011	2012	2013	2014	Comments
Pennsylvania cont.	Appalachian cont.	Shale, cont.	Flowback and produced water	-	-	-	180	740	1,100	1,300	650	
			Wells	-	-	-	*1,232*	*2,434*	*4,039*	*5,015*	*5,150*	
Texas	Unspecified (entire state)	Shale, Sandstone	Flowback water - 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 water - Estimated total disposed	-	-	-	120	110	59	-	-	Estimates from Hansen et al. (2013).

[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] Pennsylvania Department of Environmental Protection. PA DEP Oil and Gas Reporting Web site. 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 fluid injected for the past few years. (Data on brine volumes injected do not differentiate hydraulically fractured wells and are therefore not presented here.) These values are interpreted as estimates of generated flowback water as based on reported quantities of "fracture water flow back" injected into Class IID wells.

8.2.3. Estimation Methodologies and Challenges

Compiling and comparing data regarding wastewater production at the wide array of oil and gas locations in the United States presents challenges, and various approaches are used to estimate wastewater volumes, both at the state and national level. Data from state agency web sites and databases can be a ready source of information, whether publicly available and downloadable or provided directly by agencies upon request. However, due to sometimes significant differences in the types of data collected, mechanisms, formats, and definitions used, data cannot always be directly compared from state to state and can be difficult to aggregate at a national level. The inconsistences encountered in data searches for this assessment agree with recent conclusions by Malone et al. (2015), who noted inconsistences among 10 states with unconventional oil and gas activity in the accessibility, usability, completeness, accuracy, and cost of various types of data (e.g., wells drilled, production, waste, Class IID wells).

One challenge associated with using state production data to estimate the volume of wastewater nationally or regionally is the lack of consistency in data collection (U.S. GAO, 2012). Some states do not include a listing of wastewater (usually listed as produced water volumes) in their publicly available oil and gas production reports, while others do. State tracking of wastewater volumes may or may not include information that helps in determining 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) include information on disposal and management methods along with production data, and others do not.

Given these limitations, 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 will 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 flowback and 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 wells' 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 labeled by or 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 volume, wastewater characteristics are important for understanding the potential impacts of management and disposal of hydraulic fracturing wastewater on drinking water resources. Chapter 7 provides in-depth detail on produced water chemistry. This section provides brief highlights of the important features of wastewater composition as well as the characteristics of the residuals produced during wastewater treatment.

8.3.1. Wastewater

This section briefly discusses why the composition of hydraulic fracturing wastewaters needs to be considered when planning for wastewater management, especially if treatment or reuse are planned. Concerns associated with selected constituents are presented; treatment considerations associated with various wastewater constituents are included in Section 8.5.

8.3.1.1. Total Dissolved Solids and Inorganics

Wastewaters are generally high in total dissolved solids (TDS), especially waters from shale and tight sandstone formations, with values ranging from less than 1,000 mg/L to hundreds of thousands of mg/L (see Section 7.6.4 and Table 7-4). 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, 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 play, the minimum and maximum values shown in Table 7-4 suggest spatial variation 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 concentrations ranging from approximately 250 mg/L to 39,000 mg/L (Benko and Drewes, 2008; Van Voast, 2003) (see Appendix Table E-3). This results in fewer treatment challenges and a wider array of management options.

Although TDS has a secondary maximum contaminant level (MCL) (secondary MCLs are non-mandatory water quality standards) of 500 mg/L for aesthetic purposes, it is not considered a health-based contaminant and is therefore not regulated under the EPA's National Primary Drinking Water Regulations, although other standards may apply. For example, a maximum concentration of 500 mg/L has been used by the state of Pennsylvania for some industrial wastewater discharges. Constituents commonly found in TDS from hydraulic fracturing wastewaters may have potential impacts on health or create burdens on downstream drinking water treatment plants if discharged at high concentrations to drinking water resources. Bromide, for example, can contribute to the increased formation of disinfection by-products (DBPs) during drinking water treatment (Hammer and VanBriesen, 2012); see Section 8.6.1.

Metals (e.g., barium, cadmium, chromium, lead, copper, manganese, nickel, thallium, and zinc) present in TDS can be toxic to humans and aquatic life at certain concentrations. Health effects of these metals can include kidney damage, liver damage, skin conditions, high blood pressure, and developmental problems (U.S. EPA, 2015i). To ensure safe drinking water, the EPA has established

primary MCLs for a number of these constituents. MCLs and action levels for these metals vary from 0.002 mg/L for thallium to 1.3 mg/L for copper (U.S. EPA, 2015i). Cadmium has been found in produced water from tight gas formations at concentrations as high as 0.37 mg/L (the MCL is 0.005 mg/L), and chromium has been found at concentrations up to 0.265 mg/L (the MCL is 0.1 mg/L) (see Table 7-4).

Other constituents of concern among dissolved solids are chloride, sulfate, barium, and boron. Elevated concentrations of chloride and sulfate are of concern because of drinking water aesthetics, and the EPA has established secondary MCLs for both chloride and sulfate of 250 mg/L (U.S. EPA, 2015i; Hammer and VanBriesen, 2012). Barium has a primary MCL of 2 mg/L and has been found in some shale gas produced waters at concentrations in the thousands of mg/L (see Table 7-4). Boron is not regulated under the National Primary Drinking Water Regulations, but internal plant specifications for one CWT (e.g., the Pinedale Anticline Facility) and waste discharge requirements (WDR) permit for another (e.g., San Ardo Water Reclamation Facility) limit boron effluent concentrations to 0.75 mg/L (Shafer, 2011; Webb et al., 2009).

8.3.1.2. Organics

Less information is available about organic constituents in hydraulic fracturing wastewaters than about inorganic constituents, but there are several studies that include some analyses of organic constituents. The organic content in flowback waters can vary based on the chemical additives used and the formation but generally consists of polymers, oil and grease, volatile organic compounds (VOCs), and semi-volatile organic compounds (SVOCs) (Walsh, 2013; Hayes, 2009). Examples of other constituents detected include alcohols, naphthalene, acetone, and carbon disulfide (U.S. EPA, 2015i) (see Appendix Table E-10). Wastewater associated with CBM wells may have high concentrations of aromatic and halogenated organic contaminants that that may require treatment depending on how the wastewater will be managed or disposed of (Pashin et al., 2014; Sirivedhin and Dallbauman, 2004). Concentrations of BTEX (benzene, toluene, ethylbenzene, and xylenes), in CBM produced waters are, however, lower than in shale produced waters (see Appendix Table E-9).

Certain organic compounds are of concern in drinking water because they can cause damage to the nervous system, kidneys, and/or liver and can increase the risk of cancer if ingested over a period of time (U.S. EPA, 2006). Some organics in chemical additives are known carcinogens, including 2-butoxyethanol (2BE), naphthalene, benzene, and polyacrylamide (Hammer and VanBriesen, 2012). Many organics are regulated for drinking water under the National Primary Drinking Water Regulations. Section 8.6.4 provides further discussion of documented or potential situations in which organic constituents have or might reach drinking water resources.

8.3.1.3. Radionuclides

Radionuclides are constituents of concern in some hydraulic fracturing wastewaters, with most available data obtained for the Marcellus Shale in Pennsylvania (see Appendix Table E-8). Results from a USGS report (Rowan et al., 2011) indicate 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. There are limited data on radionuclides in wastewater from formations other than the Marcellus Shale, but information on the naturally

occurring radioactive material (NORM) in the formations themselves, in particular uranium and thorium, may suggest the potential for high levels of radionuclides in produced water, especially where TDS concentrations are also high. Sections 7.5.4 and 7.6.6 provide further information on radionuclides in formations and in produced waters.

The primary radioactive contaminants found in hydraulic fracturing wastewaters (radium, gross alpha radiation, and gross beta radiation) can increase the risk of cancer if consumed at elevated levels over time (U.S. EPA, 2015i). Therefore, the EPA has established drinking water MCLs for combined radium (radium-226 plus radium-228), gross alpha, and gross beta of 5 pCi/L, 15 pCi/L, and 4 millirems/year, respectively (see Section 8.6.2).

8.3.2. Constituents in Residuals

Depending on the water being treated and treatment processes used, treatment residuals may consist of sludges, spent media (used filter materials), or brines. Residuals can include constituents such as total suspended solids (TSS), TDS, metals, radionuclides, and organics. The treatment process tends to concentrate wastewater constituents in the residuals. As an illustration of the degree of concentration that can take place, processes such as electrodialysis and mechanical vapor recompression have been found to yield residuals streams with TDS concentrations in excess of 150,000 mg/L, from treating waters with influent TDS concentrations of approximately 50,000 – 70,000 mg/L (Hayes et al., 2014; Peraki and Ghazanfari, 2014).

Also, technologically enhanced naturally occurring radioactive material (TENORM) in wastewaters may cause residual wastes to have elevated gamma radiation emissions (Kappel et al., 2013).[1] One study calculated that typical solids produced by precipitation processes designed to remove barium and strontium from Marcellus Shale wastewater would contain between 2,571 and 18,087 pCi/g of radium in the barium sulfate precipitate (Zhang et al., 2014b). Another similar study using mass balances calculated that sludge from a sulfate precipitation process would average a radium concentration of 213 pCi/g in sludge (Silva et al., 2012). Silva et al. (2012) estimated a radium-226 concentration of 58 pCi/g in sludge from lime softening processes, a level that would necessitate disposal of low level radioactive waste.

8.4. Wastewater Management Practices

Operators have several strategies for management of hydraulic fracturing wastewaters (see Figure 8-3), with the most common choice being disposal via Class IID wells (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 CWT (often followed by reuse), evaporation (in arid regions), or in some cases, depending on state and local requirements, various other wastewater management strategies (e.g., irrigation, which involves no discharge to waters of the U.S.). The management methods shown in Figure 8-3 represent various strategies, not all of which will happen together.

[1] Technologically enhanced naturally occurring radioactive materials (TENORM) are radionuclides that have been concentrated or enhanced as the result of human activity.

At one time, treatment of unconventional oil and gas wastewaters at publicly owned treatment works (POTWs) was a common practice for wastewater management in the Marcellus region (Lutz et al., 2013). However, this practice has been essentially discontinued following a request from PA DEP that, by May 19, 2011, oil and gas operators stop sending Marcellus Shale wastewater to 15 POTWs and CWTs that discharged to surface waters (U.S. EPA, 2015h).

Each of these wastewater management strategies may potentially lead to an impact on drinking water resources during some phase of their execution. Such impacts may include accidental releases during transport (see Chapter 7), discharges of treated wastewaters from CWTs or POTWs where treatment for certain constituents has been inadequate, migration of constituents in wastewaters that have been applied to land, leakage from on-site storage pits (see Chapter 7), inappropriate management of residuals (e.g., leaching from landfills or land application), or accumulation of constituents in sediments near outfalls of CWTs or POTWs that have treated hydraulic fracturing wastewater.

A reliable census of nationwide wastewater management practices is difficult to assemble due to a lack of consistent and comparable data among states, but Table 8-2 illustrates the variability in the primary wastewater management methods using available qualitative and quantitative sources. Disposal via underground injection predominates in most regions. Reuse is most prevalent in the Appalachian Basin in Pennsylvania. Moderate reuse occurs in the Arkoma (OK, AR) and Anadarko (OK, TX) basins, and use of CWTs occurs predominantly in Pennsylvania.

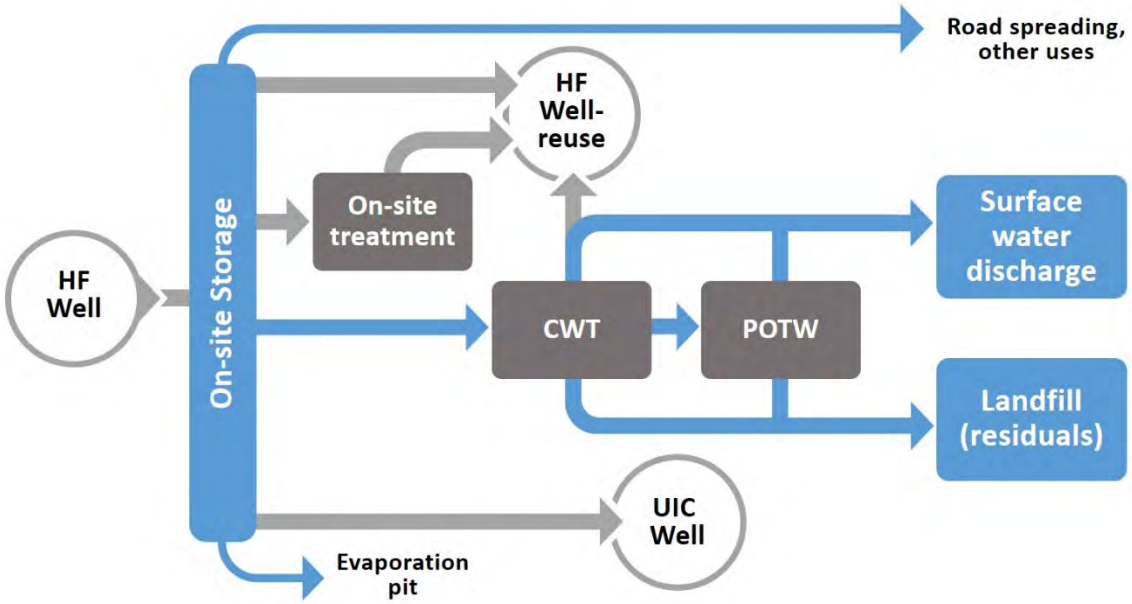

Figure 8-3. Schematic of wastewater management strategies.

Table 8-2. Hydraulic fracturing wastewater management practices in recent years.

Source: (U.S. EPA, 2015q).

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 Class IID 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 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 Class IID wells; new CWT facilities are under construction	Mixed
Fort Worth	Barnett	Shale Gas	X	XXX	X[a]	Reuse not typically effective due to high TDS early in flowback and abundance of Class IID 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 not typically cost effective due to high TDS early in flowback and abundance of Class IID wells	Mixed

Basin	Formation	Resource type	Reuse	Injection for disposal	CWT facilities	Notes	Available data[b]
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
Williston	Bakken	Shale Oil	X	XXX		Reuse limited but is being evaluated	Mixed

[a] CWT facilities in these formations are operator owned.

[b] This column indicates the type of data on which EPA based the number of X's. In most cases, EPA used a mixture of qualitative and quantitative data sources along with engineering judgment to determine the number of X's.

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.

Management choices are affected by cost and a number of other factors, including the chemical properties of the wastewater; the volume, duration, and flow rate of the water generated; the logistical feasibility of various options; the availability of necessary infrastructure; federal, state, and local regulations; and operator discretion (U.S. GAO, 2012; NPC, 2011a). The economics (such as transport, storage, and disposal costs) and availability of various treatment and disposal methods are of primary importance (U.S. GAO, 2012). For example, as of early 2015, Pennsylvania has nine operating Class IID wells within the state, whereas Texas has nearly 7,900 (U.S. EPA, 2015q).

The availability and use of management strategies may change in a region over time as oil and gas development increases or decreases, changing the volumes of wastewater that need to be handled on a local, state, and regional level (see Text Box 8-1 for more information on hydraulic fracturing wastewater management in Pennsylvania). Figure 8-4 illustrates shifting wastewater management practices in Pennsylvania over the last several years as shale gas development has proceeded in the Marcellus Shale. On-site reuse (labeled as "Reuse HF" in Figure 8-4) has grown. Also, most CWT management of Marcellus wastewater in recent years has been at zero-discharge facilities (i.e., for reuse) (an estimated 80% in 2012 and 90% in 2013) (PA DEP, 2015a). Combined with the volumes managed via on-site reuse, Pennsylvania reuse rates are approximately 85% to 80%. In contrast, wastewater disposal data for Colorado (see Figure 8-5) show a steady use of injection wells (injected on lease) since 2000, and an apparent decrease in the use of onsite pits (state data were filtered for formations indicated in the literature to be targets for hydraulic fracturing).

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, 2014c). This production increase has led to larger volumes of wastewater that require appropriate management (Vidic et al., 2013; Gregory et al., 2011; Kargbo et al., 2010). The rapid increase in wastewater generated from oil and gas wells used for hydraulic fracturing has led to many changes in the wastewater disposal practices in the oil and gas industry. Changes have been most evident in Pennsylvania, which has experienced more than a 1,400% increase in natural gas production since 2000 (EIA, 2014c).

Lutz et al. (2013) estimated that total wastewater generation in the Marcellus region increased 570% between 2004 and 2013 and concluded that this increase has created stress on the existing wastewater disposal infrastructure. In 2010, in response to concerns over elevated TDS in the Monongahela River basin and studies linking high TDS (and in particular high bromide levels) to elevated DBP levels in drinking water systems (PA DEP, 2011a), PA DEP amended Chapter 95 Wastewater Treatment Requirements under the Clean Streams Law for new discharges of TDS in wastewaters. This regulation is also known informally as the 2010 TDS regulation. The regulation disallowed any new indirect discharges (i.e., discharges to POTWs) of hydraulic fracturing waste and set limits of treated discharges from 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 requested that oil and gas well operators transporting unconventional wastewater to the eight CWTs and seven POTWs that were exempt from the 2010 TDS regulation voluntarily stop discharging to these facilities. 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 (PA DEP, 2011a).

Between early 2011 and late 2011, although reported wastewater flows more than doubled, Marcellus drilling companies in Pennsylvania reduced their wastewater flows to CWTs that were exempt from the 2010 TDS regulation by 98%, and discharge to 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 has increased, POTW treatment volumes have decreased, tracking of wastewater has improved, and wastewater transportation distances have decreased (Rahm et al., 2013). Maloney and Yoxtheimer (2012) analyzed data from 2011 and found that reuse of flowback water increased to 90% by volume. Disposed flowback water comprised 8% of the total volume. Brine water, which was defined as formation water, was reused (58%), disposed via injection well (27%), or sent to industrial waste treatment plants (14%). Of all the fluid wastes in the analysis, brine water was most likely to be transported to other states (28%). They also concluded that wastewater disposal to municipal sewage treatment plants declined nearly 100% from the first half of 2011 to the second half.

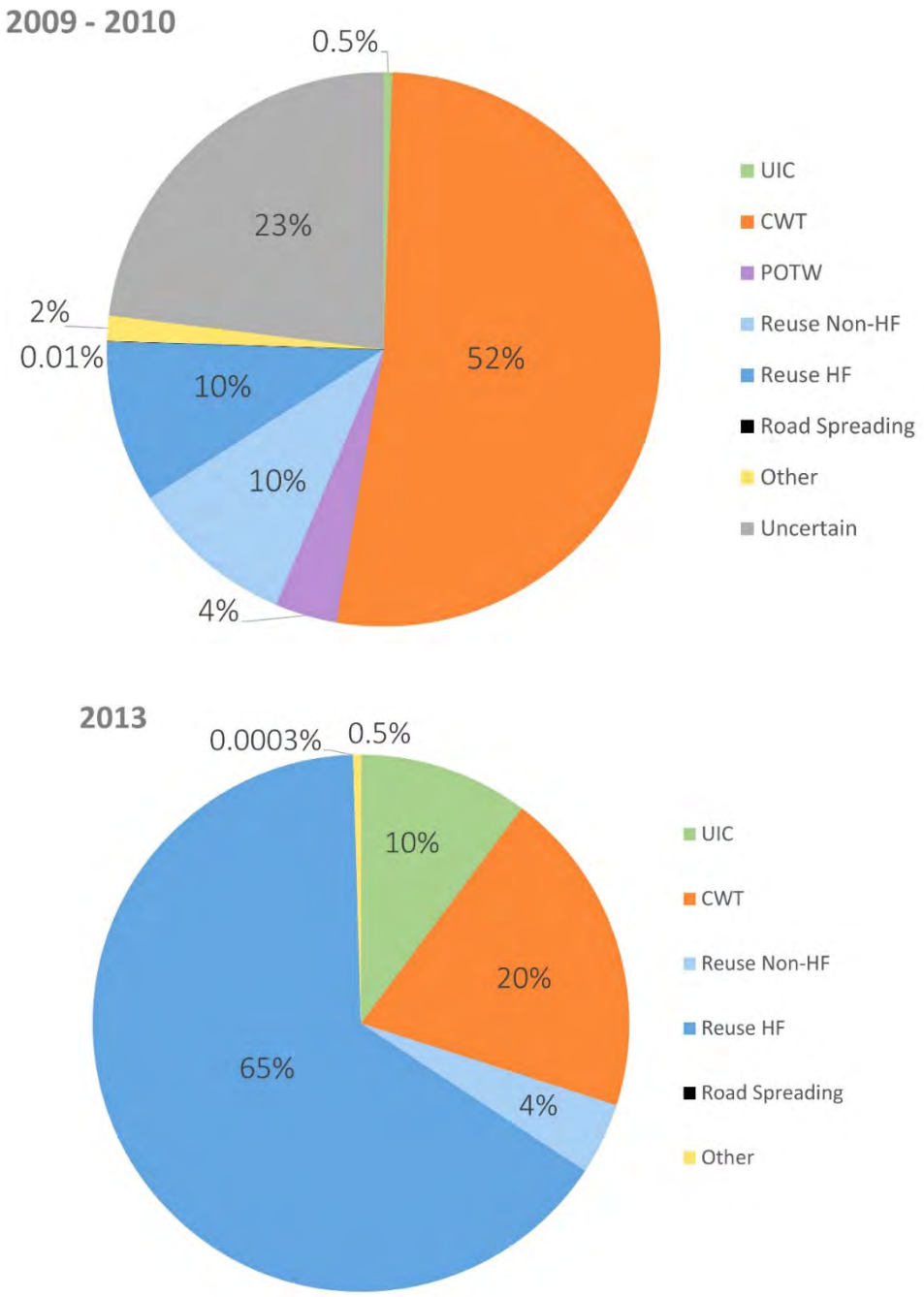

Figure 8-4. Percentages of Marcellus Shale wastewater managed via various practices for (top) the second half of 2009 and first half of 2010 (total estimated volume of 216 Mgal), and (bottom) 2013 (total estimated volume of 1.3 billion gallons).

"Reuse HF" indicates on-site reuse. Source: Waste data from PA DEP (2015a).

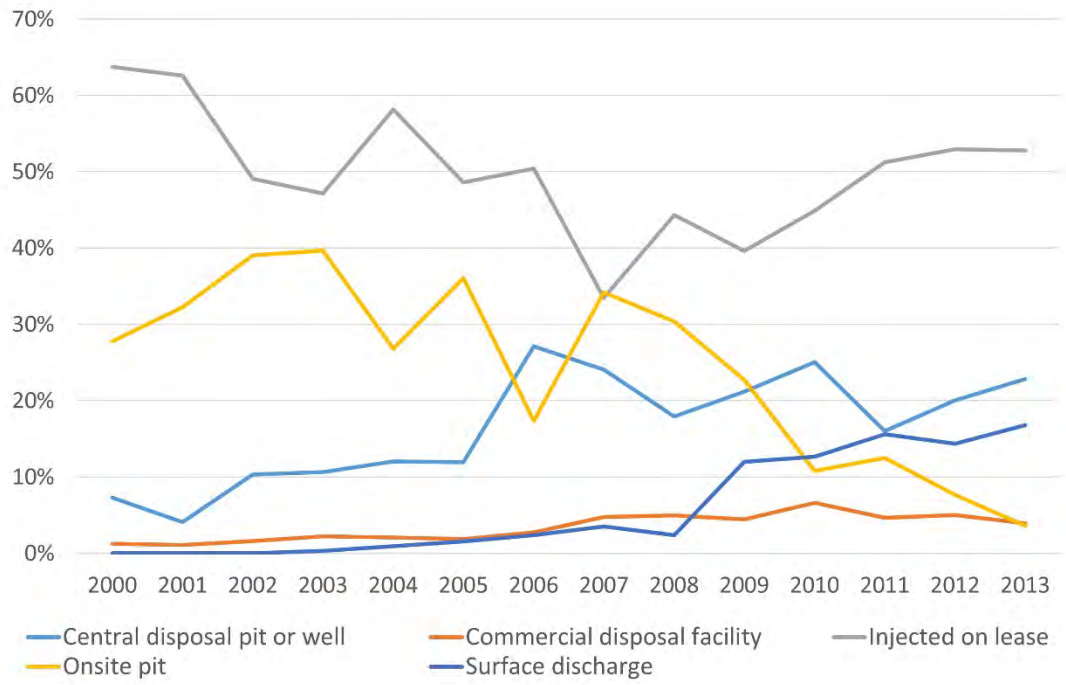

Figure 8-5. Management of wastewater in Colorado in regions where hydraulic fracturing is being performed.

Source: Production data from COGCC (2015).

Regulations also affect management options and vary geographically. At the Federal level, existing oil and gas effluent limitations guidelines and standards (ELGs) can be found under 40 CFR Part 435. These ELGs apply to conventional and unconventional oil and gas extraction facilities in various subcategories (e.g., Offshore, Onshore, Stripper Wells), with the exception of CBM discharges, which are not subject to the existing regulations. Subpart C, the Onshore subcategory, prohibits the discharge of wastewater pollutants to waters of the U.S. from onshore oil and gas extraction facilities. This "zero-discharge standard" means that oil and gas produced water pollutants cannot be directly discharged to surface waters. Operators have met these regulations through underground injection, reuse, or transfer of produced water to POTWs and/or CWTs. West of the 98th meridian (the arid western portion of the continental United States), discharges of wastewater from onshore oil and gas extraction facilities may be permitted for direct discharge to waters of the U.S. if the produced water has a use in agriculture or wildlife propagation when discharged into navigable waters. Definitions in 40 CFR 435.51(c) explain that 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 such use during periods of discharge. The regulations at 40 CFR 435.52 specify that the only allowable discharge is produced water, with an oil and grease concentration not exceeding 35 milligrams per liter (mg/L). The regulations prohibit the discharge of waste pollutants into navigable waters from any source (other than produced water) associated with

production, field exploration, drilling, well completion, or well treatment (i.e., drilling muds, drill cuttings, produced sands).

Unpermitted discharges of wastes related to hydraulic fracturing have been described in a number of instances. In Pennsylvania, discharges of brine into a storm drain that 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.

The following section provides an overview of hydraulic fracturing wastewater management methods, with some discussion of the geographic and temporal variations in practices. Discussion is provided on common treatment and disposal methods including on-site storage, underground injection, CWTs, reuse of hydraulic fracturing fluids, and evaporation methods. This section also provides discussion on past treatment of hydraulic fracturing wastewater at POTWs. Other management practices are also covered. Brief descriptions of treatment technologies applicable to hydraulic fracturing wastewater are available in Appendix F.

8.4.1. Underground Injection

Oil and gas wastewater may be disposed of via Class II injection wells regulated under the Underground Injection Control (UIC) Program under the Safe Drinking Water Act (SDWA)[1]. Class II wells include those used for enhanced oil recovery (IIR), disposal (IID), and hydrocarbon storage (IIH). Nationwide, injection wells dispose of a large fraction of wastewater from the oil and gas industry, including wastewater associated with hydraulic fracturing. A 2009 study notes that the oil and gas industry in the United States generated about 882 billion gal (21 billion bbl or 3.34 trillion L) of produced water in 2007 (Clark and Veil, 2009). More than 98% of this volume was managed via some form of underground injection, with 40% injected into Class II wells. However, 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 on data injection volumes specific to hydraulic fracturing operations that are compiled and able to be compared among states. Also, wastewater management methods are not well tracked in all states. Regional numbers of Class IID wells and generally low reuse rates (see Section 8.4.3), however, are consistent with Class IID wells being a primary means of wastewater management in many areas with hydraulic fracturing activity.

This assessment does not address whether there are documented or potential impacts on drinking water resources associated with the injection of hydraulic fracturing wastewaters into Class IID wells. However, should the feasibility of managing hydraulic fracturing wastewater via

[1] States may be given federal approval to run a UIC program under Section 1422 or 1425 of SDWA.

underground injection be limited in any way or become less economically advantageous, operators will likely adjust their wastewater management programs to favor other local practices such as treatment and discharge or reuse. Any new wastewater management decisions would then have to be evaluated in terms of potential impacts on drinking water resources.

The decision to inject hydraulic fracturing wastewater into Class IID wells depends, in part, on cost and on the proximity of the production well to the disposal well (and, therefore, transportation costs). For oil and gas producers, underground injection is usually the least expensive management strategy unless significant trucking is needed to transport the wastewater to a disposal well (U.S. GAO, 2012).

Class IID wells are not distributed uniformly among states due to differences in geology (including depth and permeability of formations), permitting, and historical demand for disposal of oil and gas wastewater. Table 8-3 shows the numbers of active Class IID wells across the United States, with the total count at a little over 27,000. The greatest numbers of wells are found in Texas, Oklahoma, and Kansas. For example, Texas has nearly 7,900 Class IID wells, with an estimated daily disposal volume of approximately 400 million gal per day (MGD) (1.5 billion L/day) (see Table 8-3). This large disposal capacity in Texas 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, Class IID wells are a relatively small portion of Marcellus wastewater management in Pennsylvania (about 10% in 2013 and the first half of 2014) (PA DEP, 2015a) because the state has nine injection wells as of early 2015. Wastewater is generally transported out of state when being managed through injection into Class IID wells. The local availability of Class IID wells and the capacity to accept large volumes of wastewater may begin to be affected by recent state actions concerning seismic activity associated with injection (U.S. EPA, 2014f).

Table 8-3. Distribution of active Class IID wells across the United States.

Source: U.S. EPA (2015q)**.**

State	Nearby basins with hydraulic fracturing	Number of active Class IID wells (2012-2014)	Average disposal rate per well (GPD/well)[a]	Total state disposal rate (MGD)

State	Nearby basins with hydraulic fracturing	Number of active Class IID wells (2012-2014)	Average disposal rate per well (GPD/well)[a]	Total state disposal rate (MGD)
AK	North Slope	45	182,000	8.2
OH	Appalachian	188	8,900	1.7
WV		66	7,180	0.47
PA		9	6,380	0.057
NY		10[b]	3,530	0.035
VA		12	17,500	0.21
TN		0	0	0
MD		0	0	0
NC	Multiple basins	0	0	0
KS	Cherokee, Anadarko, Arkoma	5,516	20,900	120
OK		4,622[c]	35,900	170
AR		611[d]	30,900	19
MO		11	1,270	0.014
CO	Denver-Julesburg, Green River, Piceance, Uinta	294	50,200	15
WY		330	-- [e]	-- [e]
UT		109	74,400	8.1
NE		113	18,100	2.0
TX	Fort Worth, Western Gulf, Permian, San Juan, Raton	7,876	54,200	430
NM		736	48,600	36
IN	Illinois	183	3,580	0.66
IL		1,054	-- [e]	-- [e]
KY		58	1,750	0.10
MI	Michigan	779[c]	16,600	13
CA	San Joaquin	826	77,800	64

State	Nearby basins with hydraulic fracturing	Number of active Class IID wells (2012-2014)	Average disposal rate per well (GPD/well)[a]	Total state disposal rate (MGD)
LA	TX-LA-MS Salt	2,448	42,100	100
MS		499	69,500	35
AL		85	44,200	3.8
ND	Williston	395	31,600	12
MT		199	31,100	6.2
SD		21	10,200	0.21
All other states (NV, FL, OR, IA, and WA)[f]		42	89,400	3.8
Total (not including missing states)		27,137	40,400	1,040

[a] Typical injection volumes per well are based on historical annual volumes for injection for disposal divided by the number of active Class IID wells during the same year (primarily data from 2007 to 2013).
[b] These wells are not currently permitted to accept unconventional oil and gas extraction wastewater.
[c] With the exception of Oklahoma and Michigan, wells on tribal lands have not been intentionally included. Wells on tribal lands may be counted if state databases contained them.
[d] Only 24 of the 611 active Class II wells in Arkansas are in the northern half of the state, close to the Fayetteville formation.
[e] Disposal rates and/or number of Class IID wells is unknown.
[f] These are states that have minimal oil and gas activity. The number of wells shown for these states may include all types of Class II wells (e.g., Class II enhanced recovery wells) and therefore is an upper estimate. All other states not listed in this table have minimal oil and gas activity and no active Class IID wells.

8.4.2. Centralized Waste Treatment Facilities

A CWT facility is generally defined as a facility that accepts industrial materials (hazardous, non-hazardous, solid, or liquid) generated at another facility (off-site) for treatment and/or recovery (EPA, 2000). (A POTW treats local municipal wastewater.) As a group, CWTs that accept oil and gas wastewater offer a wide variety of treatment capabilities and configurations. The fate of treated effluent at CWTs also varies, and can include the following: reuse in fracturing operations, direct discharge (to a receiving water under a National Pollution Discharge Elimination System (NPDES) permit), indirect discharge (to a POTW), or a combination of these. Zero discharge facilities do not discharge to either surface water or a POTW; effluent is generally used for reuse, although evaporation or land application may also be done. Some CWTs may be configured so that they only partially treat the waste stream if allowed by the end use (a reuse application that does not require TDS removal). Potential impacts on drinking water resources associated with treatment in CWTs will depend upon whether the CWT treats adequately for constituents of concern prior to discharge to surface water or to a POTW, and whether treatment residuals are managed appropriately.

Clean Water Act (CWA) regulations only apply to facilities that discharge treated wastewater to surface waters or POTWs. For zero-discharge facilities, Pennsylvania and Texas have adopted

regulations to control permitting. PA DEP issues permits (General Permit WMGR123) 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 Table 8-7 as an example of a zero-discharge facility[1]). The Texas Railroad Commission (TXRRC) regulates and categorizes wastewater recycling facilities into different categories: off-lease commercial recycling facilities (capable of being moved from one location to another) and stationary commercial recycling facilities. The Texas regulations also promote oil and gas wastewater treatment for reuse and water sharing (see http://www.rrc.state.tx.us/rules/rule.php).

Wastewater from hydraulically fractured wells can be transported by truck or pipeline to and from a CWT (Easton, 2014); this may present a vulnerability for spills or leaks (see Chapter 7). The treated wastewater from CWTs may be integrated with other sources of water (for example, treated municipal wastewater, storm water drainage, or other treated industrial waste streams) for reuse applications (Easton, 2014).

8.4.2.1. Numbers and Locations of CWTs

Although there are CWTs serving hydraulic fracturing operations throughout the country, including the Barnett and Fayetteville shale plays plus oil fields in Texas and Wyoming, historically the majority have served Marcellus Shale operations. This is likely because the low availability of injection wells (Boschee, 2014) in Pennsylvania necessitates other forms of management. An EPA study (U.S. EPA, 2015q) identified 73 CWT facilities that have either accepted or plan to accept hydraulic fracturing wastewater (see Table 8-4). Of these, 39 are located in Pennsylvania. Most of these are zero-discharge facilities; they do not discharge to surface waters or POTWs, and they often do not include TDS removal. According to EPA research (U.S. EPA, 2015q), the number of CWT facilities serving operators in the Marcellus and Utica Shales has increased since the mid-2000s as the number of wells drilled in the Marcellus and Utica Shales has increased, growing from roughly five CWTs 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 wells available relative to the rest of the state (U.S. EPA, 2015q).

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 are available to treat wastewater from the Eagle Ford (beginning in 2011 and 2013), both equipped with TDS removal, and one zero-discharge facility with TDS removal is located in the Barnett Shale region (operational beginning in 2008). In Wyoming, the four facilities in the region of the Mesaverde/Lance formations (operations beginning between 2006 and 2012; two zero-discharge and two with multiple discharge options) are all capable of TDS removal (U.S. EPA, 2015q).

[1] The facility is also permitted for indirect discharge to the Williamsport Sewer Authority.

Table 8-4. Number, by state, of CWT facilities that have accepted or plan to accept wastewater from hydraulic fracturing activities.

Source: U.S. EPA (2015q).

State	Formation(s) served where hydraulic fracturing occurs	Zero-discharge CWT facilities[a]		CWT facilities that discharge to surface water or POTW[a]		Discharging CWT facilities with multiple discharge options[a]		Total known facilities
		Non-TDS removal treatment	TDS removal treatment	Non-TDS removal treatment	TDS removal treatment	Non-TDS removal treatment	TDS removal treatment	
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	23	7 (3)	6	0	0	3 (1)	39
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, Lance	0	2	0	0	0	2	4
Total		45	13	7	0	1	7	73

[a] Number of facilities also includes facilities that have not yet opened but are under construction, pending permit approval, or in the planning stages. Facilities that are not accepting process wastewater from hydraulic fracturing activities but plan to in the future are noted parenthetically.

Because few states maintain a comprehensive list of CWT facilities and the count provided by the EPA (U.S. EPA, 2015q) includes facilities that plan to accept unconventional oil and gas wastewaters, the data in Table 8-4 do not precisely reflect the number of facilities currently available for handling hydraulic fracturing wastewaters. Additional discussion of CWTs in unconventional oil and gas fields are reviewed in the literature for areas including the Barnett (Hayes and Severin, 2012b) and the Fayetteville (Veil, 2011) as well as other oil fields in Texas and Wyoming (Boschee, 2014, 2012). In addition, news releases and company announcements indicate that new wastewater treatment facilities are being planned (Greenhunter, 2014; Geiver, 2013; Purestream, 2013; Alanco, 2012; Sionix, 2011).

Based on oil and gas waste disposal information available from PA DEP (PA DEP, 2015a) dating back to 2009, the estimated volumes of Marcellus wastewater sent to CWTs range from approximately 113 Mgal (428 million L) in the latter half of 2009 and first half of 2010, to about 183 Mgal (693 million L) in 2011, and about 252 Mgal (954 million L) in 2013. These constitute about 52% of the total wastewater volume in 2009-2010, about 25% in 2011, and 20% in 2013, indicating that although total amounts of wastewater have increased (see Table 8-1), the percentage managed through CWTs has decreased.

Among the Marcellus wastewater sent to CWTs, an estimated 35% was sent to zero-discharge facilities in Pennsylvania (those with general permits) in the latter half of 2010, and 42% was sent to facilities with NPDES permits (indicating that they can discharge to surface waters). About 23% went to CWTs whose permit types were more difficult to ascertain, generally outside of Pennsylvania. By 2013, the portion sent to zero-discharge facilities had risen to 90%, with about 5% sent to CWTs with NPDES permits and 5% sent to CWTs whose discharge permit type is not clear. The high percentage sent to zero-discharge CWTs is consistent with the concerted focus on reuse in Pennsylvania, although CWTs with NPDES permits also often provide treated wastewater for reuse, further limiting discharges to surface waters. The waste records do not indicate if a CWT has more than one permit type.

8.4.2.2. Residuals Management

Certain treatment processes at CWTs produce liquid or solids residuals as a by-product of that process. The residuals produced depend on the constituents in the treated water and the treatment process used. Residuals can consist of sludges (from precipitation, filtration, settling units, and biological processes); spent media (media requiring replacement or regeneration from filtration, adsorption, or ion exchange processes); concentrated brines (from membrane processes and some evaporation processes); and regeneration and cleaning chemicals (from ion exchange, adsorption, and membrane processes) (Fakhru'l-Razi et al., 2009). Residuals from CWTs can constitute a considerable fraction of solid waste in an oil or gas production area. Chiado (2014) found that solid wastes from hydraulic fracturing in the Marcellus accounted for 5% of the weight of waste deposited in landfills in the area, with some area landfills reaching as high as 60% landfill mass coming from hydraulic fracturing activities.

Management of Solid Residuals

CWTs may apply additional treatment 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 applied, or incinerated (Morillon et al., 2002). Pollutants may accumulate in sludge, which may limit land application as a disposal option. For example, wastes containing TENORMs can be problematic due to the possibility of radon emissions from the landfill (Walter et al., 2012). In some states, many landfills that are specifically permitted to accept TENORM have criteria written into their permits, including gamma exposure rate (radiation) levels and radioactivity concentration limits. Most non-hazardous landfills have limits on maximum radiation that can be accepted. For example, Pennsylvania requires alarms to be set at all municipal landfills, with a trigger set at 10 μR/hr above background radiation (Pa Code Title 25, Ch. 273.223

c). 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 (TX Code Ch 4 Section F Section 4.620). Some states have volumetric limitations on TENORM in their permits (e.g., Colorado).

Solid residual wastes have the potential to impact the quality of drinking water resources if contaminants leach to groundwater or surface water. In a recent study by PA DEP, radium was detected in leachate from 34 of 51 landfills, with radium-226 concentrations ranging from 54 to 416 pCi/L, and radium-228 ranging from 2.5 to 1,100 pCi/L (PA DEP, 2015b). Countess et al. (2014) studied the potential for barium, calcium, sodium, and strontium to leach from sludges generated at a CWT handling hydraulic fracturing wastewaters in Pennsylvania. Tests used various strong acid solutions (to simulate the worst case scenario) and weak acid digestions (to simulate environmental conditions). The extent of leaching varied by constituent and by fluid type; the data illustrate the possibility of leaching of these constituents from landfills.

Management of Liquid Residuals

Practices for management of liquid residual streams are generally the same as for untreated hydraulic fracturing wastewaters, although the reduced volumes tend to lower costs (Hammer and VanBriesen, 2012). Concentrations of contaminants, however, will be higher. Liquids mixed with other wastes can be disposed of in landfills if the liquid concentration is low enough. 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 (e.g., drinking water utilities) (see Section 8.6). Because some constituents of concentrated residuals can pass through or impact municipal wastewater treatment processes (Linarić et al., 2013; Hammer and VanBriesen, 2012), these residuals may not be appropriate for discharge to a POTW. Elevated salt concentrations, in particular, can reduce or inhibit microbiological treatment at municipal wastewater systems such as activated sludge treatment (Linarić et al., 2013).

8.4.3. Water Reuse for Hydraulic Fracturing

Water reuse in hydraulic fracturing operations has increased in recent years, with wastewaters being used to formulate hydraulic fracturing fluids for subsequent fracturing jobs (Boschee, 2014, 2012; Gregory et al., 2011; Rassenfoss, 2011). Wastewater may be reused after some form of treatment (sometimes only settling), depending on the reuse water quality requirements, and it may be supplied for use in hydraulic fracturing through various routes. Reused water is discussed in Chapter 4 of this report (Water Acquisition) as well as in this chapter, though in a different context. The water reuse rate described in this chapter is the amount or percentage of generated wastewater that is managed by being provided to operators for use in additional 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.

Hydraulic fracturing wastewater reuse reduces costs associated with other forms of wastewater management, and the economic benefits and feasibility of reuse can be expected to figure into ongoing wastewater management decisions. However, although reuse minimizes other forms of wastewater management on a local and short-term basis (e.g., those involving direct or indirect

discharge to surface waters), reuse can result in the accumulation of dissolved solids (e.g., salts and TENORMs) as the process returns water to the subsurface. For example, data from a PA DEP study (PA DEP, 2015b) suggests that hydraulic fracturing fluids that include reused wastewater already contain radium-226 and radium-228. Eventually, wastewaters with a component that has been reused more than once will need to be definitively managed, either through treatment or injection. Residuals from treatment will also require proper management to avoid potential impacts on water resources (see Section 8.4.2.2) (Kappel et al., 2013).

8.4.3.1. Factors in Considering Reuse

In making the decision whether to manage wastewater via reuse, operators have several factors to consider (Slutz et al., 2012; NPC, 2011a):

- Wastewater generation rates compared to water demand for future fracturing operations,
- Wastewater quality and treatment requirements for use in future operations,
- The costs and benefits of wastewater management for reuse compared with other management strategies,
- Available infrastructure and treatment technologies, and
- Regulatory considerations.

Among these factors, costs may be the most significant driver, weighing the costs of transportation from the generating well to the treatment facility and to the new well against the costs for transport to alternative locations (a disposal well or CWT). Trucking large quantities of water can be relatively expensive (from $0.50 to $8.00 per barrel), rendering on-site treatment technologies and reuse potentially economically competitive in some settings (Dahm and Chapman, 2014; Guerra et al., 2011). Also, logistics, including proximity of the water sources for aggregation, may be a factor in implementing reuse. For example, 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.

Regulatory factors may facilitate reuse. In 2013, the Texas Railroad Commission adopted rules intended to encourage statewide water conservation. These rules facilitate reuse by eliminating the need for a permit when operators reuse on their own lease or transfer the fluids to another operator for use in hydraulic fracturing (Rushton and Castaneda, 2014). Data for the years after 2013 will allow evaluation of whether reuse increases.

Recommended compositional ranges for base fluid may shift in the future as fracturing fluid technology continues to develop. Development of fracturing mixture additives that are brine-tolerant have allowed for the use of high TDS wastewaters (up to tens of thousands of mg/L) for reuse in fracturing (Tiemann et al., 2014; GTI, 2012; Minnich, 2011). Some new fracturing fluid systems are claimed to be able to tolerate salt concentrations exceeding 300,000 mg/L (Boschee, 2014). This greater flexibility in acceptable water chemistry can facilitate reuse both logistically and economically by reducing treatment needs. Additional discussion of the water quality feasible for reuse and examples of recommended constituent concentrations are included in Appendix F.

Reuse rates may also fluctuate with changes in the supply and demand of treated wastewater and the availability of fresh water. Flowback may be preferable to later-stage produced water for reuse because 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. Flowback water also tends to have lower TDS concentrations than later-stage produced water; in the Marcellus, TDS has been shown to increase from tens of thousands to about 100,000 mg/L during the first 30 days (Barbot et al., 2013; Maloney and Yoxtheimer, 2012) (see Chapter 7). The changing production rate and quality of wastewaters generated in a region as more wells go into production need to be taken into account, as well as possible decreases in the demand for reused water as plays mature (Lutz et al., 2013; Hayes and Severin, 2012b; Slutz et al., 2012).

8.4.3.2. Reuse Rates

Reliable information on reuse practices throughout the United States is hampered by a limited amount of data that are available and represent different regions of the country. In Table 8-5, estimates have been compiled from various literature sources. Reuse rates are highest in the Appalachian Basin, associated primarily with the Marcellus Shale. Documentation of reuse practices is also more readily available for that region than for other parts of the country.

A number of studies have estimated reuse rates for Marcellus wastewater. Although the reported values can differ substantially (see Table 8-5), the data point to a steep increase in reuse since 2008, with rates increasing from 0% to 10% in 2008 to upwards of 90% in 2013. As an example, an analysis of waste disposal information from the PA DEP for Marcellus wells in Pennsylvania (Hansen et al., 2013) reports an increase in reuse from 9% (7.17 million gal or 27.1 million L) of total wastewater volumes in 2008 to 56% (343.79 million gal or 1.3014 billion L) in 2011. During that same timeframe, the authors report that disposal via brine/industrial waste treatment plants increased from 32% in 2008 to 70% in 2009, and then declined to 30% in 2011. Because some industrial waste treatment plants can treat wastewater for reuse, some of the volumes indicated by Hansen et al. (2013) as managed by this route may have ultimately been used for fracturing, meaning that the 56% value for 2011 is most likely an underestimate.

Table 8-5. Estimated percentages of reuse of hydraulic fracturing wastewater.

Play or Basin	Source and Year	2008	2009	2010	2011	2012	2013
East Coast							
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, WV	Hansen et al. (2013)			88	73	65 (partial year)	
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
Marcellus, PA	Rassenfoss (2011)			~67 overall (general estimate) 96 (one specific 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, PA	Rahm and Riha (2014)				55-80 (general estimate – appears to cover recent years)		
Gulf Coast & Midcontinent							
Fayetteville	Veil (2011)			20 (single company target)			
West Permian	Nicot et al. (2012)				0		
Midland Permian	Nicot et al. (2012)				2		
Anadarko	Nicot et al. (2012)				20		
Barnett	Nicot et al. (2012)				5		
Barnett	Rahm and Riha (2014)				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	Argonne National Laboratory (2014)						0
Haynesville	Rahm and Riha (2014)				5 (general estimate – appears to cover recent years)		
West Coast & Upper Plains							
Bakken	Argonne National Laboratory (2014)						0

According to Maloney and Yoxtheimer (2012), about 331 million gal (7.9 million bbl or 1.25 billion L) of flowback and about 381 million gal (about 9.1 million bbl or 1.4 billion L) of produced water (excluding flowback) were generated in the Marcellus in 2011. For flowback and produced water

combined, about 72% was reused. Of the flowback, 90% was managed through reuse (other than road spreading). Of produced brine water, 55.7% was reused (with 11.6% treated in CWTs and 27.8% injected into Class IID wells in Ohio). Reuse is higher in the northeastern part of the Marcellus; in the southwestern portion, easier access to Class IID wells in Ohio makes disposal by injection more feasible (Rahm et al., 2013).

Data from Marcellus wastewater management reports submitted to PA DEP (PA DEP, 2015a) were compiled for this assessment; the data suggest that rates of reuse for hydraulic fracturing (as indicated by a waste disposal method of either "Reuse Other than Road Spreading" or a zero-discharge CWT) increased from about 28% in the second half of 2010 to about 60% in 2011, 83% in 2013, and 89% in the first half of 2014. These values may be underestimates because wastewater treated at facilities with NPDES permits can be provided to operators for reuse, and the permit types for some facilities could not be determined. Among the forms of reuse, on-site reuse ("Reuse Other than Road Spreading") has risen steadily over the past few years, from about 8% in the second half of 2010 to about 48% in 2011, 62% in 2012, and nearly 70% in the first half of 2014.

Outside of the Marcellus region, a lower percentage of wastewater from hydraulic fracturing operations is reused. According to published literature, in Texas in 2011, 0% to 5% of wastewater was reused in most basins, with the exception of the Anadarko Basin (20%) (Nicot and Scanlon, 2012); see Table 8-5. 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) (Argonne National Laboratory, 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; Colorado Water Conservation Board; Colorado Oil and Gas Conservation Commission, 2014). The fact sheet discusses piping and trucking wastewater to CWTs in the Piceance Basin to treat for reuse.

8.4.4. Evaporation

In drier climates of the western United States, natural evaporation may be an option for treatment of hydraulic fracturing wastewater (see Figure 8-6). Production data from the California Department of Conservation's Division of Oil, Gas, and Geothermal Resources (DOGGR) (California Department of Conservation, 2015), for example, lists "evaporation-percolation" as the management method for 23% to 30% of the wastewater from Kern County over the last few years. However, data on volumes of wastewater managed are not readily available for all states where this practice is employed.

Evaporation is a simple water management strategy that consists of transporting wastewater to a pond or pit with a large surface area and allowing passive evaporation of the water from the surface (Clark and Veil, 2009). The rate of evaporation depends on the quality of the wastewater as well as the size, depth, and location of the pond. Evaporation also depends on local humidity, temperature, and wind (NETL, 2014). The residual brine or solid can be disposed of in an underground injection well or landfill (see Section 8.4.3.2 for more details). In colder, dry climates, a freeze-thaw

evaporation method has been used to purify water from oil and gas wastewater (Boysen et al., 1999).

Figure 8-6. Lined evaporation pit in the Battle Creek Field (Montana).

Source: DOE (2006). Permission from ALL Consulting.

Alternatively, operators may transport wastewater by truck to an off-site commercial facility. Commercial evaporation facilities exist in Colorado, Utah, New Mexico, and Wyoming (NETL, 2014; DOE, 2004). Nowak and Bradish (2010) described 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 bbl or 320 million L). The Utah facility, open since 2009, consists of 13 ponds with a total capacity of 218.4 million gal (5.2 million bbl or 826.7 million L). Each facility receives 420,000 to 1.47 million gal (10,000 to 35,000 bbl or 1.6 million to 5.56 million L) per day of wastewater from oil and gas production companies in the area. Evaporation pits are subject to state regulatory agency approval and must meet state standards for water quality and quantity (Boysen et al., 2002). Impacts on drinking water resources from evaporation pits might arise if a pit is breached due to extreme weather or other factors affecting infrastructure and if leaking wastewater reaches a surface water body; such events as related specifically to evaporation pits appear not to have not been evaluated in the literature, and their prevalence is unknown.

8.4.5. Publicly Owned Treatment Works

Prior to the development of unconventional resources, POTWs were used to treat wastewater and other wastes from conventional oil and gas operations in some eastern states. Although this is not a common treatment method for oil and gas wastes in the United States, the small number 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 continued to be used to treat wastewater, including wastes originating from new unconventional oil and gas wells (Kappel et al., 2013; Soeder and Kappel, 2009). However, unconventional wastewater from the Marcellus region is difficult to treat at POTWs due to elevated concentrations of halides, heavy metals, organic compounds, radionuclides, and salts (Lutz et al., 2013; Schmidt, 2013). Most of these constituents have the potential to pass through the unit treatment processes commonly used in POTWs and can be discharged into receiving waters (Cusick, 2013; Kappel et al., 2013). In addition, research has found that sudden, extreme salt fluctuations can disturb POTW biological treatment processes (Linarić et al., 2013; Lefebvre and Moletta, 2006). In order to meet NPDES requirements, POTWs used to blend the hydraulic fracturing wastewater with incoming municipal wastewater. For example, Ferrar et al. (2013) note that, per PA DEP requirements, one facility could only accept up to 1% of their influent volume from unconventional oil and gas wastewater per day.

The annual reported volume of oil and gas produced wastewater treated at POTWs in the Marcellus Shale region peaked in 2008 and has since declined to virtually zero (see Figure 8-7). This decline has been attributed to stricter discharge limits for TDS for POTWs in Pennsylvania and widespread voluntary compliance on behalf of oil and gas operators with the May 2011 request from PA DEP to cease sending Marcellus Shale wastewater to 15 treatment plants (including both POTWs and CWTs) by May 19, 2011 (Rahm et al., 2013). To comply with the request, the oil and gas industry in Pennsylvania accelerated the transition of wastewater deliveries from POTWs to CWTs for better removal of metals and suspended solids (Schmidt, 2013). However, treated effluent from CWTs may be delivered to POTWs for additional treatment assuming treatment processes at POTWs are not adversely affected and the POTWs can continue to meet NPDES discharge limits (Hammer and VanBriesen, 2012). General Pretreatment Regulations and State and local regulations typically govern the pre-treated water volumes and qualities that can be accepted by the POTW.

Although operators stopped sending Marcellus Shale wastewater to POTWs in May of 2011, conventionally produced wastes have continued to be processed at POTWs in Pennsylvania, although at small volumes (29 Mgal and 20 Mgal for the years 2010 and 2011, respectively) (Wilson and Vanbriesen, 2012).

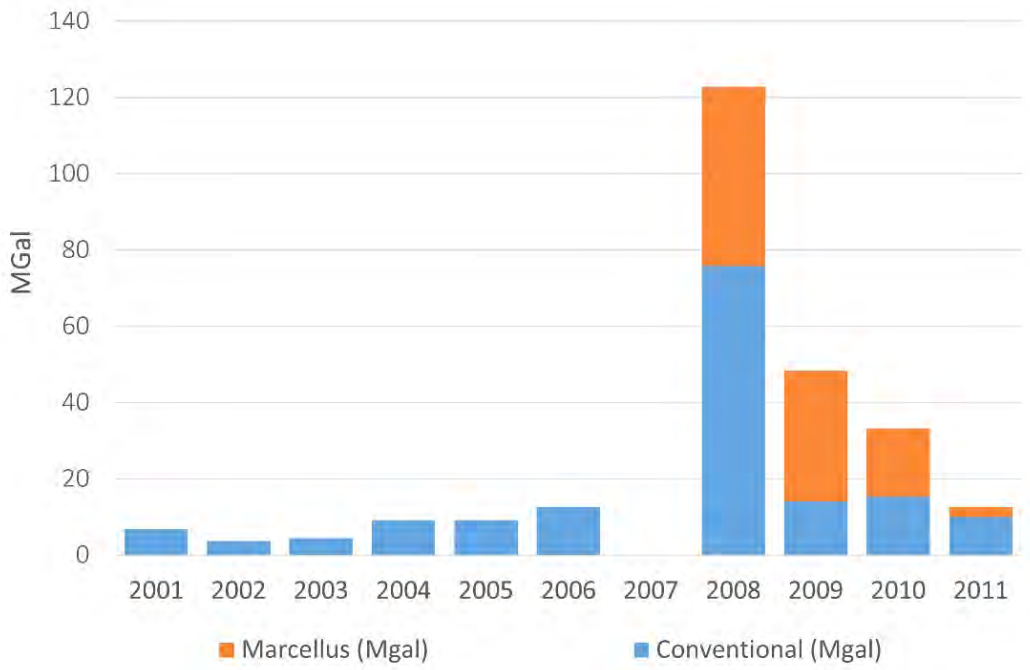

Figure 8-7. Oil and gas wastewater volumes discharged to POTWs from 2001-2011 in the Marcellus Shale.

Source: Lutz et al. (2013).

At least one study has evaluated POTW effluent chemistry before and after the cessation of treatment of hydraulic fracturing wastewater. Ferrar et al. (2013) collected effluent samples from two POTWs and one CWT facility in Pennsylvania before and after the 2011 PA DEP request. Results from POTW effluent samples collected while the facilities were still treating Marcellus Shale wastewater showed that concentrations of several analytes (barium, manganese, strontium, TDS, and chloride) were greater than various drinking water and surface water criteria (i.e., EPA MCLs and secondary MCLs for drinking water, surface water quality standards for aquatic life, and/or surface water standards for human consumption of aquatic organisms). Results for effluent samples collected after the POTWs stopped receiving Marcellus wastewater showed a statistically significant decrease in the concentrations of several of these constituents. In particular, one of the two POTWs showed a decrease in average barium concentration from 5.99 mg/L to 0.141 mg/L, a decrease in the average strontium concentration from 48.3 mg/L to 0.236 mg/L, and a decrease in the average bromide concentration from 20.9 mg/L to <0.016 mg/L. Influent concentrations at the other POTW were lower (0.55 mg/L for barium, 1.63 mg/L for strontium, and 0.60 for bromide), but significant decreases in these constituents were also seen in the effluents (0.036 mg/L barium, 0.228 mg/L strontium, and 0.119 for bromide); this POTW had continued to accept conventional oil and gas wastewater. The authors conclude that the decreases in the concentrations of the various constituents indicate that the elevated concentrations in the first samplings can be attributed to the contribution of wastewater from unconventional natural gas development.

8.4.6. Other Management Practices and Issues

Additional strategies for wastewater management in some states include discharging to surface waters and land application. Wastewater from CBM fracturing and production, in particular, generally has lower TDS concentrations than wastewater from other types of unconventional plays and lends itself more readily to beneficial use. Below is a discussion of these other management practices.

8.4.6.1. Land Application, Including Road Spreading

Land application has been done using brines from conventional oil and gas production. Road spreading can be done for dust control or de-icing. Although recent data are not available, an American Petroleum Institute (API) survey estimated that approximately 75.6 million gal (1.8 million bbl or 286 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 wells for dust control or 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 concentration (for radium and sodium, respectively), attributed to road spreading of wastewater from conventional oil and gas wells for de-icing purposes (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, or migration of brines to groundwater. Snowmelt may carry salts or other chemicals from the application site, with the possibility of transport increasing 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 ground water in the northern United States; by the 1990s, 24% of public supply wells in the Chicago area had chloride concentrations exceeding 100 mg/L (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 ground water (531 ppm in winter and 1,360 ppm in

summer (Bair and Digel, 1990). The amount of salt contributed to drinking water resources due to road application of hydraulic fracturing wastewaters has not been quantified.

In managing solid wastes from oil and gas production, a study on land application of oilfield scales and sludges suggested that radium in samples became more mobile after incubation with soil under moist conditions, due to microbial processes and interactions with the soil and water (Matthews et al., 2006). Overall, potential effects from land application on drinking water resources are not well understood.

Additionally, drill cuttings must be managed; in some places they are left in the reserve pit (pit for waste storage), allowed to dry and, buried on-site (Kappel et al., 2013). More, commonly, however, drill cuttings are disposed of in landfills (Chiado, 2014); about half of Marcellus drill cuttings are disposed of in Pennsylvania, while the rest are trucked to Ohio or West Virginia (Maloney and Yoxtheimer, 2012).

8.4.6.2. Management of Coalbed Methane Wastewater

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 (e.g., lower TDS content) than wastewater from other hydraulically fractured wells, which 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 requirements of the intended use (Hulme, 2005; DOE, 2003, 2002). Although specific volumes managed through the various practices below are not well documented, qualitative information and considerations for feasibility are available and presented below.

CBM wastewater quality, which can range from an average of nearly 1,000 mg/L TDS in the Powder River Basin to an average of about 4,700 mg/L in the San Juan Basin (see Appendix Table E-3), plays a large role in how the wastewater is managed. In basins with higher TDS such as the San Juan, Uinta, and Piceance, nearly all the wastewater is disposed of in injection wells. Wastewater may also be injected for aquifer storage and recovery, with the intention of later recovering the water for some other use (DOE, 2003).

Discharge to rivers and streams for wildlife, livestock, and agricultural use, a management option governed by the CWA, may be permitted in some cases. To be discharged, the wastewater must meet technology-based limitations established by the permit authority and any applicable water quality water quality standards. Direct discharge to streams (with or without treatment) is possible where wastewater is of higher quality. This is a more common method of wastewater management in basins such as the Raton Basin in Colorado and the Tongue River drainage of the Powder River Basin in Montana (NRC, 2010).

Agricultural uses include livestock watering, crop irrigation, and commercial fisheries. Livestock watering with CBM wastewater is a common practice, and irrigation is an area of active research (e.g., Engle et al., 2011; NRC, 2010). Irrigation with treated CBM 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. Approximately 13% of CBM wastewater in the Powder River Basin in Wyoming, and 26% to 30% in Montana, is used for irrigation (NRC, 2010).

As noted above, a degree of treatment is needed for some uses. Plumlee et al. (2014) examined the feasibility, treatment requirements, and cost 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 CBM wastewater for stream augmentation or crop irrigation was estimated to cost between $0.26 and $0.27 a barrel and disposal costs ranged from $0.01 per barrel (pipeline collection system with impoundment) to $2.00 per barrel (hauling for disposal or treatment).

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, in western states, senior water rights claims in over-appropriated basins, may also determine use of CBM wastewater (Wolfe and Graham, 2002).

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 sand tight sand formations ranging from less than 1,000 mg/L TDS to hundreds of thousands of mg/L TDS (DOE, 2006). Wastewaters on the lower end of the TDS spectrum could be reused in many of the same ways as CBM wastewaters, 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).

Documented potential uses for wastewater in the western United States include livestock watering, irrigation, supplementing stream flow, fire protection, road spreading, and industrial uses, with each having their own water quality requirements and applicability (Guerra et al., 2011). Guerra et al. summarized the least conservative TDS standards for five possible uses in the western United States that include 500 mg/L for drinking water (the secondary MCL), 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 treatment for TDS removal based on a maximum TDS concentration of 10,000 mg/L. Wastewater from 10% of unconventional wells were estimated to meet the criterion of 1,000 mg/L TDS for surface water discharge (Guerra et al., 2011).

A 2006 Department of Energy (DOE) study points out that the quality necessary for use in agriculture depends on the plant or animal species involved. Other important factors include the sodium adsorption ratio and concentrations of TDS, calcium, magnesium, and other constituents

(DOE, 2006). The authors note 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).

8.5. Summary and Analysis of Wastewater Treatment

A variety of individual treatment techniques and combinations of techniques may be employed for removal of hydraulic fracturing wastewater constituents of concern. These include methods commonly employed in municipal wastewater treatment as well as more advanced processes such as desalination. Treatment technologies are selected based on the water quality of the wastewater to be treated and the effluent concentration required for the intended management method(s) (i.e., reuse, discharge to POTW, and discharge to surface water body). For example, if reuse is planned, the level of treatment will depend on the water quality needed to formulate the new fracturing fluid.

This section discusses treatment technologies that are most effective for removing specific hydraulic fracturing wastewater constituents. It provides information on the unit processes appropriate for treating different types of constituents as well as challenges associated with their use. Considerations when designing a treatment system are also discussed for both centralized and on-site (i.e., mobile) facilities.

8.5.1. Overview of Treatment Processes for Hydraulic Fracturing Wastewater

This section provides a brief overview of the treatment technologies used to treat hydraulic fracturing wastewater; Appendix F provides more in-depth descriptions of these technologies.

The most basic treatment need for oil and gas wastewaters, including those from hydraulic fracturing operations is separation to remove suspended solids and oil and grease, done using basic separation technologies (e.g., hydrocyclones, dissolved air or induced gas flotation, media filtration, or biological aerated filters). Other treatment processes that may be used include media filtration after chemical precipitation for hardness and metals (Boschee, 2014), adsorption technologies, including ion exchange (organics, heavy metals, and some anions) (Igunnu and Chen, 2014), a variety of membrane processes (microfiltration, ultrafiltration, nanofiltration, RO), and distillation technologies. In particular, advanced processes such as RO or distillation methods (e.g., mechanical vapor recompression (MVR)) are needed for significant reduction in TDS (Drewes et al., 2009; LEau LLC, 2008; Hamieh and Beckman, 2006). An emerging technology is electrocoagulation, which has been used in mobile treatment systems to treat hydraulic fracturing wastewaters (Halliburton, 2014; Igunnu and Chen, 2014). Removal efficiencies for hydraulic fracturing wastewater constituents by treatment technology are provided in Appendix F.

8.5.2. Treatment of Hydraulic Fracturing Waste Constituents of Concern

The constituents prevalent in hydraulic fracturing wastewater include suspended solids, TDS, anions (e.g., chloride, bromide, and sulfate), metals, radionuclides, and organic compounds (see Section 8.3 and Chapter 7). If the end use of the wastewater necessitates treatment, a variety of technologies can be employed. This section discusses effective unit processes for removing these constituents and provides examples of treatment processes being used in the field as well as

emerging technologies. Table 8-6 provides an overview of influent and effluent results at various CWTs for the constituents of concern listed in this section and the specific technology(ies) used to remove them.

Table 8-6. Studies of removal efficiencies and influent/effluent data for various processes and facilities.

Constituents of concern	Location and results				
	Pinedale Anticline Water Reclamation Facility, Wyoming (Shafer, 2011)	**Maggie Spain Water-Recycling Facility, Barnett Shale, Texas (Hayes et al., 2014)**	**Judsonia, Sunnydale, Arkansas (U.S. EPA, 2015f)**	**9-month study treating Marcellus Shale waste using thermal distillation (Boschee, 2014; Bruff and Jikich, 2011)**	**San Ardo Water Reclamation Facility, San Ardo, California (Conventional oil and gas) (Dahm and Chapman, 2014; Webb et al., 2009)**
TSS	Results not reported.	90% Inf. = 1,272 mg/L Eff. = 9 mg/L Chemical oxidation, coagulation, and clarification	No influent data. Eff.: <4 mg/L Meets NPDES Permit Settling, biological treatment, and induced gas flotation	>90% Inf.: 35 to 114 mg/L Eff.: <3 to 3 mg/L 100 micron mesh bag filter	Results not reported.
TDS	>99% Inf. = 8,000 to 15,000 mg/L Eff. = 41 mg/L RO	99.7% Inf. = 49,550 mg/L Eff. = 171 mg/L MVR (3 units in parallel)	Results not reported. MVR	98% Inf.: 22,350 to 37,600 mg/L Eff.: 9 to 400 mg/L Thermal distillation	97% Inf. = 7,000 mg/L Eff. = 180 mg/L Ion exchange softening and double-pass RO

Constituents of concern	Location and results				
	Pinedale Anticline Water Reclamation Facility, Wyoming (Shafer, 2011)	**Maggie Spain Water-Recycling Facility, Barnett Shale, Texas (Hayes et al., 2014)**	**Judsonia, Sunnydale, Arkansas (U.S. EPA, 2015f)**	**9-month study treating Marcellus Shale waste using thermal distillation (Boschee, 2014; Bruff and Jikich, 2011)**	**San Ardo Water Reclamation Facility, San Ardo, California (Conventional oil and gas) (Dahm and Chapman, 2014; Webb et al., 2009)**
Anions	Chloride: >99% Inf. = 3,600 to 6,750 mg/L Eff. = 18 mg/L Sulfate: 99% Inf. = 10 to 100 mg/L Eff. = non-detect RO	Sulfate: 98% Inf. = 309 mg/L Eff. = 6 mg/L Chemical oxidation, coagulation, clarification, and MVR	Sulfate: No influent data. Eff.: 12 mg/L Meets NPDES Permit MVR	Bromide: >99% Inf.: 101 to 162.5 mg/L Eff.: <0.1 to 1.6 mg/L Chloride: 98% Inf.: 9,760 to 16,240 mg/L Eff.: 2.9 to 184.2 mg/L Sulfate: 93% Inf.: 20.4 to <100 mg/L Eff.: <1 to 2.2 mg/L	Chloride: >99% Inf. = 3,400 mg/L Eff. = 11 mg/L Double-pass RO Sulfate: 6% Inf. = 133 mg/L Eff. = 125 mg/L
				Fluoride: 96% Inf.: <2 to <20 mg/L Eff.: <0.2 to 0.42 mg/L Thermal distillation	Sulfuric acid is added after RO to neutralize the pH so no sulfate removal is expected.

Constituents of concern	Location and results				
	Pinedale Anticline Water Reclamation Facility, Wyoming (Shafer, 2011)	**Maggie Spain Water-Recycling Facility, Barnett Shale, Texas (Hayes et al., 2014)**	**Judsonia, Sunnydale, Arkansas (U.S. EPA, 2015f)**	**9-month study treating Marcellus Shale waste using thermal distillation (Boschee, 2014; Bruff and Jikich, 2011)**	**San Ardo Water Reclamation Facility, San Ardo, California (Conventional oil and gas) (Dahm and Chapman, 2014; Webb et al., 2009)**
Metals	Boron: 99% Inf. = 15 to 30 mg/L Eff. = non-detect Ion exchange	Iron: >99% Inf. = 28 mg/L Eff. = 0.1 mg/L For iron, 90% attributed to chemical oxidation, coagulation, and clarification Boron: 98% Inf. = 17 mg/L Eff. = 0.4 mg/L Barium: >99% Inf. = 15 mg/L Eff. = 0.1 mg/L Calcium: >99% Inf. = 2,916 mg/L Eff. = 3.2 mg/L	Cobalt: No influent data. Eff.: <0.007 mg/L Tin: No influent data. Eff.: <0.1 mg/L Arsenic: No influent data. Eff.: <0.001 mg/L Cadmium: No influent data. Eff.: <0.0001 mg/L Chromium: No influent data. Eff.: <0.007 mg/L Copper: No influent data. Eff.: <0029 mg/L	Copper: >99% Inf. = <0.2 to <1.0 mg/L Eff. = <0.02 to <0.08 mg/L Zinc: inf below detect Inf. = <0.2 to <1.0 mg/L Eff. = <0.02 to 0.05 mg/L Barium: >99% Inf. = 260.5 to 405.5 mg/L Eff. = <0.1 to 4.54 mg/L Strontium: 98% Inf. = 233 to 379 mg/L Eff. = 0.026 to 3.93 mg/L Iron: Inf. = 13.9 to 22.9 mg/L Eff. = <0.02 to 0.06 mg/L Manganese: 98% Inf. = 2 to 2.9 mg/L Eff. = <0.02 to 0.04 mg/L	Sodium: 98% Inf. = 2,300 mg/L Eff. = 50 mg/L Boron: >99% Inf. = 26 mg/L Eff. = 0.1 mg/L RO with elevated influent pH

Constituents of concern	Location and results				
	Pinedale Anticline Water Reclamation Facility, Wyoming (Shafer, 2011)	**Maggie Spain Water-Recycling Facility, Barnett Shale, Texas (Hayes et al., 2014)**	**Judsonia, Sunnydale, Arkansas (U.S. EPA, 2015f)**	**9-month study treating Marcellus Shale waste using thermal distillation (Boschee, 2014; Bruff and Jikich, 2011)**	**San Ardo Water Reclamation Facility, San Ardo, California (Conventional oil and gas) (Dahm and Chapman, 2014; Webb et al., 2009)**
Metals, cont.		Magnesium: >99% Inf. = 316 mg/L Eff. = 0.4 mg/L Sodium: >99% Inf. = 10,741 mg/L Eff. = 14.3 mg/L Strontium: >99% Inf. = 505 mg/L Eff. = 0.5 mg/L MVR	Lead: No influent data. Eff.: <0.001 mg/L Mercury: No influent data. Eff.: <0.005 mg/L Nickel: No influent data. Eff.: 0.002 mg/L Silver: No influent data. Eff.: <0.0002 mg/L Zinc: No influent data. Eff.: 0.02 mg/L Cyanide: No influent data. Eff.: <0.01 mg/L Meets NPDES permit except for TMDLs for hexavalent chromium and mercury	Boron: 97% Inf. = <1 to 3.12 mg/L Eff. = 0.02 to 0.06 mg/L Calcium: 98% Inf. = 1,175 to 1,933 mg/L Eff. = 0.36 to 22.2 mg/L Lithium: 99% Inf. = 9.1 to 14.3 mg/L Eff. = non-detect to 0.13 mg/L Magnesium: 98% Inf. = 109.8 to 176.8 mg/L Eff. = <0.1 to 2.04 mg/L Sodium: 98% Inf. = 4,712 to 7,781 mg/L Eff. = 0.37 to 87.9 mg/L Arsenic: 82% Inf. = <0.01 to 0.028 mg/L Eff. = <0.005 mg/L Titanium: 86% Inf. = <0.01 to 0.037 mg/L Eff. = <0.005 mg/L	

Constituents of concern	Location and results				
	Pinedale Anticline Water Reclamation Facility, Wyoming (Shafer, 2011)	**Maggie Spain Water-Recycling Facility, Barnett Shale, Texas (Hayes et al., 2014)**	**Judsonia, Sunnydale, Arkansas (U.S. EPA, 2015f)**	**9-month study treating Marcellus Shale waste using thermal distillation (Boschee, 2014; Bruff and Jikich, 2011)**	**San Ardo Water Reclamation Facility, San Ardo, California (Conventional oil and gas) (Dahm and Chapman, 2014; Webb et al., 2009)**
Metals, cont.			Settling, biological treatment, induced gas flotation, and MVR	Thermal distillation	
Radio-nuclides	Results not reported.	Results not reported.	Not regulated under permit – believed to be absent.	Radium-226: 97% - 99% Inf. = 130 to 162 pCi/L Eff. = 0.224 to 2.87 pCi/L Radium-228: 97% - 99% Inf. = 45 to 85.5 pCi/L Eff. = 0.259 to 1.32 pCi/L Gross Alpha: 97% - >99% Inf. = 161 to 664 pCi/L Eff. = 0.841 to 6.49 pCi/L Gross Beta: 98% - >99% Inf. = 79.7 to 847 pCi/L Eff. = 0.259 to 1.57 pCi/L Thorium 232: 71% - 90% Inf. = 0.055 to 0.114 pCi/L Eff. = 0.011 to 0.016 pCi/L Thermal distillation	Results not reported.

Constituents of concern	Location and results				
	Pinedale Anticline Water Reclamation Facility, Wyoming (Shafer, 2011)	**Maggie Spain Water-Recycling Facility, Barnett Shale, Texas (Hayes et al., 2014)**	**Judsonia, Sunnydale, Arkansas (U.S. EPA, 2015f)**	**9-month study treating Marcellus Shale waste using thermal distillation (Boschee, 2014; Bruff and Jikich, 2011)**	**San Ardo Water Reclamation Facility, San Ardo, California (Conventional oil and gas) (Dahm and Chapman, 2014; Webb et al., 2009)**
Organics	O&G: 99% Inf. = 50 to 2,400 mg/L Eff. = non-detect BTEX: 99% Inf. = 28 to 80 mg/L Eff. = non-detect Gasoline range organics: RO: 99% Inf. = 88 to 420 mg/L Eff. = non-detect Diesel range organics: 99% Inf. = 77 to 1,100 mg/L Eff. = non-detect Methanol: 99% Inf. = 40 to 1,500 mg/L Eff. = non-detect Oil-water separator, anaerobic and aerobic biological treatment, coagulation, flocculation, flotation, sand filtration, membrane bioreactor, and ultrafiltration	TPH: >80% Inf. = 388 mg/L Eff. = 4.6 mg/L BTEX: 94% Inf. = 3.3 mg/L Eff. = 0.2 mg/L TOC: 48% Inf. = 42 mg/L Eff. = 22 mg/L MVR	Biochemical oxygen demand: No influent data. Eff.: <2 mg/L O&G: No influent data. Eff.: <5 mg/L Benzo (k) fluoranthene: No influent data. Eff.: <0.005 mg/L Bis (2-Ethylhexyl) Phthalate: No influent data. Eff.: <0.001 mg/L Butyl benzyl phthalate: No influent data. Eff.: <0.001 mg/L Meets NPDES permit Settling, biological treatment, induced gas flotation, and MVR	Acetone: 93% Inf. = 8.71 to 13.8 mg/L Eff. = 0.524 to 0.949 mg/L Toluene: >80% Inf. = 0.0083 to 0.0015 mg/L Eff. = non-detect to 0.0013 mg/L Methane: >99% Inf. = 0.748 to 5.49 mg/L Eff. = non-detect to 0.0013 mg/L DRO: 0 to 82% Inf. = 4 to 7.1 mg/L Eff. = 0.99 to 4.9 mg/L O&G: No removal Thermal distillation	Results not reported.

8.5.2.1. Total Suspended Solids

The reduction of TSS is typically required for reuse. Hydraulic fracturing wastewaters containing suspended solids can plug the well and damage equipment if reused for other fracking operations (Tiemann et al., 2014; Hammer and VanBriesen, 2012). For treated water that is discharged, the EPA has a secondary treatment standard for POTWs that limits TSS in the effluent to 30 mg/L (30-day average). In addition, most advanced treatment technologies require the removal of TSS prior to treatment to avoid operational problems such as membrane fouling/scaling and to extend the life of the treatment unit. TSS can be removed by several processes, such as coagulation, flocculation, sedimentation, and filtration (including microfiltration and media and bag and/or cartridge filtration), and with hydrocyclones, dissolved air flotation, freeze-thaw evaporation, electrocoagulation, and biological aerated filters (Boschee, 2014; Igunnu and Chen, 2014; Drewes et al., 2009; Fakhru'l-Razi et al., 2009) (see Appendix F).

Technologies that remove TSS have been employed in the Marcellus Shale (sedimentation and filtration) (Mantell, 2013a); Utica Shale (chemical precipitation and filtration) (Mantell, 2013a); Barnett Shale (chemical precipitation and inclined plate clarifier, >90% removal) (Hayes et al., 2014); and Utah (electrocoagulation, 90% removal) (Halliburton, 2014). Details of examples of operating treatment facilities are provided in Table 8-6.

8.5.2.2. Total Dissolved Solids

The TDS concentration of hydraulic fracturing wastewater is a key treatment consideration, with the TDS removal needed dependent upon the intended use of the treatment effluent. POTW treatment and basic treatment processes at a CWT (i.e., chemical precipitation, sedimentation, and filtration) are not reliable methods for removing TDS. Reduction requires more advanced treatment processes such as RO, nanofiltration, thermal distillation (including MVR), evaporation, and/or crystallization (Olsson et al., 2013; Boschee, 2012; Drewes et al., 2009). RO and thermal distillation processes can treat waste streams with TDS concentrations up to 45,000 mg/L and more than 100,000 mg/L, respectively (Tiemann et al., 2014). As noted in section 8.5.1, pretreatment (e.g., chemical precipitation, flotation, etc.) is typically needed to remove constituents that may cause fouling or scaling or to remove specific constituents not removed by a particular advanced process. Extremely high TDS waters may require a series of advanced treatment processes to remove TDS to desired levels. However, the cost of treating high-TDS waters may preclude facilities from choosing treatment if other options such as deep well injection are available and more cost-effective (Tiemann et al., 2014). Emerging technologies such as membrane distillation and forward osmosis are also showing promise for TDS removal and require less energy compared to other desalination processes (Shaffer et al., 2013).

Examples of facilities with advanced technologies and their effectiveness in reducing TDS concentrations in hydraulic fracturing wastewaters from conventional and unconventional resources are summarized in Table 8-6.

8.5.2.3. Anions

Although chemical precipitation processes can reduce concentrations of multivalent anions such as sulfate, monovalent anions (e.g., bromide and chloride) are not removed by basic treatment

processes and require more advanced treatment such as RO, nanofiltration, thermal distillation (including MVR), evaporation, and/or crystallization (Hammer and VanBriesen, 2012).

Ion exchange and adsorption are effective treatment processes for removing fluoride but not typically the anions of concern in hydraulic fracturing wastewaters (bromide, chloride, sulfate) (Drewes et al., 2009). Emerging technologies applicable to TDS will typically remove anions. However, issues discussed above, such as the potential for scaling, still apply.

8.5.2.4. Metals and Metalloids

Chemical precipitation, including lime softening and chemical oxidation, is effective at removing metals (e.g., sodium sulfate reacts with metals to form solid precipitates such as barium sulfate) (Drewes et al., 2009; Fakhru'l-Razi et al., 2009). However, as mentioned in Section 8.5.2.3, chemical precipitation does not adequately remove monovalent ions (e.g., sodium, potassium), and the produced solid residuals from this process typically require further treatment, such as de-watering (Duraisamy et al., 2013; Hammer and VanBriesen, 2012). Media filtration can remove metals if coagulation/oxidation is implemented prior to filtration (Duraisamy et al., 2013). Advanced treatment processes such as distillation (with pH adjustment to prevent scaling), evaporation, RO, and nanofiltration can remove dissolved metals and metalloids (Hayes et al., 2014; Igunnu and Chen, 2014; Bruff and Jikich, 2011; Drewes et al., 2009). However, if metal oxides are present or formed during treatment, they must be removed prior to RO and nanofiltration processes to prevent membrane fouling (Drewes et al., 2009). Also, boron is not easily removed by RO, achieving less than 50% rejection (the percentage of a constituent captured and thus removed by the membrane) at neutral pH (rejection is greater at higher pH values) (Drewes et al., 2009). Ion exchange can be used to remove other metals such as calcium, magnesium, barium, strontium, and certain oxidized heavy metals such as chromate and selenate (Drewes et al., 2009). Adsorption can remove metals but is typically used as a polishing step to prolong the replacement/regeneration of the adsorptive media (Igunnu and Chen, 2014).

The literature provides examples of facilities able to reduce metal and metalloid concentrations in conventional and unconventional hydraulic fracturing wastewaters, some of which are provided in Table 8-6. The facilities in Table 8-6 have achieved removals of 98%–99% for a number of metals. Other work demonstrating effective removal includes a 99% reduction in barium using chemical precipitation (Marcellus Shale region) (Warner et al., 2013a) and over 90% boron removal with RO (at pH of 10.8) at two California facilities (Webb et al., 2009; Kennedy/Jenks Consultants, 2002). However, influent concentration must be considered together with removal efficiency to determine whether effluent quality meets the requirements dictated by end use or by regulations. In the case of the facility described by Kennedy/Jenks Consultants (2002) the boron 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.

Newer treatment methods for metals removal include electrocoagulation (Halliburton, 2014; Gomes et al., 2009) and electrodialysis (Banasiak and Schäfer, 2009). Testing of electrocoagulation has been performed in the Green River Basin (Halliburton, 2014) and the Eagle Ford Shale (Gomes et al., 2009). While showing promising results in some trials, results of these early studies have

illustrated challenges, with removal efficiencies affected by factors such as pH and salt content. Membrane distillation has also shown promise in removing heavy metals and boron in wastewaters (Camacho et al., 2013).

8.5.2.5. Radionuclides

Several processes (e.g., RO, nanofiltration, and thermal distillation) are effective for removing radionuclides (Drewes et al., 2009). Ion exchange can be used to treat for specific radionuclides such as radium (Drewes et al., 2009). Chemical precipitation of radium with barium sulfate has also been shown to be a very effective method for removing radium (Zhang et al., 2014b).

Data on radionuclide removals achieved in active treatment plants are scarce. The literature does provide some data from the Marcellus Shale region on use of distillation and chemical precipitation (co-precipitation of radium with barium sulfate). The nine-month pilot-scale study conducted by Bruff and Jikich (2011) showed that distillation treatment could achieve high removal efficiencies for radionuclides (see Table 8-6), and Warner et al. (2013b) reported that a CWT achieved over 99% removal of radium via co-precipitation of radium with barium sulfate. However, in both studies, radionuclides were detected in effluent samples, and the CWT was discharging to a surface water body during this time (Warner et al., 2013b; Bruff and Jikich, 2011); see Section 8.6.2. Effluent from distillation treatment was found to contain up to 6.49 pCi/L for gross alpha (from 249 pCi/L prior to distillation) (Bruff and Jikich, 2011). Between 2010 and 2012, samples of wastewater effluent from a western PA CWT contained a mean radium level of 4 pCi/L (Warner et al., 2013a).

8.5.2.6. Organics

Because hydraulic fracturing wastewaters can contain various types of organic compounds that each have different properties, specific treatment processes or series of processes are used to target the various classes of organic contaminants. Effectiveness of treatment depends on the specific organic compound and the technology employed (see Appendix F). It should be noted that in many studies, rather than testing for several organic constituents, researchers often measure organics in terms of biochemical oxygen demand and/or chemical oxygen demand, which are an indirect measure of the amount of organic compounds in the water. Organic compounds may also be measured and/or reported in groupings such as total petroleum hydrocarbons (TPH) (which include gasoline range organics (GROs) and diesel range organics (DROs)), oil and grease, VOCs (which include BTEX), and SVOCs.

Based on examples found in literature, facilities have demonstrated the capability to treat for organic compounds in hydraulic fracturing wastewaters using a single process or a series of processes (Hayes et al., 2014; Bruff and Jikich, 2011; Shafer, 2011) (see Table 8-6). The processes can include anaerobic and aerobic biological treatment, coagulation, flocculation, flotation, filtration, bioremediation, ultrafiltration, MVR, and dewvaporation. Forward osmosis is an emerging technology that may be promising for organics removal in hydraulic fracturing wastewaters because it is capable of rejecting the same organic contaminants as commercially-available pressure-driven processes (Drewes et al., 2009).

8.5.2.7. Estimated Treatment Removal Efficiencies

There are relatively few studies that have evaluated the ability of individual treatment processes to remove constituents from hydraulic fracturing wastewater and present the resulting water quality. Furthermore, although a specific technology may demonstrate a high removal percentage for a particular constituent, if the influent concentration of that constituent is extremely high, the constituent concentration in the treated water may still exceed permit limits and/or disposal requirements. Appendix Table F-4 presents the results of simple calculations pairing average hydraulic fracturing wastewater concentrations from Chapter 7 with treatment process removal efficiencies reported in the literature in Table F-2.

As an example, radium in wastewater from the Marcellus Shale and Upper Devonian sandstones can be in the thousands of pCi/L. With a 95% removal rate, chemical precipitation may result in effluent that still exceeds 100 pCi/L. Distillation and reverse osmosis might produce effluent with concentrations in the tens of pCi/L. A radium concentration of 120 pCi/L, however, could be reduced to less than 5 pCi/L by RO or distillation. Wastewater with barium concentrations in the range of 140 – 160 mg/L (e.g., the Cotton Valley and Mesaverde tight sands) might be reduced to concentrations under 5 mg/L by distillation and roughly 11-13 mg/L by RO. Barium concentrations in the thousands of mg/L would be substantially reduced by any of several processes but might still be relatively high and could exceed 100 m g/L. Table F-4 also illustrates the potential for achieving low concentrations of organic compounds in wastewater treated with freeze-thaw evaporation or advanced oxidation and precipitation.

This analysis is intended to highlight the potential impacts of influent concentration on treatment outcome and to illustrate the relative capabilities of various treatment processes for an example set of constituents. Removal efficiencies would differ and likely be greater with a full set of pretreatment and treatment processes that would be seen in a CWT (see Table 8-6).

8.5.3. Design of Treatment Trains for CWTs

Based on the chemical composition of the hydraulic fracturing wastewater and the desired effluent water quality, a series of treatment technologies will most likely be necessary. The possible combinations of unit processes to formulate treatment trains are extensive. One report identified 41 different treatment unit processes that have been used in the treatment of oil and gas wastewater and 19 unique treatment trains (combinations of unit processes) (Drewes et al., 2009). Fakhru'l-Razi et al. (2009) also provide examples of process flow diagrams that have been used in pilot-scale and commercial applications for treating oil and gas wastewater. Figure 8-8 shows the treatment train for the Pinedale Anticline Facility, which includes pretreatment for dispersed oil, VOCs, and heavy metals and advanced treatment for removal of TDS, dissolved organics, and boron. This CWT can either discharge to surface water or provide the treated wastewater to operators for reuse.

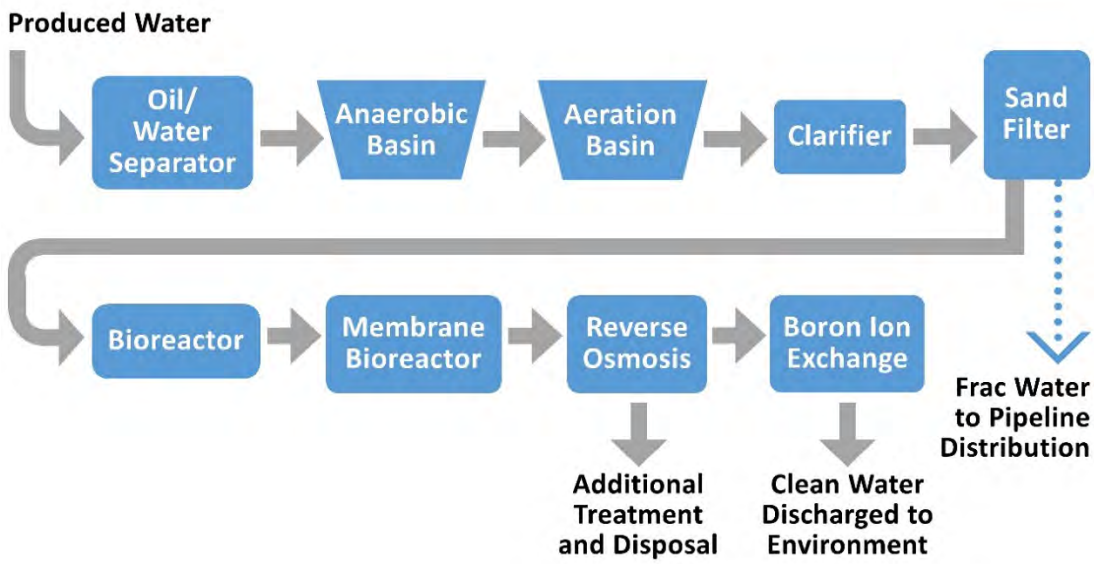

Figure 8-8. Full discharge water process used in the Pinedale Anticline field.

Source: Boschee (2012).

Table 8-7 provides information on some CWTs in locations across the country and the processes they employ. The table also notes for each facility whether data are readily available on effluent quality. Comprehensive and systematic data on influent and effluent quality from a range of CWTs that treat to a variety of water quality levels is difficult to procure, rendering it challenging to understand removal efficiencies and resulting effluent quality, especially when a facility offers a range of water quality products (e.g., for reuse vs. discharge). For those facilities with NPDES permits, discharge monitoring report (DMR) data may be available for some constituents, although if the facility does not discharge regularly, these data will be sporadic.

CWTs such as the Judsonia Central Water Treatment Facility in Arkansas, the Casella-Altela Regional Environmental Services, and Clarion Altela Environmental Services (see Table 8-7) facilities have NPDES permits and use MVR or thermal distillation for TDS removal. As of March 2015, the Pinedale Anticline Facility and the Judsonia Facility appear to be the only CWTs in Table 8-7 discharging to a surface water body.

Table 8-7. Examples of centralized waste treatment facilities.

Facility	State	Description of Unit Processes	Does CWT have a NPDES permit for discharge?	Does CWT provide effluent for reuse?	Does CWT have advanced process for TDS removal?	What is the status of the facility as of January 2015?	Are effluent quality data available through literature search?
Pinedale Anticline Water Reclamation Facility[a]	WY	Oil/water separation, biological treatment, aeration, clarification, sand filtration, bioreactor, membrane bioreactor, RO, and ion exchange	No - However, facility is permitted to discharge under 40 CFR 435 Subpart E (WY0054224). Facility is permitted to discharge up to 25% of its effluent stream	Yes	Yes, RO (Boschee, 2014, 2012)	The treatment plant produces treated water for reuse and for discharge to surface water. The website indicates the facility is in operation and is recycling to support drilling operations and is discharging to the New Fork River (http://hswater.squarespace.com/pinedale-anticline/).	Yes – DMR data available on Wyoming DEQ website. Some information can also be obtained from Shafer (2011).
SEECO – Judsonia Water Reuse Recycling Facility	AR	Settling, biological treatment, induced gas flotation, and MVR	Yes - AR0052051	Yes	Yes, MVR	The treatment plant provides treated water for reuse and for discharge to surface water. Based on DMR data from late 2014-early 2015, the system is discharging treated water to a surface water body, though intermittently.	DMR data available

Facility	State	Description of Unit Processes	Does CWT have a NPDES permit for discharge?	Does CWT provide effluent for reuse?	Does CWT have advanced process for TDS removal?	What is the status of the facility as of January 2015?	Are effluent quality data available through literature search?
Eureka Resources – Williamsport 2nd Street Facility	PA	Settling, oil/water separation, chemical precipitation, clarification, MVR. Can treat with or without TDS removal.	No - However, future plans to install RO for direct discharge capability	Yes	Yes, MVR	Per Ertel et al. (2013), the facility provides treatment wastewater for reuse and indirect discharge. The facility treats entirely or almost entirely hydraulic fracturing wastewater.	No
Standing Stone Facility, Bradford County	PA	Settling, oil/water separation, chemical precipitation, clarification, MVR, crystallization	Yes - PA0232351	Yes	Yes, MVR, crystallizer	The facility can provide treated wastewater for reuse and also has received an NPDES permit for direct discharge. The facility treats hydraulic fracturing wastewater.	No

Facility	State	Description of Unit Processes	Does CWT have a NPDES permit for discharge?	Does CWT provide effluent for reuse?	Does CWT have advanced process for TDS removal?	What is the status of the facility as of January 2015?	Are effluent quality data available through literature search?
Wellington Water Works	CO	Dissolved air flotation, pre-filtration, microfiltration with ceramic membranes, activated carbon adsorption. Water is pumped to an aquifer storage and recovery well. Water is then extracted and treated with RO (Alzahrani et al., 2013).	Permit number issued by CO (61879)	Yes	Yes, RO but only after the water is sent to an aquifer storage and recovery well	Per Stewart (2013b), the facility is providing treated wastewater for reuse, for agricultural use, to a shallow well to augment the municipal drinking water supply, and for discharge to the Colorado River.	No
Casella Altela Regional Environmental Services (CARES) McKean Facility	McKean County, PA	Pretreatment system (not defined in literature) and thermal distillation	Yes – PA0102288	Yes	Yes – thermal distillation	The treatment plant is capable of reuse and recycle for fracturing operations and surface water discharge of excess water. However, the facility's website indicates it is only treating water for reuse/recycle as of early 2015 (http://caresforwater.com/location/cares-mckean).	No - just NPDES discharge requirements

Facility	State	Description of Unit Processes	Does CWT have a NPDES permit for discharge?	Does CWT provide effluent for reuse?	Does CWT have advanced process for TDS removal?	What is the status of the facility as of January 2015?	Are effluent quality data available through literature search?
Clarion Altela Environmental Services (CAES) Facility	Clarion County, PA	Pretreatment system (not defined in literature) and thermal distillation	Yes – PA0103632	Yes	Yes – thermal distillation	The treatment plant capable of reuse and recycle for fracturing operations and surface water discharge of excess water. However, the facility's website indicates it is only treating water for reuse/recycle as of early 2015 (http://caeswater.com/technology/).	No – just NPDES discharge requirements
Terraqua Resource Management (aka. Water Tower Square Gas Well Wastewater Processing Facility)	Lycoming County, PA	Equalization tanks, oil-water separation via chemical addition (sulfuric acid, emulsion breaker), pH adjustment, coagulation, flocculation, inclined plate clarifier, sand filtration	Yes – PA0233650 Permit pending approval for discharge to stream (as of 4/17/2009)	Yes	No – However, TARM recognizes that they can't discharge, until they install TDS treatment	According to its website (last updated 2012), the facility reuses/recycles treated water for fracturing operations (http://www.tarmsolutions.com/solutions/).	No
Maggie Spain Water-Recycling Facility	Decatur, TX	Settling, flash mixer with lime and polymer addition, inclined plate clarifier, surge tank, MVR	No	Yes	Yes – MVR	A 17-month pilot study using a commercial-scale mobile treatment facility was concluded in 2011. The status is unclear as of early 2015.	Yes – Some information can be obtained from Hayes et al. (2014).

Facility	State	Description of Unit Processes	Does CWT have a NPDES permit for discharge?	Does CWT provide effluent for reuse?	Does CWT have advanced process for TDS removal?	What is the status of the facility as of January 2015?	Are effluent quality data available through literature search?
Fountain Quail/NAC Services - Kenedy	Kenedy, TX	Oil-water separator, coagulation, flocculation, sedimentation, filtration, MVR.	No	Yes	Yes – MVR	According to its website, the facility reuses/recycles treated water for fracturing operations (http://www.aqua-pure.com/operations/shale/ford/ford.html).	No
Purestream - Gonzales facility	Gonzales, TX	Induced gas flotation and MVR	No	Yes	Yes - MVR	Per Dahm and Chapman (2014) commercial operations deployed March 2014 for reuse/recycle for fracturing operations.	No
LINN Energy Fyre Ranch - Granite Wash	Wheeler County, TX	Induced gas flotation and MVR	No	Yes	Yes - MVR	AVARA system installed for reuse/recycle in June 2014. http://purestream.com/index.php/water-management/vapor-recompression/photos-and-videos	No

Facility	State	Description of Unit Processes	Does CWT have a NPDES permit for discharge?	Does CWT provide effluent for reuse?	Does CWT have advanced process for TDS removal?	What is the status of the facility as of January 2015?	Are effluent quality data available through literature search?
Fluid Recovery Service Josephine Facility[b]	PA	Oil-water separator, aeration, chemical precipitation with sodium sulfate, lime, and a polymer, inclined plate clarifier	Expired - PA0095273	No	No	The facility claims to have stopped accepting Marcellus wastewater September 30, 2011 (Ferrar et al., 2013). It treats conventional oil and gas wastewater. The facility will be upgrading to include evaporative technology that will enable it to attain monthly average TDS levels of 500 mg/L or less.	Yes – Some effluent results obtained from Ferrar et al. (2013) and Warner et al. (2013a). Also minimal DMR data from the EPA.
Fluid Recovery Service Franklin Facility[b]	PA	Oil-water separator, aeration, chemical precipitation with sodium sulfate, lime, and a polymer, inclined plate clarifier	Expired - PA0101508	No	No	This facility is not accepting wastewater from hydraulic fracturing operations as of January 2015. The facility will be upgrading to include evaporative technology that will enable it to attain monthly average TDS levels of 500 mg/L or less.	Minimal DMR data from the EPA.

Facility	State	Description of Unit Processes	Does CWT have a NPDES permit for discharge?	Does CWT provide effluent for reuse?	Does CWT have advanced process for TDS removal?	What is the status of the facility as of January 2015?	Are effluent quality data available through literature search?
Hart Resources-Creekside Facility[b]	PA	Oil-water separator, aeration, chemical precipitation with sodium sulfate, lime, and a polymer, inclined plate clarifier	Expired - PA0095443	No	No	This facility is not accepting wastewater from hydraulic fracturing operations as of January 2015. The facility will be upgrading to include evaporative technology that will enable it to attain monthly average TDS levels of 500 mg/L or less.	Minimal DMR data from the EPA.

[a] For Pinedale Anticline Water Reclamation Facility, surface water discharges are permitted under 40 CFR 435 Subpart E (beneficial use subcategory agricultural and wildlife water) not 40 CFR 437 (the discharge permit for CWTs). For the purposes of this assessment, this facility is included with CWTs.

[b] As of May 15, 2013, these facilities are under an administrative order (AO). According to the AO, these facilities must comply with a monthly effluent limit for TDS not to exceed 500 mg/L. This will allow them to treat high-saline wastewaters typical of unconventional oil and gas operations. To meet the requirements of the AO, they have applied to PADEP for a NPDES permit and are planning to install treatment for TDS.

8.6. Potential Impacts on Drinking Water Resources

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), with one study using probability modeling indicating that 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). Whether drinking water resources are affected by hydraulic fracturing wastewater depends at least in part upon the characteristics of the wastewater, the form of discharge or other management practice, and the processes used if the wastewater is treated. Other site-specific factors (e.g., size of receiving water and volume of wastewater) determine the magnitude and nature of potential effects, but a thorough exploration of local factors is beyond the scope of this assessment. The majority of hydraulic fracturing wastewater is either injected into a disposal well or, in the case of the Marcellus region, reused for other hydraulic fracturing jobs. Potential impacts on drinking water resources may occur on a local level through several routes: treated wastewater may be discharged directly from centralized waste treatment facilities (CWTs) or indirectly from publicly owned treatment works (POTWs) that receive CWT effluent; sediments in water bodies receiving effluent may accumulate contaminants; spills or leaks may be associated with on-site storage or transportation (see Chapter 7); and in previous years, hydraulic fracturing wastewater treated at POTWs was discharged to surface waters.

It has been suggested that the most significant effects of hydraulic fracturing on surface water quality are related to discharges of partially treated wastewater, although these effects vary according to region (Kuwayama et al., 2015). A recent study (Bowen et al., 2015) concluded that there is currently no clear 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. These authors note that available national level databases have limitations for assessing this question.

Pits and impoundments associated with waste management may have impacts on drinking water resources and are discussed in Chapter 7. In addition, unauthorized discharge of wastewater is a potential mechanism for impacts on drinking water resources. Descriptions of several incidents and resulting legal actions have been publicly reported. However, such events are not generally described in the scientific literature, and the prevalence of this type of activity is unclear.

Important considerations regarding the potential impact of hydraulic fracturing wastewater on a receiving waterbody include whether constituents in the wastewater are known to have health effects, if they are regulated drinking water contaminants, or if they may give rise to regulated compounds. For some classes of constituents, such as disinfection by-product (DBP) precursors, considerable research exists. For others, information is limited regarding their concentrations in effluents and whether they are likely to affect drinking water at intakes. The following subsections identify several classes of constituents known to occur in hydraulic fracturing wastewater, discuss whether potential impacts are likely, and provide specific examples of information gaps.

8.6.1. Bromide and Chloride

Bromide and chloride are two constituents commonly found in high-total dissolved solids (TDS) hydraulic fracturing wastewater. As noted in section 8.3.1.1, chloride is a regulated contaminant with a secondary MCL standard of 250 mg/L. Bromide is not regulated but is of concern due to its 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 can be of concern because the limited availability of underground injection for disposal can result in a higher rate of discharge of treated wastewater to surface waters compared to other parts of the country. In response to concerns in part over bromide in discharges, operators in Pennsylvania have discontinued the practice of sending wastewater from hydraulic fracturing operations to POTWs (States et al., 2013). Also, CWTs have been shifting towards treatment of those wastewaters for reuse rather than discharging to surface water bodies (Hammer and VanBriesen, 2012).

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 trihalomethanes in finished drinking water. The authors noted that source water containing 50 μg/L bromide resulted in treated water with approximately 62% of its finished water total trihalomethanes consisting of bromoform, dibromochloromethane, and bromodichloromethane. Source water containing 150 μg/L bromide resulted in finished water TTHMs composed of approximately 83% brominated species. Allegheny River bromide concentrations measured during the study ranged from less than 25 μg/L to 299 μg/L, with the highest bromide concentrations measured under low-flow conditions. Industrial wastewater sites accounted for approximately 50% of the increase in bromide load as water moved downriver.

In addition, a related constituent, iodide can be a constituent in hydraulic fracturing wastewater (see Chapter 7). Although its effects have not been as well documented as those associated with bromide (Xu et al., 2008), iodide raises some of the same concerns (such as DBP formation) as bromide does (Parker et al., 2014; Krasner, 2009). Iodinated DBPs are not regulated by the EPA as of early 2015.

As discussed in Section 8.5, 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 treatment plants with intakes downstream of these discharges may receive water with correspondingly higher levels of bromide and chloride and may have difficulty complying with Safe Drinking Water Act (SDWA) regulations related to DBPs.

8.6.1.1. Effects on Receiving Streams

Studies show that discharges from oil and gas wastewater treatment facilities can elevate TDS, bromide, and chloride levels in receiving waters (States et al., 2013; Wilson and Van Briesen, 2013). Wilson and Van Briesen (2013) measured bromide, chloride, and other constituents at water intakes downstream of wastewater discharges for three years in the Monongahela River in western Pennsylvania. By evaluating water chemistry data in the context of flow measurements, the authors

attributed an overall decrease in bromide concentrations from 2010 to 2012 to a decrease in bromide loading; they note that this is likely to be associated with a decrease in management of fossil fuel wastewater at treatment plants that discharge to surface water.

Although treatment plant effluents will be diluted upon reaching the receiving water, the dilution may not be adequate to avoid water quality problems if there are existing pollutant loads in the waterbody from contributors such as acid mine drainage or power plant effluents (Ferrar et al., 2013). Warner et al. (2013a) evaluated effluent from the Josephine Brine Treatment Facility (which treated both conventional and unconventional oil and gas wastewater at the time of the study) and concluded that even a 500 to 3,000-fold dilution of the wastewater would not reduce bromide levels to background. In addition, downstream levels of chloride in the receiving stream were elevated, with a downstream value of 88 mg/L as compared to an upstream value of 18 mg/L.

A study by Hladik et al. (2014) focused on sampling at sites downstream and near the outfalls of plants that treated oil and gas wastewater in Pennsylvania. The authors documented brominated and iodinated DBPs (e.g., dibromochloronitromethane (DBNM); dibromoiodomethane) at the outfalls of CWTs and POTWs and noted that this DBP signature was different than for those plants that did not accept oil and gas wastewater. For example, concentrations of dibromochloronitromethane ranged from 0.26 to 8.7 μg/L, and dibromoiodomethane was measured at 0.98 and 1.3 μg/L; neither compound was detected at an upstream site or at the outfall of the POTW not accepting oil and gas wastewater. These brominated and iodinated compounds are considered more toxic than other types of DBPs (Richardson et al., 2007). Hladik et al. note that these elevated DBP levels could contribute to DBPs at downstream drinking water intakes and can also be an indicator of the potential for more highly brominated and iodinated DPBs forming in drinking treatment plants downstream of these discharges (Hladik et al., 2014). The sites studied by Hladik et al. (2014) received wastewater from both conventional and unconventional oil and gas development.

Research suggests that a relatively small portion of hydraulic fracturing wastewater effluent can notably affect DBP formation. In laboratory studies, Parker et al. (2014) diluted hydraulic fracturing wastewater from the Marcellus and Fayetteville shales with Allegheny and Ohio River waters and then disinfected the mixtures. In chlorinated samples containing as little as 0.01% hydraulic fracturing wastewater, the THM composition shifted significantly away from chloroform species to a greater representation of brominated and iodinated species.

Elevated concentrations of bromide in effluents can place a burden on downstream drinking water treatment systems. States et al. (2013) studied influent and finished water at the Pittsburgh Water and Sewer Authority (PWSA) drinking water system, concluding that elevated bromide in the source water led to elevated total trihalomethanes (TTHM) formation in the treated drinking water. The authors also noted a substantial increase in the percentage of brominated TTHMs (States et al., 2013), as discussed above. 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).

8.6.1.2. Modeling

The EPA's contaminant modeling shows that that the strategies most likely to reduce bromide impacts on downstream users include reducing effluent concentrations (e.g., discharging flowback versus produced water), discharging during higher stream flow periods, and using a pulsing or intermittent discharge. Weaver et al. (In Press) developed a computer model to estimate river and stream bromide concentrations after treated water discharges. The model utilizes existing data for bromide concentrations in produced water, flowback, and mixtures, combined with existing stream flow data from USGS stations in Pennsylvania. The model parameters include steady state versus transient inputs to receiving waters, high and low streamflow months, varying effluent concentration and types (produced, flowback, and mixed). For steady-state scenarios in the model, bromide concentrations are lowest under high flow conditions with lower concentrations of effluent (flowback and mixed water).

A source apportionment study conducted by the EPA considered the relative contributions of bromide, chloride, nitrate, and sulfate from CWTs primarily treating hydraulic fracturing wastewater to the Allegheny River Basin and to water at two downstream public water system intakes on the Allegheny River (U.S. EPA, 2015p). The Allegheny River and its tributaries receive runoff and discharges containing an array of contaminants, including these anions. Contaminant sources include discharges from CWTs for oil and gas wastewater, runoff from acid mine drainage and mining operations, discharges from coal-fired electric power stations, industrial wastewater treatment plant effluents, and POTW discharges. The Allegheny River is also the water supply for thirteen public water systems that serve over 500,000 people in western Pennsylvania.

In Pennsylvania, wastewater produced from hydraulic fracturing of the Marcellus formation has been mostly diverted from CWTs and POTWs that discharge to public waters in the state (Hammer and VanBriesen, 2012). Wastewater produced from hydraulic fracturing of non-Marcellus formations, however, continues to be sent to surface-discharging facilities on the Allegheny River.

The source apportionment study considered contributions of bromide, chloride, nitrate and sulfate to public water supplies from CWTs and other upriver sources by: developing chemical source profiles, or fingerprints, for discharges upstream of the public water system intakes; characterizing water quality in the river upstream and downstream of the CWTs, electric generating stations, and industrial facilities; characterizing the water quality at the public water system intakes; and analyzing the sampling data collected with the EPA Positive Matrix Factorization (PMF) receptor model in order to quantify relative contributions of contaminant sources to the anions found at the public water system intakes. The study focused on low-flow conditions.

CWTs and coal-fired power plants with flue gas desulfurization were found to contribute bromide to the two public water supply intakes. Although acid mine drainage also contributed bromide, its contribution was minor (9% at one intake) compared to the contributions from the CWTs (89% and 37% at the two intakes) and coal-fired power plants (50-59% at one intake). The CWTs, coal-fired power plants, and acid mine drainage combined accounted for 88–89% of the bromide at one intake and 96% of the bromide at the other intake.

8.6.1.3. Summary

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. Tighter restrictions on TDS in effluent from POTWs and CWTs have led to a reduction in in-stream bromide concentrations. Advanced treatment processes at CWTs such as reverse osmosis, distillation, evaporation, or crystallization can reduce chloride, bromide, and iodide in surface waters. Strategies such as reducing effluent concentrations, discharging during higher stream flow periods, and utilizing a pulsing or intermittent discharge could also reduce the potential impact of elevated TDS on drinking water treatment plants.

8.6.2. Radionuclides

Potential impacts on drinking water resources from technologically enhanced naturally occurring radioactive material (TENORMs) associated with hydraulic fracturing wastewater may arise from a number of sources, including: treated wastewater that does not have adequately reduced radionuclide concentrations, accumulation of radionuclides in surface water sediments downstream of wastewater treatment plant discharge points, migration from soils that have accumulated radionuclides from previous activities such as pits or land application, and inadequate management of treatment plant solids that have accumulated radionuclides (such as filter cake).

In Pennsylvania between 2007 and 2010, TENORM-bearing produced wastewaters were sent to POTWs, which are generally not required to monitor for radioactivity (Resnikoff et al., 2010). Although the practice of management of Marcellus waters via POTWs has declined, there is still potential for input of radionuclides to surface waters via discharge of CWT effluents either directly to surface waters or indirectly through discharge to POTWs.

Data regarding TENORM content in oil and gas wastes that are treated and discharged to surface waters are limited. However, a recent study by the Pennsylvania Department of Environmental Protection (PA DEP) (PA DEP, 2015b) provides information that helps fill this data gap. The study began in 2013 and examined radionuclide (radium-226, radium-228, K-40, gross alpha, gross beta) levels at 29 wastewater plants in Pennsylvania that cover a range of both sources and treatment plant types, including POTWs, CWTs that treat oil and gas wastewaters and can discharge to surface water or a POTW, and zero liquid discharge facilities treating oil and gas wastewater. Four of the 10 discharging CWTs sampled during the study discharged to surface water under a National Pollution Discharge Elimination System (NDPES) permit, and the others discharged to POTWs. Six of the POTWs in the study received effluent from a CWT along with municipal wastewater. The CWTs in the study are not described as receiving exclusively Marcellus wastewater, but the study itself was motivated by concerns over an increase in radionuclides in oil and gas wastes observed during the expansion of Marcellus Shale production.

The POTWs receiving influent from CWTs treating oil and gas wastewater (along with municipal wastewater influent) had average effluent radium-226 concentrations of 103 pCi/L (unfiltered) and 129 pCi/L (filtered) (filtration is used to remove very fine particulates from the water). Those POTWs not receiving influent from CWTs treating oil and gas wastewater effluent had higher average radium-226 values in unfiltered samples (145 pCi/L) and lower values for filtered samples

(47 pCi/L). For perspective, the maximum contaminant level (MCL) for radium-226 plus radium-228 is 5 pCi/L. For reference, radium-226 in river water generally ranges from 0.014 pCi/L to 0.54 pCi/L (0.5 to 20 mBq/L) (IAEA, 2014). The results of the POTW sampling are inconclusive as to whether the effluents from POTWs receiving CWT-treated oil and gas wastewater are routinely higher than the effluents from those without this type of influent.

For the CWTs in the PA DEP study, average radium-226 content in the effluents was an order of magnitude higher than in effluents from the POTWs (1,840 pCi/L unfiltered, 2,100 pCi/L, filtered). The effluent averages were similar to averages for the influent concentrations, although median concentrations in the effluents were much lower than in the influents. Effluent from zero-discharge facilities averaged 2,610 pCi/L radium-226 and 295 pCi/L radium-228, although these effluents would most likely be reused as fracturing fluid (PA DEP, 2015b). The authors do note a potential for environmental effects from spills of influent or effluent from zero-discharge facilities.

Warner et al. (2013a) noted that if the activities of radium-226 and radium-228 in Marcellus brine influent at the CWT they studied are similar to those reported by other researchers (Rowan et al., 2011), then the CWT achieved a 1,000-fold reduction in radium content via a process of radium coprecipitation with barium sulfate. The detection of radium in effluents from this CWT (mean values of 4 pCi/L of radium-226 and 2 pCi/L of radium-288) even with what may be high treatment removal efficiency underscores the fact that effluent concentrations depend not only upon the treatment processes used but also the influent concentration.

An additional concern related to evaluation of radionuclide concentrations in wastewater is that the high TDS content of hydraulic fracturing wastewater can result in poor recovery of chemical constituents when using wet chemical techniques, leading to underestimations of constituent concentrations. In particular, recovery for radium may be as low as <1% (Nelson et al., 2014). Underestimation of radium content may lead to failure in identifying an impact or potential impact on drinking water resources.

In addition to concerns over of the potential for TENORM in discharges to surface waters, there are may be a legacy of accumulation of radionuclides in surface water sediments. Studies of effluent, stream water, and stream sediment associated with a CWT in western Pennsylvania that has treated both conventional and unconventional oil and gas wastewaters indicate that radium-226 levels in stream sediment samples at the point of discharge are approximately 200 times greater than upstream and background sediments. This indicates the potential for accumulation of contaminants in localized areas of wastewater discharge facilities (Warner et al., 2013a). Although the CWT in question also accepted conventional oil and gas wastewater, Warner et al. (2013a) 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 interpret this as an indication that the radium accumulated in the sediments originated from the discharge of treated unconventional oil and gas wastewater. Another study, however, 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 (Skalak et al., 2014). Accumulation of contaminants in sediment may be dependent on treatment processes and their removal rates for

various constituents as well as stream chemistry and hydrologic characteristics. Contamination with radium-226 would be potentially be long lived; the half-life of radium-226 is approximately 1,600 years, while the half-life of radium-228 is 5.76 years.

The recent PA DEP study (PA DEP, 2015b) found that the radium-226 content in sediments near the discharge points for POTWs receiving treated oil and gas effluent from CWTs (along with their municipal wastewater influent) exceeds typical background soil levels of approximately 1 to 2 pCi/g of radium-226 and radium-228. The authors conclude that wastewater effluent is the most likely source for the radium in these samples. Results indicate an average of 9.00 pCi/g radium-226 and 3.52 pCi/g radium-228 in sediments near outfalls of POTWs. Sediments at 4 CWTs receiving oil and gas wastewater and that discharge to surface water have much higher average concentrations of 84.2 pCi/g for radium-226 and 19.8 pCi/g for radium-228. However, the concentrations of radium in the sediments does not correlate with concentrations of radium in the effluents suggesting that sorption over time affects the concentration of radium in the sediments (PA DEP, 2015b).

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. In particular, radium has a high affinity for iron and manganese (hydr)oxides in sediment. 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 (hydro)oxides (Porcelli et al., 2014; Gonneea et al., 2008). Warner et al. (2013a) speculate that the discharge of saline CWT effluent into less saline stream water 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 redox processes that may affect iron and manganese minerals in the sediments.

Other solids may contain radionuclides; filter cake samples from treatment at POTWs were found by PA DEP (2015b) to have radium contents greater than typical soil concentrations, and they exhibited a large variation. Filter cake from CWTs had radium concentrations higher than in POTW filter cake. The authors conclude that although the risk to workers and the public from handling and temporary storage of these materials is minimal, there may be environmental risks from spills or long term disposal. There could be impacts on surface waters through spills or effects on ground waters from landfill leachate.

Radionuclide accumulation in CWTs or POTWs may continue to affect the plant even after discontinuing treatment of high radionuclide wastewater. Radium can adsorb onto scales in pipes and tanks and will also co-precipitate calcium, barium, and strontium in sulfate minerals (USGS, 2014e). Pipe scale in oil and gas production facilities can have radium concentrations as high as 154,000 pCi/g, although concentrations of less than 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 equipment may end up in

landfills and then leach into groundwater or run off to a surface water body (USGS, 2013c). Although barium sulfate phases are relatively insoluble, one study demonstrates that barium sulfate scales that were buried in soil could be reduced by microbially mediated processes, allowing release of co-precipitated elements such as radium due to leaching by rainwater (Swann et al., 2004). 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.

Accumulation of radionuclides (potassium, thorium, bismuth, radium, and lead) has been evaluated in two pits in Texas that have stored fluids associated with hydraulic fracturing (Rich and Crosby, 2013). Gamma radiation in these pits has been found to vary from 8 to 23 pCi/g, with beta radiation varying from 6 to 1329 pCi/g (Rich and Crosby, 2013). Although the study sample size was small, the results suggest that radionuclides associated with sediments from some reserve pits could have potential impacts on surface waters or ground waters. This could happen through migration of affected sediments or soils to surface waters or through leaching to ground water.

Salt and radionuclide accumulation can occur near road spreading sites; one study in Pennsylvania found a 20% increase in radium concentrations in soils near roads where wastewaters from conventional operations had been spread for de-icing (Skalak et al., 2014). Accumulation of radionuclides in soils near roads presents a vehicle for potential impacts on drinking water resources. The extent to which hydraulic fracturing wastewater contributes to this depends upon state-level regulations regarding whether hydraulic fracturing wastewater can be used for road spreading.

Effluents 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 measurement may therefore serve as an effective screening mechanism for overall radionuclide concentrations in hydraulic fracturing wastewater. This in turn can help in evaluating management strategies. Portable gamma spectrometers allow rapid screening of wastewater effluents. Sediments may also be measured for radionuclide concentrations at discharge points.

8.6.3. 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 mg/L (see Table 7-10), surface waters may be impacted if discharges from CTWs or POTWs indirectly receiving oil and gas wastewater via CWTs are not managed appropriately. Spills may also affect surface waters.

Common treatment processes, such as coagulation, are effective at removing many metals (see Section 8.5.2.4). A request by the EPA for effluent sampling from seven facilities in Pennsylvania treating oil and gas wastewaters 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, 2015d, e). However, metals such as barium and strontium have been found to range from low to elevated in some CWT effluents. For the year 2011,

for example, effluent from a Pennsylvania CWT had average barium levels ranging from 9 to 98 mg/L (PA DEP, 2015a). That facility was operating with a barium removal stage and was treating both conventional and hydraulic fracturing wastewater, although effluent concentrations dropped after May, 2011. The facility is scheduled to upgrade its TDS removal capabilities.

Data collected by the EPA between October 2011 and February 2013 at seven Pennsylvania facilities indicate effluent barium concentrations ranging from 0.35 to 25 mg/L (median of 3.5 mg/L and average of 6.7 mg/L). Strontium concentrations ranged from 0.36 to 546 mg/L (median of 297 mg/L and mean of 236 mg/L (U.S. EPA, 2015e). A December 2010 effluent sampling effort in at a discharging CWT in Pennsylvania reported average barium and strontium concentrations of 27 mg/L and nearly 3,000 mg/L, respectively (eight samples from one plant) (Volz et al., 2011). The facility treats conventional oil and gas wastewaters, and it also received Marcellus wastewater until September, 2011.

Limited data are available on metal concentrations in wastewater and treated effluents that are directly discharged; additional information would be needed to assess whether there will be downstream effects on drinking water utilities. NPDES discharge permits, which restrict TDS discharge concentrations, will likely reduce metal effluent concentrations due to the additional treatment necessary to minimize TDS.

8.6.4. 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). Generally, lower concentrations of BTEX occur in wastewater from coalbed methane (CBM) production (see Appendix Table E-9). Processes such as aeration or dissolved air flotation can remove volatile organic compounds (VOCs) during treatment, but if treatment is not adequate, the VOCs may reach water resources. The average concentration of benzene in a December 2010 sampling effort was 12 μg/L in the discharge of a Pennsylvania CWT (Volz et al., 2011). The facility was receiving wastewater from both conventional and unconventional operations at that time. Ferrar et al. (2013) measured mean concentrations of benzene, toluene, ethylbenzene, and xylene in effluents from the same facility, and mean concentrations among the four compounds ranged from about 2 to 46 μg/L. Concentrations were lower for samples taken after May 19, 2011 than before, and the effect was considered statistically significant. The treatment processes at this facility do not include aeration.

Leakage from pits or spills creates another potential route of entry to drinking water resources. VOCs have been measured in groundwater near the Duncan Oil Field in New Mexico, downgradient of an unlined pit storing oil and gas wastewater (Sumi, 2004; Eiceman, 1986). VOCs and oil were also found in groundwater about 213 feet (65m) downgradient from an unlined pit in Oklahoma (Kharaka et al., 2002).

8.6.5. 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 a half-life estimation of 1-4 weeks in the environment (Wess et al., 1998). The EPA has not classified 2-BE (or other glycol ethers) for carcinogenicity. 2-BE was detected in the discharge of a Pennsylvania CWT at concentrations of 59 mg/L (Volz et al., 2011). Ferrar et al. (2013) detected 2-BE in the effluents 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 effluents from hydraulic fracturing wastewater treatment systems.

Polycyclic aromatic hydrocarbons are another common group of semi-volatile organic compounds (SVOCs) in oil and gas wastewater. They have been detected in soils 164 feet (50 m) downgradient of an unlined pit in New Mexico (Sumi, 2004; Eiceman, 1986). PAHs were also found in birds in wetlands fed by oil and gas wastewater discharges in Wyoming (Ramirez, 2002).

8.6.6. Oil and Grease

Oil and gas wastewater often contains oil and grease from the formation or from oil-based drilling fluids. Typically, oil and grease are separated from the wastewater before discharge either by a heat treatment or by allowing gravity separation followed by skimming. If these processes are inefficient, oil and grease may 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 with a standpipe. 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). In a study by the U.S. Fish and Wildlife Service regarding permitted oil and gas discharges between 1996 and 1999 from Wyoming oil fields, 15% of the 62 discharges to Wyoming wetlands reviewed showed visible oil sheens in the receiving water and 10 of the sites sampled exceeded discharge limits of 10 mg/L of oil and grease (Ramirez, 2002).

8.7. Synthesis

Hydraulic fracturing operations produce fluids during the flowback and production phases (collectively called wastewater) of a production well, along with liquid and solid treatment residuals from treatment processes. A variety of management strategies may be considered, with cost frequently a driving factor. Available information suggests that Class IID wells regulated under the Underground Injection Control (UIC) Program are the most frequently used wastewater management practice, but reuse, discharge after treatment, and various other uses are also employed.

8.7.1. Summary of Findings

Hundreds of billions of gallons of wastewater are generated annually in the United States by the oil and gas industry, although national level estimates are difficult to reliably obtain. It is also difficult to produce a nationwide estimate of the amount of wastewater that is attributable specifically to hydraulic fracturing because some states do not specifically identify wastewater from hydraulic fracturing operations in their available wastewater data.

The total amount of wastewater produced in an area corresponds generally to oil and gas production and, therefore, may increase if hydrocarbon production increases in a region. Geographically, a large portion of oil and gas wastewater in the United States is reported to be generated in the western part of the country, including contributions from both conventional and unconventional resources. For some states, estimates of hydraulic fracturing wastewater volumes can be made using publicly available production or waste data. Annual estimates compiled in this way range from hundreds of millions to billions of gallons of wastewater generated per state per year. Direct comparisons among these state data are problematic, however, because of a great deal of variability in state data collection, including differences in the years for which data are available, and challenges in definitively identifying wells that have been hydraulically fractured (to distinguish hydraulic fracturing wastewater from that generated from wells that are not hydraulically fractured). Within a given state, however, estimated volumes in areas where hydraulic fracturing is practiced extensively have generally increased over the last several years, along with numbers of wells contributing to total wastewater volumes. For example, the data made available by PA DEP illustrate that the total volume of wastewater generated correlates generally with a significant increase in volume of hydrocarbon production and with the number of production wells. As hydraulic fracturing activities increase and the number of wells increases, the amount of hydraulic fracturing wastewater generated is likely to increase.

8.7.1.1. Wastewater Management Practices

Hydraulic fracturing wastewater is managed in a variety of ways, including disposal through Class IID wells; minimal treatment and reuse in subsequent fracturing operations; more complete treatment followed by discharge, disposal, or reuse; evaporation; and other uses such as irrigation (when the wastewater quality is adequate). Unauthorized discharges of hydraulic fracturing wastewaters have been documented; such discharges could potentially impact drinking water resources, but estimates of the frequency of occurrence cannot be developed with the available data.

As of 2015, available information suggests that wastewater management practices involve extensive use of Class II wells to manage wastewater from most of the major unconventional plays in the United States, with the notable exception of the Marcellus Shale region in Pennsylvania. More than 98% of wastewater in the oil and gas industry is estimated to be injected into Class II wells annually (including wells for enhanced oil recovery and disposal) (Clark and Veil, 2009). Based on data compiled from 2012 and 2014, there are about 25,000 Class IID wells in the United States (U.S. EPA, 2015q). In particular, large numbers of active injection wells are found in Texas (7,876 or

29%), Kansas (5,516 or 20%), Oklahoma (4,622 or 17%), Louisiana (2,448 or 9%), and Illinois (1,054 or 4%).

Use of Class IID wells is likely driven by the availability of Class IID wells within reasonable transportation distance and the cost of transporting (and injecting) the wastewaters. In the oil and gas industry, Class IID wells have generally been the most economically favorable wastewater management practice (U.S. GAO, 2012). In Pennsylvania, there are only nine Class IID wells as of February 2015, and a significant growth of gas production using hydraulic fracturing in the Marcellus is generating increasing amounts of wastewater. Treatment and reuse are becoming increasingly popular in the Marcellus Shale region and are in more widespread use in comparison to other oil and gas producing parts of the country.

Reuse of hydraulic fracturing wastewater to formulate fracturing fluid in subsequent hydraulic fracturing jobs varies considerably on a national level, and reliable estimates are not available for all areas. As of 2014–2015, the greatest amount of reuse occurs in Pennsylvania, where the scarcity of Class IID wells to receive Marcellus wastewater drives this practice. Recent estimates of wastewater reuse in Pennsylvania range as high as 90% or more. Waste disposal data from the PA DEP (2015a) indicate that much of the reuse happens on-site. Operators also report some reuse of wastewater in other regions such as the Haynesville Shale, the Fayetteville Shale, the Barnett Shale, and the Eagle Ford Shale, although at much lower volume percentages (about 5 – 20%) compared with practices in the Marcellus Shale region. Increased reuse and recycling of hydraulic fracturing wastewaters has the added benefit of providing an additional water supply for hydraulic fracturing fluid formulation in areas where water scarcity is a concern. If, however, hydraulic fracturing activity slows, demand for wastewater for reuse will also decrease, and other forms of wastewater management will be needed.

The decision to reuse/recycle depends upon several factors, including the volume and rate of production of the wastewater and whether these are suitable for water needs for ongoing fracturing activities in the area. The composition of the water, in particular the TSS and TDS content, and whether the water quality can be accommodated in the fracturing practices in an area can also influence reuse, including decisions about what type of pretreatment or treatment may be needed to make reuse or recycling feasible.

Treatment facilities (either centralized waste treatment facilities (CWTs) or systems designed for on-site use) can be permitted to treat oil and gas wastewaters. Treatment can be followed by discharge to a surface water body or to a POTW, or the treated effluent may be used for reuse. Most CWTs treating hydraulic fracturing wastewater are located in Pennsylvania (39 facilities), and a number of CWTs (11) are located in Ohio. More are under construction or pending approval. Most are "zero-discharge" and do not have the treatment capacity to reduce TDS; their effluent is reused for hydraulic fracturing. Specialized on-site, mobile, or semi-mobile treatment facilities can be used by operators to handle wastewater without the expense of long-distance transportation and can be customized to produce an effluent that meets the water quality needs of the intended disposal or reuse plans.

Treatment of hydraulic fracturing wastewaters by publicly owned treatment works (POTWs) was previously practiced in Pennsylvania. POTWs are not designed for the high TDS content of Marcellus wastewaters, and stricter discharge limits for TDS in Pennsylvania, as well as a positive response to a request from Pennsylvania DEP that operators stop sending Marcellus wastewater to POTWs and some CWTs, led to the practice being discontinued in 2011. (Some POTWs in Pennsylvania still accept oil and gas wastewaters from conventional operations, including conventional wells that have undergone hydraulic fracturing.)

Management plans will necessarily need to change with time as hydraulic fracturing activities in a region change. The volumes of wastewater also change during the life of a well. The chemical composition of the wastewater changes during the transition from the flowback period and into the production phase. In addition, the demand for reused water to support ongoing fracturing activities will change. Taken in aggregate, these factors may influence costs and choices associated with hydraulic fracturing wastewater management, especially if Class IID wells are limited in a particular area for any reason.

8.7.1.2. Treatment and Discharge

One of the most frequently cited concerns regarding hydraulic fracturing wastewater, especially from shale plays and tight sand plays, is the high TDS content, which poses challenges for treatment, discharge, and reuse. Conventional treatment processes such as sedimentation, filtration methods, flotation, chemical precipitation and ion exchange can remove constituents such as oil and grease, major cations, metals, and TSS. Because these processes do not remove monovalent ions (e.g., chloride, bromide, sodium), reducing TDS in these high-salinity wastewaters requires more advanced processes such as reverse osmosis (RO), electrodialysis, and distillation methods. Distillation methods appear to be the approach of choice for newer CWT facilities that are designed to lower TDS. RO, while highly effective, does have limits to TDS concentrations (less than approximately 40,000 mg/L) that it can treat (Shaffer et al., 2013; Younos and Tulou, 2005).

Hydraulic fracturing wastewater discharged from treatment facilities without advanced TDS removal processes has been shown to cause elevated TDS, bromide, and chloride levels in receiving waters in Pennsylvania. Existing literature indicates that bromide and chloride are important wastewater constituents with regard to potential burdens on downstream drinking water treatment facilities. Bromide in particular is of concern due to the formation of disinfection by-products (DBPs) during disinfection. 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 DBPs (and iodinated DBPs) are more toxic than other species of DBPs. Modeling suggests that very small percentages of hydraulic fracturing wastewater in a river used as a source for drinking water treatment plants may cause a notable increase in DBP formation.

Radionuclides (in particular radium-226 and radium-228) in some hydraulic fracturing wastewaters pose concerns for the quality of discharges if they are not adequately treated. Possible elevated radionuclide content in treatment residuals is also a consideration. In Marcellus Shale gas production wastewater, radium-226, radium-228, gross alpha, and gross beta are most cited as the

radioactive constituents of concern, and concentrations can range up to thousands of pCi/L. Fewer data exist on uranium content in wastewaters, and data are also limited on radionuclide concentrations in wastewaters from other unconventional plays. A confounding issue in evaluating radium concentrations is underestimation when using traditional wet chemical methods with high-TDS waters. A variety of treatment processes can be used for removal of radium, ranging from conventional methods such as chemical precipitation and filtration to more advanced and costly techniques, such as reverse osmosis or distillation (including mechanical vapor recompression). Whether the effluent from such treatment contains elevated radium, however, will depend upon influent concentrations as well as treatment removal efficiency.

Other potential effects on drinking water resources may result from discharges or spills of hydraulic fracturing wastewaters containing elevated concentrations of barium and other metals. Again, the management strategy and treatment choices will affect the likelihood of such impacts.

8.7.2. Factors Affecting the Frequency or Severity of Impacts

On a regional scale, potential effects on drinking water resources from hydraulic fracturing wastewater will depend upon the mix of wastewater management strategies used, and potential impacts may change through time if the quantity of hydraulic fracturing wastewater changes and strategies to manage the wastewater change. For example, if use of Class IID wells becomes restricted in parts of the country where they are currently commonly used, the emphasis may shift, at least locally, from use of Class IID wells and towards the use of treatment and either discharge or reuse. Although reuse delays the discharge of wastewater by directing it to ongoing fracturing activities, reuse may ultimately concentrate constituents such as radionuclides (depending upon the ratio of recycled to new water). If a stream of wastewater or portion of wastewater has been used for more than one hydraulic fracturing event and is eventually intended for disposal, the method of disposal will need to be appropriate for the quality of the wastewater.

Potential effects on drinking water resources from hydraulic fracturing wastewaters that undergo treatment depend upon the quality and quantity of discharges to receiving waters (discharge could occur directly after treatment at a CWT or indirectly after discharge to a POTW). Hydraulic fracturing wastewater management can consider appropriate levels of treatment and blending so that the resulting TDS content in a receiving water will not result in formation of DBPs during subsequent drinking water treatment and will not impair biological treatment processes.

The volumes of discharges relative to the receiving water body size are important local factors to consider in evaluating whether elevated concentrations can be anticipated at downstream drinking water intakes. Small drinking water systems drawing water from smaller streams in affected areas would likely face greater challenges in dealing with high bromide and chloride levels in source waters. Furthermore, other potential impacts on surface water and shallow ground water may exist due to spills of either untreated wastewater or effluent from zero-discharge CWTs, and there will be site-specific factors such as distance to a water body or depth to the water table to consider (see Chapter 5).

Results from existing literature and recent PA DEP data suggest that cumulative impacts from radionuclides may occur in sediments at or near discharge points from facilities that treat and discharge oil and gas wastewater (or have done so in the past). There may be consequences for downstream drinking water systems if the sediments are disturbed or entrained due to dredging or flood events. Similarly, some organic constituents may not be removed during treatment, and potential effects on receiving waters and sediments will depend upon the properties of the specific constituents, their concentrations, and the treatment used.

The possibility of radionuclides affecting receiving waters and sediments will depend upon the technologically enhanced naturally occurring radioactive material (TENORM) content of the wastewater and the treatment processes used. Although radionuclide contamination at drinking water intakes due to treated hydraulic fracturing fluid has not been detected, a recent PA DEP study (PA DEP, 2015b) has revealed radium in effluents from both CWTs handling oil and gas wastewater and POTWs receiving effluent from such facilities. The concentrations in the CWT effluents were considerably higher than in the POTW effluents. The site selection criteria for this study included some Pennsylvania wastewater facilities whose influents include wastewater from unconventional operations or where radioactivity was measured in the influent, sludges, or effluents (CWTs may also receive conventional wastewater). In regions where unconventional plays are known to be enriched in radionuclides, analysis of TENORMs in untreated hydraulic fracturing wastewaters, selection of appropriate treatment processes, and monitoring of TENORMs in treatment effluent and receiving waters could help address potential impacts on drinking water resources. Gross alpha and gross beta measurements or gamma spectroscopic analyses could be used as initial screening methods for radionuclides. Enrichment of TENORMs in waste products from treatment processes also requires appropriate management to reduce potential impacts.

Other management strategies such as irrigation, road spreading, and evaporation are less frequently employed for hydraulic fracturing wastewaters. Irrigation or land application may have potential effects on surface waters depending upon the constituents in the wastewater (e.g., salts and radionuclides), the distance from the site of application to a receiving water, and whether stormwater management measures exist that mitigate runoff. Distance to the water table, precipitation, and the hydrogeologic properties of the soil and sediment will influence whether migration of these constituents results in contamination of shallow ground water.

8.7.3. Uncertainties

A full understanding of the practices being used for management of hydraulic fracturing wastewaters is limited by a lack of available data in a number of areas. It is difficult to assemble a complete, national- or regional-level picture of wastewater generation and management practices 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 make such information available, and it can be difficult to identify wastewater volumes specifically associated with hydraulic fracturing activity (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. Data are also

generally difficult to locate for production volumes, chemical composition, masses, and management and disposal strategies for residuals.

Among management practices, up-to-date information on the volumes of hydraulic fracturing wastewaters disposed of via underground injection in different states are 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.

Assessment of the potential effects of hydraulic fracturing on drinking water resources is also limited by relatively few data on effluent quality from CWTs that receive oil and gas wastewaters (including those associated with hydraulic fracturing) and POTWs that receive CWT effluents. If a CWT can discharge to surface water (e.g., the CWT has a NPDES permit), some monitoring data may be available that will provide information on effluent quality, but the list of monitored constituents may be limited.

In evaluating the treatment effectiveness of full scale facilities, relatively few data exist on the quality of both influents and effluents from treatment facilities, although some manufacturers of patented CWT systems publicize information on treatment effectiveness. A better understanding of the pollutant removal capabilities of facilities would be helped by influent and effluent sampling, timed so that effluent samples are representative of influent samples to the degree possible. There are limited analyses of influent and effluent samples for a wide range of constituents associated with hydraulic fracturing fluids and wastewaters (e.g., major cations and anions, radionuclides, metals, VOCs, SVOCs, diesel range organics (DROs), and total petroleum hydrocarbons (TPH)). Analyses are needed in which the methods are appropriate for the TDS content of the sample. Radium in particular needs to be analyzed using a method suitable for high-salt samples, otherwise concentrations may be underestimated. Continued work towards ensuring that analytical methods exist for the highly complex matrixes often encountered with oil and gas wastewater would provide better certainty in the results of chemical analyses.

Monitoring of surface waters, even screening with a simple TDS proxy such as conductivity, would be needed to help assess how often hydraulic fracturing activities (including spills or discharges of wastewater) affect receiving waters; such data are lacking except for some studies in the Marcellus Shale region. 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 waste water treatment residuals.

8.7.4. Conclusions

Oil and gas operations in the United States generate billions of gallons of wastewater daily; 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 due to lack of consistent data regarding wastewater volumes. Available information indicates that the majority of this water is injected into Class IID wells regulated under the Underground Injection Control (UIC) program, although in some areas of the country, wastewater is reused (either with our without treatment) for new hydraulic fracturing jobs. In the Marcellus Shale region in

Pennsylvania, the majority of wastewater is currently reused. Wastewater may also be treated in a CWT and discharged to a surface water body or to a POTW, or in certain settings, used for various other uses (e.g., irrigation) if water quality allows. Impacts on drinking water resources may result from inadequate treatment prior to discharge or spills. Particular constituents of concern in wastewater from hydraulic fracturing, especially in the Marcellus Shale region, include bromide and radionuclides. There is limited information regarding the influents and effluents from facilities that treat wastewater from hydraulic fracturing operations.

Text Box 8-2. Research Questions Revisited.

What are the common treatment and disposal methods for hydraulic fracturing wastewater, and where are these methods practiced?

- The majority of hydraulic fracturing wastewater in the United States is disposed of via underground injection wells. As of 2014-2015, most states where hydraulic fracturing occurs have an adequate number of Class IID injection wells regulated under the Underground Injection Control (UIC) program. The Marcellus Shale region, especially the northeastern region, is an exception. Wastewater treatment for reuse is increasing in the Marcellus shale region and may continue to increase in western shale plays as the practice becomes encouraged and economically favorable.

How effective are conventional POTWs and commercial treatment systems in removing organic and inorganic contaminants of concern in hydraulic fracturing wastewater?

- Publicly owned treatment works (POTWs) using basic treatment processes cannot effectively reduce elevated total dissolved solids (TDS) concentrations in hydraulic fracturing wastewater. Centralized waste treatment facilities (CWTs) with advanced treatment processes can remove TDS constituents with removal efficiencies ranging from 97% to over 99% as demonstrated at facilities that use treatment processes such as mechanical vapor recompression, distillation, and reverse osmosis (see Table 8-6). Advanced treatment processes have been shown to remove certain contaminants found in hydraulic fracturing wastewater (see Table 8-6). Indirect discharge, where wastewater is pretreated by a CWT and sent to a POTW, may be an effective option for hydraulic fracturing wastewater treatment (with restrictions on contaminant concentrations in the pretreated wastewater that is sent to a POTW). This option would require careful planning to ensure that the pretreated wastewater blended with POTW influent is of appropriate quality and quantity to prevent deleterious effects on biological processes in the POTW or the pass-through of contaminants.
- Facilities that treat wastewater for reuse and employ only basic treatment are unable to remove all contaminants in hydraulic fracturing wastewater. Depending on the water quality requirements for a particular site, these lower quality treated waters may be of adequate quality for reuse on subsequent hydraulic fracturing operations (and will be less costly). Some organic compounds (BTEX, some alcohols, 2-butoxyethanol) may not be removed by the processes employed in CWTs if they don't include specific processes that target these compounds (e.g., distillation, advanced oxidation, adsorption).

What are the potential impacts on drinking water treatment facilities from surface water disposal of treated hydraulic fracturing wastewater?

- Inadequate bromide and iodide removal from treated hydraulic fracturing wastewater has the greatest potential to affect surface water quality and place a burden on downstream drinking water treatment facilities that use chlorine-based disinfection due to the formation of DBPs. Radionuclides, metals, and trace organic compounds in effluents from CWTs may also be of concern if present in treated wastewater or if they accumulate in sediments downstream of discharge points. These constituents have reached drinking water resources via some discharges, although sampling data for effluents and receiving waters are limited. As of 2014-2015, there is no evidence that these contaminants have affected drinking water facilities, but data are lacking for concentrations of these constituents at drinking water intakes in regions with hydraulic fracturing.

8.8. References for Chapter 8

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Chapter 9

Identification and Hazard Evaluation of Chemicals across the Hydraulic Fracturing Water Cycle

9. Identification and Hazard Evaluation of Chemicals across the Hydraulic Fracturing Water Cycle

9.1. Introduction

Chapters 4 through 8 of this assessment each present a stage of the hydraulic fracturing water cycle and the mechanisms by which activities in those stages produce potential impacts on drinking water resources. In contrast, this chapter presents and integrates what is known about chemicals *across* stages of the hydraulic fracturing water cycle (i.e., used in hydraulic fracturing fluids and detected in hydraulic fracturing wastewater). The discussion is focused on available information about (1) chronic toxicity values—specifically, the available noncancer oral reference values (RfVs) and cancer oral slope factors (OSFs)—of chemicals that could occur in drinking water resources; and (2) properties of chemicals that could affect their occurrence in drinking water resources (see Chapters 5 and 7).[1,2] To the extent that information was available to do so, knowledge of toxicological and chemical properties was combined to illustrate an approach that may provide preliminary insights about the relative hazard potential that chemicals could pose to drinking water resources.

Risk assessment and risk management decisions will be informed by the scientific information on the toxicity of chemicals in hydraulic fracturing fluid and wastewater, which recent authors note is incomplete (Goldstein et al., 2014). 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). However, that report did not characterize the potential toxicity of many of the other compounds known to occur in hydraulic fracturing fluids or wastewater. More recently, Kahrilas et al. (2015) reviewed the toxicity and physicochemical properties of biocides used in hydraulic fracturing. Stringfellow et al. (2014) examined the toxicity and physicochemical properties of several classes of chemicals that are reportedly used in hydraulic fracturing; however, this study only reported acute toxicity (from lethal doses), which may differ from the effects of low-dose, chronic exposure to these chemicals. Wattenberg et al. (In Press) assessed the acute and chronic toxicity data that was available for 168 chemicals from the FracFocus database that had at least 25 reports of use in North Dakota. The authors found that 113 of these chemicals had some health hazard data available, but determined that there were significant data gaps, particularly with regards to what is known about the potential chronic toxicity of these chemicals. Overall, available

[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. In the context of this chapter, the term RfV refers to reference values for noncancer effects occurring via the oral route of exposure and for chronic durations, except where noted. Source: IRIS Glossary (U.S. EPA, 2011d).

[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.

information indicates that there may be hundreds of chemicals associated with the hydraulic fracturing water cycle for which toxicological data is limited or unavailable.

Furthermore, the potential public health impact of hydraulic fracturing processes is not well understood (Finkel et al., 2013; Colborn et al., 2011). Potential public health implications are highlighted in the recent studies by McKenzie et al. (2014) and Kassotis et al. (2014), but as of early 2015, there is a lack of published, peer-reviewed epidemiological or toxicological studies that have examined health effects resulting from water contamination due to hydraulic fracturing. However, numerous authors have noted that with the recent increase in hydraulic fracturing operations there may be an increasing potential for significant public health and environmental impacts via ground and surface water contamination (Goldstein et al., 2014; Finkel et al., 2013; Korfmacher et al., 2013; Weinhold, 2012).

This chapter provides a compilation of the chemicals used or released during the fracturing process, and information about their potential health effects. The data are presented in this chapter as follows.

Section 9.2 discusses how ten information sources, including the EPA's analysis of the FracFocus database (U.S. EPA, 2015a), were used to create a list of chemicals used in or detected in various stages of the hydraulic fracturing water cycle. This chemical list was initially presented in the EPA's 2012 interim progress report (U.S. EPA, 2012f), and has been updated in this assessment with additional chemicals from FracFocus. The consolidated chemical list includes chemicals that are 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 flowback or produced water. Although over half of the chemicals cited on this list are listed in the EPA FracFocus database, this chapter is not meant to be interpreted as a hazard evaluation of the chemicals listed in the EPA FracFocus database alone.

Section 9.3 provides an overview of the methods that were used for gathering information on toxicity and physicochemical properties for all chemicals that were identified in Section 9.2, and outlines the number of chemicals that had available data on these properties. For toxicological data, the primary focus is on peer-reviewed, selected chronic oral RfVs and OSFs. This section also discusses additional potential sources of toxicity information: estimates of toxicity predicted using Quantitative Structure Activity Relationship (QSAR) modeling, or toxicological information available on the EPA's Aggregated Computational Toxicology Resource (ACToR) database. 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 (see below) do not necessarily apply to other routes of exposure, such as inhalation or dermal exposure. In addition, this analysis is focused on individual chemicals rather than mixtures of chemicals used as additives. Furthermore, the propensity for a chemical to pose a physical hazard (e.g. the flammability and explosiveness of stray gas methane) are not considered here.

Many chemicals reported in hydraulic fracturing were identified as being of interest in previous chapters of this report. This includes the most frequently used chemicals in hydraulic fracturing fluid (Chapter 5), the most and least mobile chemicals in hydraulic fracturing fluid (Chapter 5), and inorganic chemicals and pesticides that may be detected in flowback and produced water (Chapter 7). The available selected chronic oral RfVs and OSFs for these chemicals are summarized in Section 9.4.

Section 9.5 describes the hazard identification and hazard evaluation of chemicals for which data was available on toxicity, occurrence, and physicochemical properties.[1,2] For hazard identification, the selected chronic oral RfVs and OSFs and health effects for these chemicals are presented and summarized. To illustrate one approach to integrate toxicity, occurrence and physicochemical properties data to generate a hazard potential score, a multicriteria decision analysis (MCDA) framework was developed. In this context, occurrence and physicochemical property data were used as metrics to estimate the likelihood that a chemical could impact drinking water resources. Chemicals considered in these hazard evaluations include a subset of chemicals from the FracFocus database, as well as a subset of chemicals that have been detected in flowback and produced water.

In general, characterizing chemicals and their properties on a national scale is challenging and that the use and occurrence of chemicals is likely to differ between geological basins and possibly on a well-to-well basis (see Chapters 5 and 7). Therefore, for the protection of public health at the community level, chemical hazard evaluations may be most useful to conduct 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 the greatest potential human health hazard.

9.2. Identification of Chemicals Associated with the Hydraulic Fracturing Water Cycle

As the initial step towards developing a hazard evaluation, the EPA compiled a list of chemicals that are used in or released by hydraulic fracturing operations across the country (U.S. EPA, 2012f). Ten sources of information (described in Appendix A) were used to develop this list. This consolidated list was used to compile two sublists: (1) a list of chemicals known to be used in hydraulic fracturing fluids, and (2) a list of chemicals that are reported to have been detected in hydraulic fracturing flowback and produced water. It is likely that, as industry practices change, chemicals may be used or detected that are not included on these lists. In addition, those chemicals that are considered proprietary and identified as confidential business information (CBI) by well operators are not listed or considered.

[1] Hazard identification is a process for determining if a chemical or a microbe can cause adverse health effects in humans and what those effects might be. See Terms of Environment at: http://iaspub.epa.gov/sor_internet/registry/termreg/searchandretrieve/termsandacronyms/search.do.

[2] Hazard evaluation is a component of risk assessment that involves gathering and evaluating data on the types of health injuries or diseases (e.g., cancer) that may be produced by a chemical and on the conditions of exposure under which such health effects are produced. See Terms of Environment at: http://iaspub.epa.gov/sor_internet/registry/termreg/searchandretrieve/termsandacronyms/search.do.

In total, the EPA identified 1,173 chemicals as being used in hydraulic fracturing fluid and/or detected in flowback and produced water. The complete list of chemicals and associated data is available in Appendices A and B.[1]

9.2.1. Chemicals Used in Hydraulic Fracturing Fluids

Of the 1,173 total chemicals, the EPA identified 1,076 chemicals as being used in hydraulic fracturing fluids. Of these, 692 chemicals were listed in the FracFocus database, and therefore had information available in order to calculate their nationwide frequency of use (U.S. EPA, 2015a).[2] Frequency of use for individual chemicals ranged from low (481 chemicals on the list were used in less than 1% of wells nationwide) to very high (methanol was used in 73% of wells nationwide). Furthermore, only 32 chemicals (excluding water, quartz, and sodium chloride) were reported in at least 10% of the disclosures nationwide (see Section 5.4 and Table 5-2). As noted previously, the FracFocus database does not list or consider those chemicals identified as CBI. The EPA determined that approximately 70% of the disclosures in the FracFocus database contain at least one CBI chemical, and for those disclosures, the average number of CBI chemicals per disclosure was five (see Section 5.4, Text Box 5-3). Additionally, as noted previously, approximately 35% of FracFocus ingredient records were not able to be assigned standardized chemical names. These ingredient records were excluded from the EPA's analysis (see Section 5.10).

9.2.2. Chemicals Detected in Flowback and Produced Water

Of the 1,173 total chemicals, 134 were identified as having been detected in flowback or produced water. Included among these chemicals are naturally occurring organic compounds, metals, radionuclides, and pesticides. As reported in Chapter 7, concentration data in flowback or produced water are available for 75 of these 134 chemicals (see Appendix E), including inorganic contributors to salinity (Tables E-4 and E-5), metals (Tables E-6 and E-7), radioactive constituents (Table E-8), and organic constituents (Tables E-9, E-10, and E-11). 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 (Table E-10), average or median measured concentrations ranged from 2.7 μg/L for N-nitrosodiphenylamine to 400 μg/L for carbon disulfide. According to the sources listed in Appendix A, 37 of the total 134 chemicals in flowback and produced water were also identified as being used in hydraulic fracturing fluid.

9.3. Toxicological and Physicochemical Properties of Hydraulic Fracturing Chemicals

Toxicological and physicochemical data were collected as available for each of the chemicals identified in Appendix A. The criteria used to identify and select toxicity values, RfVs and OSFs (Section 9.3.1), and the method used to generate physicochemical property data (Section 9.3.2) are discussed below. A summary of the available data for these chemicals follows in Section 9.3.3. Other

[1] The list of 1,173 chemicals was finalized as of this 2015 draft assessment. There may be chemicals present in flowback and produced water that are not included on this list.
[2] The FracFocus frequency of use data presented in this chapter is based on 35,957 well disclosures.

possible sources of toxicological information, including QSAR-approaches and the EPA's ACToR database, are discussed in Section 9.3.4.

9.3.1. Selection of Toxicity Values: Reference Values (RfVs) and Oral Slope Factors (OSFs)

Toxicity information spans a wide range with respect to extent, quality and reliability. Toxicological data may include assessments from various sources including state, national, international, private and academic organizations as well as toxicity information which has not been formalized into an assessment and may be found in the scientific literature and databases including results from guideline tests, high throughput screening assays, alternative assays, and QSAR models. The sources of toxicity values – specifically, chronic oral RfVs and OSFs – selected for the purposes of this chapter are based on criteria developed specifically for this report. For many of the chemicals used in hydraulic fracturing or found in flowback or produced water there may be relevant information, including cancer and noncancer-related information, from one or more sources that were not evaluated in this chapter.

The sources of RfVs and OSFs selected 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; and 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. 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.

RfVs and OSFs available from the EPA IRIS, the EPA PPRTV program, ATSDR, and the EPA HHBP program all met the criteria for selection and inclusion as a data source (see Table 9-1). An attempt was made to identify and acquire RfVs and OSFs from all 50 states, but only the peer-reviewed state RfVs and OSFs from California met the stringent selection criteria and were included because of the state's extensive peer review process.[1] One international source for RfVs, the World Health Organization's (WHO) International Programme on Chemical Safety (IPCS) Concise International Chemical Assessment Documents (CICAD), also met the selection criteria. The International Agency for Research on Cancer (IARC) and U.S. National Toxicology Program (NTP) Report on Carcinogens also met the criteria and were used as additional sources for qualitative cancer classifications.

Table 9-1. Sources of selected toxicityRfVs and OSFs.

Source	Website

[1] 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.

Source	Website
EPA Integrated Risk Information System (IRIS)	http://cfpub.epa.gov/ncea/iris/index.cfm?fuseaction=iris.showSubstanceList
Human Health Benchmarks for Pesticides (HHBP)	http://iaspub.epa.gov/apex/pesticides/f?p=HHBP:home
EPA Provisional Peer-Reviewed Toxicity Value (PPRTV) database	http://hhpprtv.ornl.gov/index.html
Agency for Toxic Substances and Disease Registry (ATSDR) Minimum Risk Levels	http://www.atsdr.cdc.gov/toxprofiles/index.asp#bookmark05
State of California Toxicity Criteria Database	http://www.oehha.org/tcdb/index.asp
International Programme on Chemical Safety (IPCS) Concise International Chemical Assessment Documents (CICAD)	http://www.who.int/ipcs/publications/cicad/en/

EPA generally applies federal RfVs and OSFs for use in human health risk assessments. Therefore, for the purpose of hazard evaluation and making comparisons between chemicals in this chapter, only federal chronic oral RfVs and OSFs from the EPA IRIS, the EPA PPRTV program, ATSDR, and the EPA HHBP program were used. Furthermore, when a chemical had an RfV and/or OSF from more than one federal source, a modification of the EPA Office of Solid Waste and Emergency Response (OSWER) Directive 9285.7-53 tiered hierarchy of toxicity values was applied to determine which value to use. A single RfV and/or OSF was selected from the sources in this order: IRIS, HHBP, PPRTV, and ATSDR.[1] The RfVs considered from these sources included noncancer reference doses (RfDs) from the IRIS, PPRTV, and HHBP programs, and oral minimum risk levels (MRLs) from ATSDR.[2,3]

Because there are relatively few OSFs available compared to RfVs, OSFs were excluded from discussion in this chapter; however, all available OSFs are reported in Appendix G. The EPA drinking water maximum contaminant levels (MCLs) were also excluded from this analysis because they are treatment-based. MCLs are set as close to maximum containment level goal (MCLG) values as feasible. However, MCL and MCLGs values are still reported in Appendix G for the sake of completeness.

[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. See Appendix G for details.
[2] A 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. For the complete definition see Appendix G.
[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), noncancerous 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. Chronic MRL: Duration of exposure is 365 days or longer.

9.3.2. Physicochemical Properties

As presented in Chapter 5, EPI Suite™ software was used to generate data on the physicochemical properties of chemicals on the consolidated list. EPI Suite™ provides an estimation of physicochemical properties based upon chemical structure, and will additionally provide empirically measured values for these properties when they are available for a given chemical. For more details on the software and on the use of physicochemical properties for fate and transport estimation, see Chapter 5.

9.3.3. Summary of Selected Toxicological and Physicochemical Property Data for Hydraulic Fracturing Chemicals

Figure 9-1 summarizes the availability of selected RfVs and OSFs and physicochemical data for the 1,173 hydraulic fracturing chemicals identified by the EPA.

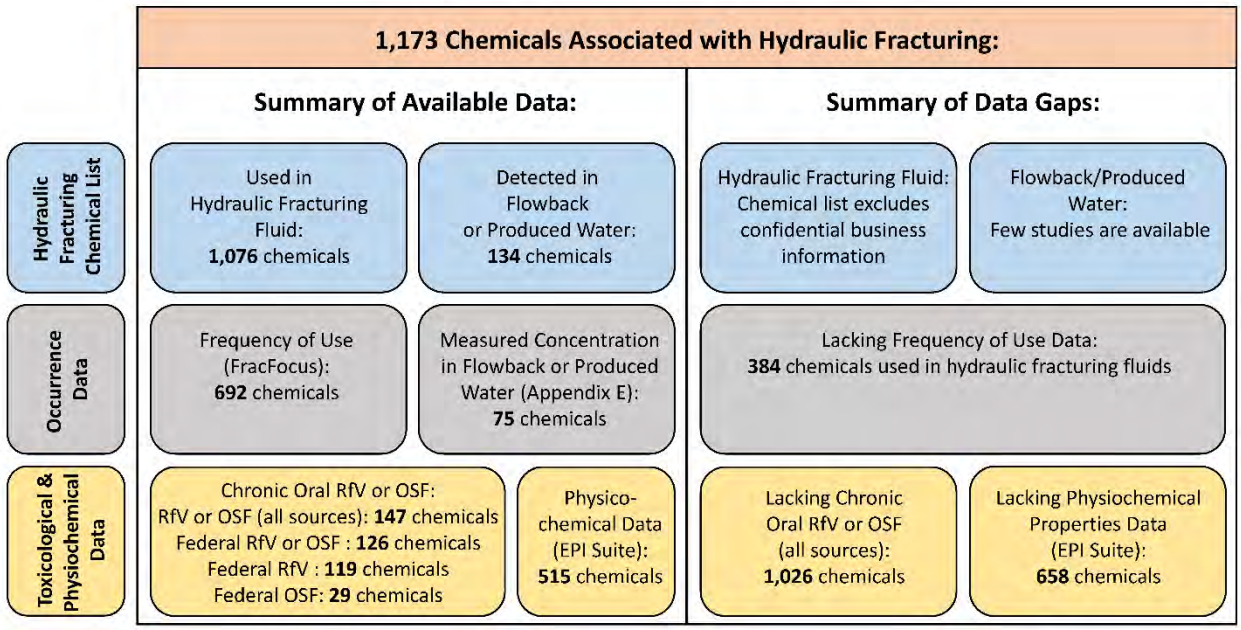

Figure 9-1. Overall representation of the selected RfVs and OSFs, occurrence data, and physicochemical data available for the 1,173 hydraulic fracturing chemicals identified by the EPA.

Of the 1,173 chemicals identified by the EPA, only 147 (13%) have federal, or state, or international chronic oral RfVs and/or OSFs from sources listed in Table 9-1. Therefore, chronic RfVs and/or OSFs from the selected sources are lacking for 87% of chemicals that the EPA has identified as associated with hydraulic fracturing. All available chronic RfVs and OSFs from the sources listed in Table 9-1 are tabulated in Appendix G. Chronic RfVs and OSFs for chemicals used in hydraulic fracturing fluids are listed in Tables G-1a through G-1c, and chronic RfVs and OSFs for chemicals

reported in hydraulic fracturing flowback and produced water are listed in Tables G-2a through G-2c.

From the U.S. federal sources that were considered here, the availability of chronic RfVs and OSFs can be summarized as follows. Of the 1,173 chemicals on the consolidated list, a total of 126 chemicals have federal chronic RfVs and/or OSFs. Of these 126 chemicals, 119 have federal chronic RfVs, and 29 have federal OSFs (see Figure 9-1). 22 chemicals have both a federal chronic RfV and a federal OSF, while 7 have a federal OSF only.

Overall, when chemicals in hydraulic fracturing fluid and chemicals in flowback are considered separately, the availability of chronic RfVs and OSFs can be summarized as follows:

- For the 1,076 chemicals used in hydraulic fracturing fluid, chronic RfVs from all of the selected federal, state, and international sources were available for 90 chemicals (8.4%). From the federal sources alone, chronic RfVs were available for 73 (6.8%), and OSFs were available for 15 (1.4%).

- For the 134 chemicals reported in flowback and produced water, chronic RfVs from all of the selected federal, state, and international sources were available for 83 chemicals (62%). From the federal sources alone, chronic RfVs were available for 70 chemicals (52%), and OSFs were available for 20 (15%).

The IRIS database was the most abundant source of the federal chronic RfVs and OSFs. IRIS had available RfDs for 77 of the total 1,173 chemicals, and OSFs for 27 chemicals. Of the other federal data sources, the PPRTV database had RfDs for 33 chemicals, and OSFs for 2 chemicals; the HHBP database had RfDs for 11 chemicals, but did not have available OSFs for any of the chemicals; and the ATSDR database had chronic oral MRLs for 27 chemicals.

In addition to these chronic values, many of the chemicals also have less-than-chronic federal oral RfVs. Subchronic or acute federal RfVs were identified for 91 chemicals on the consolidated list, including 55 chemicals used in hydraulic fracturing fluid (Table G-1d), and 56 chemicals reported in flowback or produced water (Table G-2d). There were 8 chemicals that had less-than-chronic RfVs but lacked a chronic RfV. All of these less-than-chronic RfVs were found on the PPRTV or ATSDR databases; the IRIS database did not have less-than-chronic RfVs for any of these chemicals. These values are not discussed in this report, but are provided in Appendix G as supporting information.

From the total list of 1,173 chemicals associated with hydraulic fracturing, EPI Suite™ was able to generate data on physicochemical properties for 515 (44%) of the chemicals (see Appendix A). The remaining 658 chemicals lacked the structural information necessary to generate an estimate.

9.3.4. Additional Sources of Toxicity Information

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 toxicity information. This section discusses other publicly accessible sources of toxicological data that are lower on the continuum of quality and reliability in comparison to the

selected RfVs and OSFs described above. Because the quality of these data is unknown for most chemicals, values from these data sources are not included in the hazard evaluation in this report.

9.3.4.1. Estimated Toxicity Using Quantitative Structure Activity Relationships (QSAR)

One potential source of toxicological information is QSAR software, which is able to provide estimates or predictions of toxicity based on chemical structure. QSAR models for toxicity have been used and evaluated in a number of previous studies published in the peer reviewed literature (Rupp et al., 2010; Venkatapathy et al., 2004; Moudgal et al., 2003). A key advantage to QSAR models is that they are able to rapidly and inexpensively estimate toxicity values for chemicals. Compared to toxicological studies involving animals or in vitro methods, which have monetary, time, and ethical considerations associated with them, the QSAR method requires only information on chemical structure in order to generate a toxicity estimation. These values may be of lower quality and less reliable than values generated using traditional toxicological methods. However, because they increase the available pool of toxicity information, QSAR estimates may potentially be a useful resource for risk assessors that are faced with evaluating potential exposures to data-poor chemicals.

9.3.4.2. Chemical Data Available from ACToR

An additional tool for obtaining toxicological information is the ACToR database.[1] ACToR is a large data warehouse developed by the EPA to gather and house large and disparate amounts of public data on chemicals including chemical identity, structure, physicochemical properties, in vitro assay results, and in vitro toxicology data (Judson et al., 2009). ACToR contains data on over 500,000 chemicals from over 2,500 sources, covering many domains including hazard, exposure, risk assessment, risk management, and use. Data in ACToR is organized on several levels of "assays" and "assay categories". The information available in 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.

The ACToR database was searched for information related to the total list of 1,173 chemicals associated with hydraulic fracturing.[2] For the purposes of this chapter, the database was first searched for all of the assays and assay categories that had data on these chemicals. This initial search was then filtered to only include the assay categories that are most relevant to toxicity via the oral route of exposure (drinking water). These assay categories were assigned into the following nine data classes: carcinogenicity, dose response values, drinking water criteria, genotoxicity/mutagenicity, hazard identification, LOAEL/NOAEL, RfD, slope factor, and water quality criteria. The type of data and examples of the data sources included in these data classes can be found in the ACToR database documentation.

When all assays and assay categories were considered, it was found that all but 28 of the total 1,173 chemicals had available data on ACToR. When only the relevant assays and assay categories were considered, 642 (55%) of the chemicals were found to have data on ACToR. The fraction of

[1] The ACToR database is available at: http://actor.epa.gov.
[2] The ACToR database was queried for the total list of 1,173 chemicals on April 1, 2015.

chemicals that had at least one data point in each of the nine ACToR data classes is shown in Figure 9-2. As can be seen in Figure 9-2, about half of the chemicals had some information on water quality criteria, while fewer chemicals had information on the other classes of data.

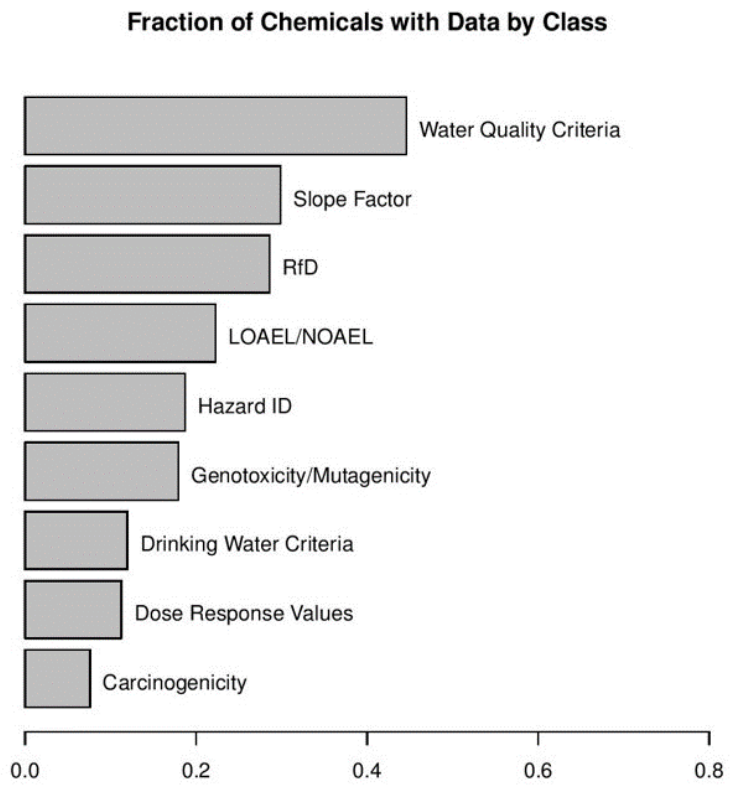

Figure 9-2. Fraction of chemicals with at least one data point in each ACToR data class.

Focusing on the 1,026 chemicals that lacked a chronic RfV and/or OSF from the selected sources described in Section 9.3.1, 497 (48%) of these chemicals had available data on ACToR. Because ACToR has a significant amount of data on potential chemical hazards, including for some data-poor chemicals, ACToR might help to fill data gaps in the ongoing effort to understand potential hazards of hydraulic fracturing chemicals. Since the quality of the non-peer reviewed values is not known, these data are not considered in the hazard evaluation.

9.4. Hazard Identification of Reported Hydraulic Fracturing Chemicals

This section focuses on 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. Federal RfVs are identified for these chemicals as available.

9.4.1. Selection of Additional Chemicals for Hazard Identification

Four subsets of chemicals were identified as being of interest in Chapter 5 (Chemical Mixing) and Chapter 7 (Flowback and Produced water):

1. Chapter 5: The most frequently used chemicals in hydraulic fracturing fluid, defined as chemicals being reported to the FracFocus database in at least 10% of well disclosures (U.S. EPA, 2015a).

2. Chapter 5: The top 20 most and least mobile chemicals from the EPA's analysis of the FracFocus database (U.S. EPA, 2015a), as determined based on the octanol-water partition coefficient (K_{ow}) from EPI Suite™.

3. Chapter 7: Inorganic chemicals that may be returned to the surface in flowback and produced water. This includes metals, inorganic ions, and naturally occurring radioactive material (NORM).

4. Pesticides occurring in flowback and produced water.

The hazard identification for these four subsets of chemicals is presented below.

9.4.2. Hazard Identification Results

9.4.2.1. Most Frequently Used Chemicals in Hydraulic Fracturing Fluid (FracFocus)

Chapter 5 listed 35 chemicals that are reported to the FracFocus database in at least 10% of well disclosures nationwide (U.S. EPA, 2015a) (Table 5-2). For 32 of these chemicals (water, quartz, and sodium chloride were excluded from this analysis), only 7 chemicals (22%) have a federal chronic RfV, as shown in Table 9-2. None of these 32 chemicals have available OSFs for cancer. For this subset of chemicals, methanol was reported to be the most frequently used chemical in the FracFocus analysis, followed by hydrotreated light petroleum distillates and hydrochloric acid, all of which were reported in greater than 60% of disclosures. Ethylene glycol, isopropanol, and peroxydisulfuric acid-diammonium salt are the only 3 additional chemicals to have been used in greater than 40% of disclosures.

Table 9-2. List of the most frequently used chemicals in hydraulic fracturing fluids, with their respective federal chronic RfVs where available.

Chemicals are ordered in the table, from high to low, based on their frequency of use from FracFocus. Includes all chemicals reported to FracFocus in at least 10% of well disclosures, excluding water, quartz, and sodium chloride.

Chemical	CASRN	RfV	Source
		Chronic RfD (mg/kg-day)	
Methanol	67-56-1	2	IRIS
Distillates, petroleum, hydrotreated light	64742-47-8	--	--
Hydrochloric acid	7647-01-0	--	--

Chemical	CASRN	RfV	Source
		Chronic RfD (mg/kg-day)	
Ethylene glycol	107-21-1	2	IRIS
Isopropanol	67-63-0	--	
Peroxydisulfuric acid, diammonium salt	7727-54-0	--	--
Guar gum	9000-30-0	--	--
Sodium hydroxide	1310-73-2	--	--
Propargyl alcohol	107-19-7	0.002	IRIS
Glutaraldehyde	111-30-8	--	--
Ethanol	64-17-5	--	--
Potassium hydroxide	1310-58-3	--	--
Acetic acid	64-19-7	--	--
Citric acid	77-92-9	--	--
2-Butoxyethanol	111-76-2	0.1	IRIS
Solvent naphtha, petroleum, heavy arom.	64742-94-5	--	--
Naphthalene	91-20-3	0.02	IRIS
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	--	--
Choline chloride	67-48-1	--	--
Phenolic resin	9003-35-4	--	--
Methenamine	100-97-0	--	--
Carbonic acid, dipotassium salt	584-08-7	--	--
1,2,4-Trimethylbenzene	95-63-6	--	--
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides	68424-85-1	--	--
Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture)	127087-87-0	--	--
Formic acid	64-18-6	0.9	PPRTV
Sodium chlorite	7758-19-2	0.03	IRIS
Nonyl phenol ethoxylate	9016-45-9	--	--
Tetrakis(hydroxymethyl)phosphonium sulfate	55566-30-8	--	--
Polyethylene glycol	25322-68-3	--	--
Ammonium chloride	12125-02-9	--	--
Sodium persulfate	7775-27-1	--	--

9.4.2.2. Most and Least Mobile Chemicals Used in Hydraulic Fracturing Fluid (FracFocus)

Chapter 5 lists the 20 most mobile chemicals (Table 5-7) and 20 least mobile chemicals (Table 5-8) from the EPA's analysis of the FracFocus database (U.S. EPA, 2015a). For these lists, mobility was determined based on K_{ow}. For the 20 most mobile chemicals, no federal chronic RfVs or OSFs were available (see Table 9-3). Similarly, for the 20 least mobile chemicals, only one chemical—di(2-ethylhexyl) phthalate—had a federal chronic RfV available (see Table 9-4).

Table 9-3. List of the 20 most mobile chemicals used in hydraulic fracturing fluid, with their respective federal chronic RfVs where available.

Chemicals are ordered in the table by lowest estimated log K_{ow}. None of these chemicals had federal chronic RfVs available.

Chemical	CASRN	Log K_{ow} (unitless)	RfV	Source
			Chronic RfD (mg/kg-day)	
1,2-Ethanediaminium, N,N'-bis[2-[bis(2-hydroxyethyl)methylammonio]ethyl]-N,N'-bis(2-hydroxyethyl)-N,N'-dimethyl-, tetrachloride	138879-94-4	-23.19	--	--
Phosphonic acid, [[(phosphonomethyl)imino] bis[2,1-ethanediylnitrilobis (methylene)]]tetrakis-	15827-60-8	-9.72	--	--
Phosphonic acid, [[(phosphonomethyl)imino] bis[2,1-ethanediylnitrilobis (methylene)]]tetrakis-, sodium salt	22042-96-2	-9.72	--	--
Phosphonic acid, [[(phosphonomethyl)imino] bis[2,1-ethanediylnitrilobis (methylene)]]tetrakis-, ammonium salt (1:x)	70714-66-8	-9.72	--	--
Phosphonic acid, (((2-[(2-hydroxyethyl)(phosphono methyl)amino)ethyl)imino]bis (methylene))bis-, compd. with 2-aminoethanol	129828-36-0	-6.73	--	--
2-Hydroxy-N,N-bis(2-hydroxyethyl)-N-methylethanaminium chloride	7006-59-9	-6.7	--	--
N-(3-Chloroallyl)hexaminium chloride	4080-31-3	-5.92	--	--
3,5,7-Triazatricyclo(3.3.1.1(superscript 3,7))decane, 1-(3-chloro-2-propenyl)-, chloride, (Z)-	51229-78-8	-5.92	--	--
(2,3-dihydroxypropyl)trimethylammonium chloride	34004-36-9	-5.8	--	--
Phosphonic acid, [[(phosphonomethyl)imino] bis[6,1-hexanediylnitrilobis(methylene)]]tetrakis-	34690-00-1	-5.79	--	--

Chemical	CASRN	Log K_{ow} (unitless)	RfV Chronic RfD (mg/kg-day)	Source
[Nitrilotris(methylene)]tris-phosphonic acid pentasodium salt	2235-43-0	-5.45	--	--
Aminotrimethylene phosphonic acid	6419-19-8	-5.45	--	--
Choline chloride	67-48-1	-5.16	--	--
Choline bicarbonate	78-73-9	-5.16	--	--
alpha-Lactose monohydrate	5989-81-1	-5.12	--	--
Lactose	63-42-3	-5.12	--	--
Tetrakis(hydroxymethyl)phosphonium sulfate	55566-30-8	-5.03	--	--
Disodium ethylenediaminediacetate	38011-25-5	-4.76	--	--
Nitrilotriacetamide	4862-18-4	-4.75	--	--
1,3,5-Triazine-1,3,5(2H,4H,6H)-triethanol	4719-04-4	-4.67	--	--

Table 9-4. List of the 20 least mobile chemicals used in hydraulic fracturing fluid, with their respective federal chronic RfVs where available.

Chemicals are ordered in the table by highest estimated log K_{ow}.

Chemical	CASRN	Log K_{ow} (unitless)	RfV Chronic RfD (mg/kg-day)	Source

Chemical	CASRN	Log K_{ow} (unitless)	RfV Chronic RfD (mg/kg-day)	Source
Sorbitan, tri-(9Z)-9-octadecenoate	26266-58-0	22.56	--	--
Fatty acids, C18-unsatd., dimers	61788-89-4	14.6	--	--
Sorbitan sesquioleate	8007-43-0	14.32	--	--
Tributyltetradecylphosphonium chloride	81741-28-8	11.22	--	--
Sodium bis(tridecyl) sulfobutanedioate	2673-22-5	11.15	--	--
1-Eicosene	3452-07-1	10.03	--	--
D&C Red 28	18472-87-2	9.62	--	--
C.I. Solvent Red 26	4477-79-6	9.27	--	--
1-Octadecene	112-88-9	9.04	--	--
Alkenes, C>10 .alpha.-	64743-02-8	8.55	--	--
Dioctyl phthalate	117-84-0	8.54	--	--
Benzene, C10-16-alkyl derivs.	68648-87-3	8.43	--	--
Di(2-ethylhexyl) phthalate	117-81-7	8.39	0.02	IRIS
1-Octadecanamine, N,N-dimethyl-	124-28-7	8.39	--	--
N,N-dimethyloctadecylamine hydrochloride	1613-17-8	8.39	--	--
Butyryl trihexyl citrate	82469-79-2	8.21	--	--
1-Hexadecene	629-73-2	8.06	--	--
Benzo(g,h,i)perylene	191-24-2	7.98	--	--
Dodecylbenzene	123-01-3	7.94	--	--
Isopropanolamine dodecylbenzene	42504-46-1	7.94	--	--

9.4.2.3. Flowback and Produced Water: Inorganics and NORM

In addition to a number of volatile and semi-volatile organic compounds presented below, Chapter 7 also discusses the appearance of inorganic constituents such as metals, inorganic ions, and naturally occurring radioactive material (NORM) in flowback and produced water. A number of metals detected in flowback and produced water that appear on the EPA's consolidated list and are noted in Chapter 7 have federal RfVs and/or OSFs listed in Appendix G (Table G-2). These metals and inorganic ions include: iron, boron, chromium, zinc, arsenic, manganese, cadmium, and strontium. These metals have oral RfVs based on a number of health effects including: neurotoxicity, developmental and liver toxicity, hyperpigmentation and keratosis of the skin, and decrements in blood copper status and enzyme activity. Chromium (VI) is classified as a known

human carcinogen by IARC and NTP, while arsenic is classified as known human carcinogen by the EPA, IARC, and NTP. Radionuclides, such as radium-226, radium-228, and uranium-238, which are naturally occurring in the formation may also return to the surface within produced water. Each of these radionuclides is classified as a known human carcinogen by the EPA and IARC.

9.4.2.4. Flowback and Produced Water: Pesticides

Lastly, it should be noted that a number of pesticides appear in the tables presented in Appendix G. These chemicals were reported as having been detected in analyses of hydraulic fracturing flowback and produced waters by several of the 10 sources cited in Appendix A; however, there is much uncertainty about why they were detected. They could have migrated to the shale formation or to the rock surrounding the shale formation, or they could have migrated into source waters used by the hydraulic fracturing operation. It is also possible that these are laboratory contaminants.

9.5. Hazard Identification and Hazard Evaluation of Selected Subsets of Hydraulic Fracturing Chemicals

As described in Section 9.4, the majority of chemicals identified in the previous chapters of this report do not have RfVs and/or OSFs from the sources meeting the criteria described in Section 9.3.1. This lack of data creates a challenge for hazard evaluation, because the potential human health effects of these chemicals are difficult to determine. On the other hand, other chemicals identified by the EPA have more data available, including chronic RfVs, data on occurrence, and data on physicochemical properties. This section focuses on the hazard evaluation of these subsets of chemicals that had data available.

When considering the hazard evaluation of chemicals in drinking water, it is important to remember that toxicity is contingent upon exposure. All chemicals, including pure water, may be toxic if they are ingested in large enough quantities. Therefore, in addition to data on health effects, hazard evaluations must also consider data on potential chemical exposure. In the context of the hazard evaluation presented in this section, chemical occurrence and physicochemical property data were used as metrics to estimate the likelihood that the chemical could reach and impact drinking water resources.

For the selected subsets of chemicals that had data available, this section discusses the known toxicological properties based on selected RfVs (hazard identification), and then illustrates one possible method for combining toxicity and exposure potential information for a more data-informed hazard evaluation. Additionally, this section presents a summary of chemicals that have occurrence data across multiple stages of the hydraulic fracturing water cycle.

9.5.1. Selection of Chemicals for Hazard Evaluation

From the overall list of 1,173 chemicals identified in this assessment, subsets of chemicals were selected for hazard evaluation if they met the following criteria:

1. Had a federal chronic oral RfV;

2. Had available data on frequency of use (in hydraulic fracturing fluids) or measured concentrations (in flowback and produced water); and
3. Had available data on physicochemical properties.

These criteria were selected for hazard evaluation for the following reasons:

1. Federal RfVs generally undergo more extensive independent peer review compared to other sources of RfVs. Additionally, as described above, there are many more chemicals with federal chronic RfVs than chemicals with federal OSFs. Therefore, although OSFs are discussed in the hazard evaluation, chronic RfVs were selected for illustrative purposes of making comparisons between chemicals.
2. Data on frequency of use (in hydraulic fracturing fluids) or measured concentration (in flowback or produced water) provide a metric to help assess the likelihood of chemical occurrence in the hydraulic fracturing water cycle. Chemicals that are used more frequently in hydraulic fracturing fluid have a greater likelihood of accidental release or dissemination due to the fact that they are present at a greater number of wells nationwide. Likewise, chemicals that occur at higher concentrations in flowback or produced water may result in greater exposures. Frequency of detection in flowback or produced water would also be a useful metric for this evaluation, but this information was not available for these chemicals.
3. Information on physicochemical properties enables the estimation of chemical persistence and mobility in the environment. This is discussed in more detail in Section 9.5.2 below.

For chemicals that are used in hydraulic fracturing fluids, the FracFocus database was the only source with reliable information on the frequency of use (U.S. EPA, 2015a). For chemicals found in flowback or produced water, data on measured concentration were only available for the 75 chemicals presented in Appendix E. Therefore, hazard evaluations were only conducted on chemicals included in these two data sources. While the other data sources listed in Appendix A provide useful information on the diversity of chemicals that may occur in the hydraulic fracturing water cycle, hazard evaluation could not be conducted on these sources in the absence of data on frequency of use or measured concentration.

Overall, 37 chemicals used in hydraulic fracturing fluid and 23 chemicals detected in flowback and produced water met the selection criteria for hazard evaluation (see Figure 9-3).

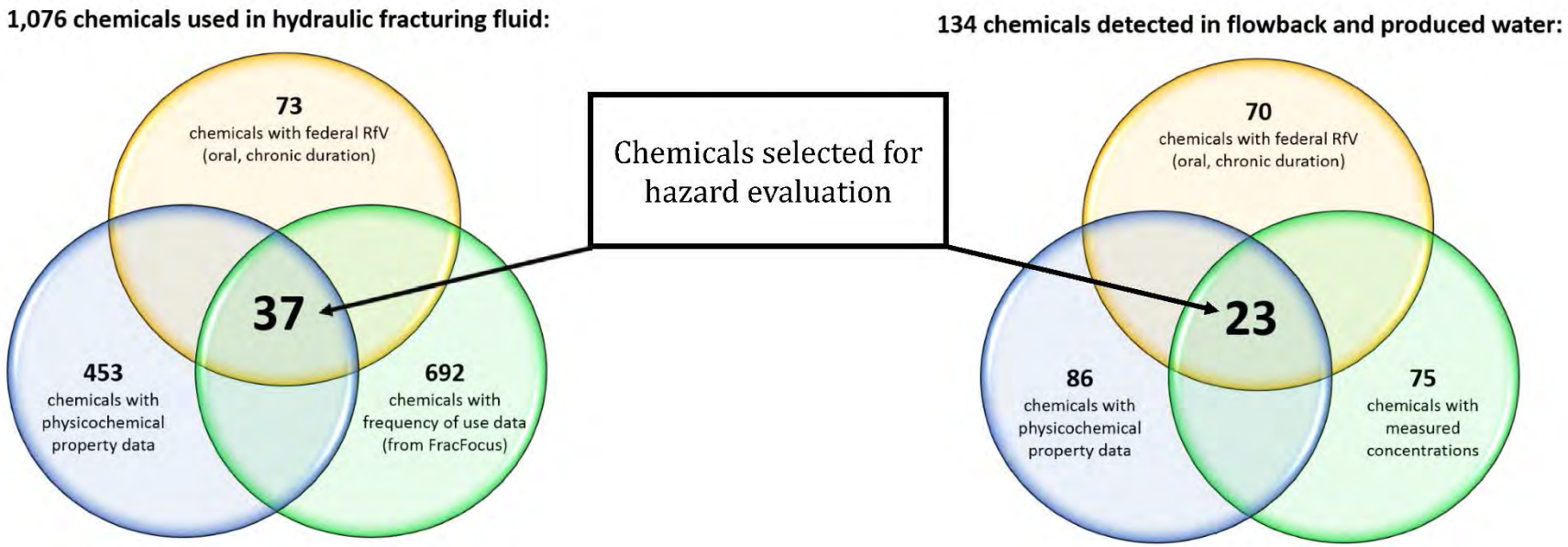

Figure 9-3. The two subsets of chemicals selected for hazard evaluation included 37 chemicals used in hydraulic fracturing fluid, and 23 chemicals detected in flowback or produced water.

9.5.2. Multi Criteria Decision Analysis (MCDA) Framework for Hazard Evaluation: Integrating Toxicity, Occurrence, and Physicochemical Data

Integration or combining of various types of data may provide insights on those chemicals that may be of greater concern than other chemicals to drinking water resources. For the purpose of this chapter, a structured but flexible Multi Criteria Decision Analysis (MCDA) approach was developed to integrate factors related to hydraulic fracturing such as chemical toxicity, occurrence, and physicochemical data. The approach described here is for illustrative purposes only, in order to demonstrate how combining of information may be informative. Alternative frameworks may be considered by risk assessors for similar analyses.

In this illustration, a MCDA framework was developed and applied to each list of chemicals identified in Section 9.5.1 and depicted in Figure 9-3 (37 chemicals used in hydraulic fracturing fluids, and 23 chemicals detected in flowback or produced water). The MCDA framework serves to place the toxicity of these chemicals in the context of factors that may increase the likelihood of impacting drinking water resources. In essence, this analysis serves to illustrate the circumstances under which drinking water resources may be affected.

MCDA is a well-established analysis tool that is used to transparently integrate multiple lines of evidence to support decision-making. For example, MCDA has been adapted as a method of selecting an optimal cleanup plan for a contaminated site (Linkov et al., 2011), and as a method of integrating chemical hazard data across multiple studies (Hristozov et al., 2014). The MCDA framework employed here is based on the method by Mitchell et al. (2013b), who developed a protocol for ranking chemical exposure potential by integrating data on physicochemical properties and commercial use. This method is similar to approaches used by the petroleum industry to quantitatively rank the potential hazards of hydraulic fracturing chemicals (see Section 5.9). Moreover, the underlying philosophy of this approach is similar to that of the EPA's Design for the Environment (DfE) Program. The DfE's Alternatives Assessment Criteria for Hazard Evaluation (U.S. EPA, 2011a) was developed as a tool for evaluating and differentiating among chemical hazards based on toxicity and physicochemical properties. Recently, this criteria and framework have been applied in the Alternatives Assessment for the Flame Retardant Decabromodiphenyl Ether (DecaBDE) and Flame Retardant Alternatives for Hexabromocyclododecane (HBCD) (U.S. EPA, 2014a, d). Aspects of MCDA methods and the DfE's Program for Alternatives Assessment are evident in the National Research Council (NRC)'s "A Framework to Guide Selection of Chemical Alternatives" document (NRC, 2014).

The methodology used to illustrate a hazard evaluation MCDA for hydraulic fracturing is outlined below, and schematic of the model is shown in Figure 9-4. 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 normalized scores were summed to develop a total composite hazard potential score for each chemical. These scores serve as a relative ranking and a means of making comparisons across chemicals. These scores are not intended to define whether or not a chemical will present a human health hazard, or indicate that one chemical is safer than another. Rather, the scores serve as a qualitative metric to identify chemicals that may be more likely to present an impact to drinking water resources, given available data on chemical properties and occurrence.

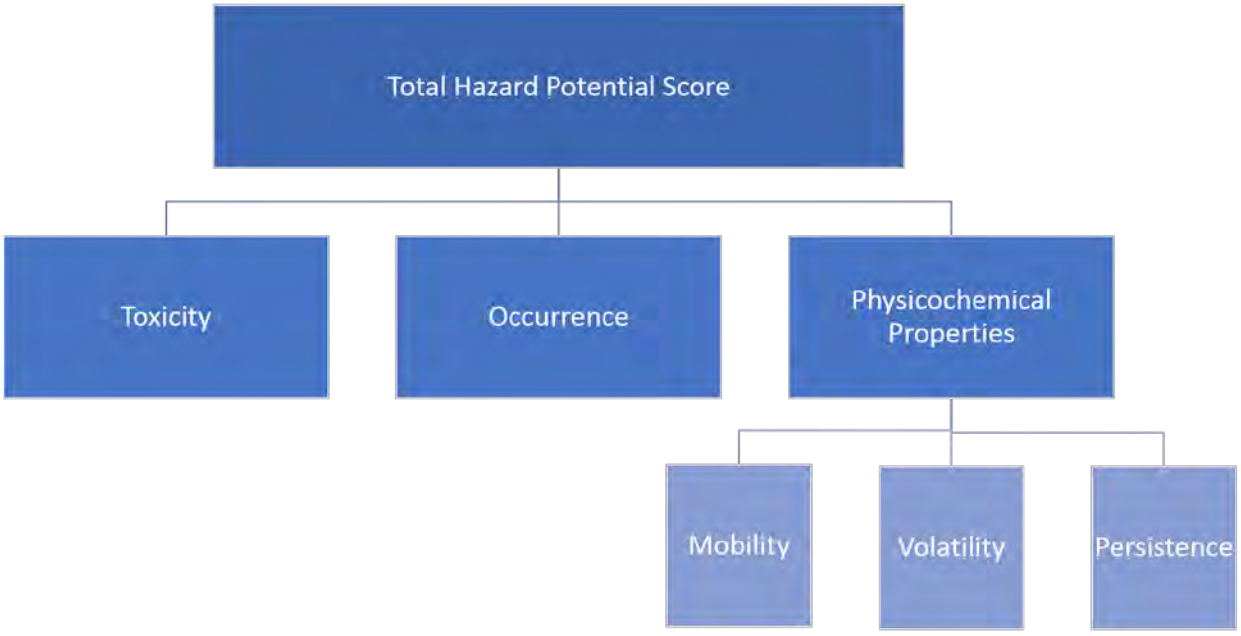

Figure 9-4. Overview of the MCDA framework applied to the hazard evaluations.

9.5.2.1. Toxicity Score

The toxicity score was based upon the federal chronic RfV, which was determined from peer reviewed sources as described in Section 9.3.1. Within each dataset (chemicals used in hydraulic fracturing fluids, or chemicals detected in flowback and produced water), toxicity was ranked based on quartiles, with each chemical assigned a toxicity score of 1 to 4 (see thresholds outlined in Table 9-5). Note that chemicals in the lowest quartile received the highest toxicity score as these chemicals have lower RfVs than for other chemicals.

9.5.2.2. Occurrence Score

This score was based on the frequency or concentration at which chemicals were reported within the hydraulic fracturing water cycle. For chemicals used in hydraulic fracturing fluids, the occurrence score was based on the nationwide number of well disclosures for each chemical from the FracFocus database. For chemicals that were detected in hydraulic fracturing flowback and produced water, the occurrence score was based on the average or median measured concentration reported in Appendix E. If the measured 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. Note that these two metrics of chemical occurrence—frequency of use, and concentration—cannot be directly compared to one another. Therefore, FracFocus chemicals and flowback and produced water chemicals were considered separately for this MCDA hazard evaluation. Within each dataset (chemicals used in hydraulic fracturing fluids, or chemicals detected in flowback and produced water), chemical occurrence was ranked based on quartiles, with each chemical assigned an occurrence score of 1 to 4, as shown in Table 9-5.

9.5.2.3. Physicochemical Properties Score

This score was based upon inherent physicochemical properties which affect the likelihood that a chemical will reach and impact drinking water resources. The thresholds chosen for ranking physicochemical properties, shown in Table 9-5, are based on previously published thresholds used in the DfE Alternatives Assessment Criteria for Hazard Evaluation (U.S. EPA, 2011a), the EPA Office of Pollution Prevention and Toxics Pollution Prevention (P2) Framework (U.S. EPA, 2005), and Mitchell et al. (2013b). When refining EPI Suite™ physicochemical properties data for input into this MCDA, empirically measured values were always used when available. If multiple estimated values were available, the most conservative value (i.e., the value resulting in the highest score according to Table 9-5) was used.

The total physicochemical properties score for each chemical was based upon three subcriteria: mobility in water, volatility, and persistence. Chemical mobility in water was assessed based upon three physicochemical properties: the octanol-water partition coefficient (K_{ow}), the organic carbon-water partition coefficient (K_{oc}), and aqueous solubility. Chemical volatility was assessed based on the Henry's law constant, which describes partitioning of a chemical between water and air. 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. Details on the evaluation and physicochemical score calculation are provided in the Chapter Annex, Section 9.8.1. 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 score.

9.5.2.4. Final MCDA Score Calculations

Each raw score (toxicity, occurrence, or physicochemical properties), calculated as described above, was standardized by scaling to the highest and lowest raw score within the set 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 x, 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 chemical x. Each standardized score (toxicity, occurrence, or physicochemical properties) falls on a scale of 0 to 1. These standardized toxicity, occurrence, and physicochemical properties scores were summed to calculate a total hazard potential score for each chemical. The total hazard potential scores fell on a scale of 0 to 3, with higher scores indicating

chemicals that are predicted to be more likely to affect drinking water resources. An example of MCDA score calculation can be found in the Annex, Section 9.8.2.

In the MCDA approach illustrated in this chapter, each factor (toxicity, occurrence, physicochemical properties) was given equal weight in the calculation of the final hazard potential score. This was done in order to prevent subjectivity and avoid biasing the results based on any individual variable that was considered in this analysis. This approach is adaptable, however. Risk assessors may choose to apply alternative weights that place more or less emphasis on the various factors being considered, in order to reflect expert judgement of a variable's relative importance. This MCDA approach may also be adapted to include other variables of interest, such as carcinogenic potential, which were not considered in the MCDA approach illustrated in this chapter.

Table 9-5. Thresholds used for developing the toxicity score, occurrence score, and physicochemical properties score in this MCDA framework.

Score	1	2	3	4
Toxicity Score				
Chronic RfV (federal)	>3rd quartile	>2nd quartile to ≤3rd quartile	>1st quartile to ≤2nd quartile	≤1st quartile
Occurrence Score				
Percentage of wells nationwide	<1st quartile	≥1st quartile to <2nd quartile	≥2nd quartile to <3rd quartile	≥3rd quartile
Concentration (µg/L)	<1st quartile	≥1st quartile to <2nd quartile	≥2nd quartile to <3rd quartile	≥3rd quartile
Physicochemical Properties Score				
Mobility score:				
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 score:				
Henry's law constant	$>10^{-1}$	$>10^{-3}$ to $\leq 10^{-1}$	$>10^{-5}$ to $\leq 10^{-3}$	$\leq 10^{-5}$
Persistence score:				
Half-life in water (days)	<16	≥16 to <60	≥60 to <180	≥180

9.5.3. Hazard Evaluation Results

Discussed below are the results of the hazard evaluations for each subset of chemicals identified in Section 9.5.1. For each subset of chemicals selected for hazard evaluation, the information presented includes: the available federal chronic oral RfV (hazard identification), followed by highlights of MCDA analyses (hazard evaluation).

For this MCDA illustration, the calculated toxicity scores, occurrence scores, physicochemical properties scores, and total hazard potential scores are provided for chemicals used in hydraulic fracturing fluids and chemicals detected in flowback/produced water, respectively. These individual scores make it possible to visualize the extent to which the total hazard potential ranking of each chemical is driven by each of the variables considered in the MCDA.

9.5.3.1. Hazard Identification: Chemical Used in Hydraulic Fracturing Fluid

As discussed above, a total of 37 chemicals used in hydraulic fracturing fluids were identified for hazard evaluation using the selection criteria described in Section 9.5.1. Some of the chemicals represented include the BTEX chemicals (benzene, toluene, ethylbenzene, xylenes) as well as naphthalene, acrylamide, phenol, 1,2-propylene glycol, ethylene glycol, 2-butoxyethanol, ethyl acetate, and methanol.

These chemicals along with their primary noncancer toxicological properties, including the point-of-departure (POD), total product of uncertainty factors applied, the federal chronic RfV, and the health effect basis for the RfV, are shown in Table 9-6.[1,2] As seen in Table 9-6, all of these chemicals had RfDs available from IRIS, PPRTV, or HHBP. These chemicals induce a variety of adverse outcomes including immune system effects, changes in body weight, changes in blood chemistry, cardiotoxicity, neurotoxicity, liver and kidney toxicity, and reproductive and developmental toxicity. The RfD values within this suite of chemicals range from 0.001–20 mg/kg-day, with (E)-crotonaldehyde having the lowest RfD (0.001 mg/kg-day) and 1,2-propylene glycol having the highest (20 mg/kg-day).

Comparison of RfVs among a set of chemicals requires a more thorough examination. For instance, to derive the final chronic RfD for a given chemical, a number of UFs may be applied to the POD. Briefly, UFs are applied to account for 5 areas of uncertainty: 1) intraspecies variability; 2)

[1] The point-of-departure (POD) is the dose-response point that marks the beginning of a low-dose extrapolation. This point can be the lower bound on dose for an estimated incidence or a change in response level from a dose-response model or a NOAEL or LOAEL for an observed incidence, or change in level of response. See http://www.epa.gov/iris/ for more information.

[2] An uncertainty factor is one of several (generally 10-fold) default factors used in operationally deriving the RfV from experimental data. The factors are intended to account for (1) variation in susceptibility among the members of the human population (i.e., inter-individual or intraspecies variability); (2) uncertainty in extrapolating animal data to humans (i.e., interspecies uncertainty); (3) uncertainty in extrapolating from data obtained in a study with less-than-lifetime exposure (i.e., extrapolating from subchronic to chronic exposure); (4) uncertainty in extrapolating from a LOAEL rather than from a NOAEL; and (5) uncertainty associated with extrapolation when the database is incomplete. See the IRIS Glossary at: http://www.epa.gov/iris/ for more information.

interspecies uncertainty; 3) extrapolation from a subchronic study; 4) extrapolating from a NOAEL; and 5) an incomplete database. A UF of 1, 3 ($10^{0.5}$), or 10 can be applied for any of these areas of uncertainty depending upon the amount and/or type data available. The maximum total UF that can be applied is 3,000; RfDs are not derived for chemicals that invoke the application of a total UF >3,000 or involves the application of the full 10-fold UF in four or more areas of uncertainty (U.S. EPA, 2002a). Therefore, those chemicals with a lower total uncertainty factor generally have more reliable and robust health effect information. For example, although (E)-crotonaldehyde has the lowest RfD, chemicals such as acrylamide, benzene, and dichloromethane have RfDs within a factor of 10 (0.002–0.006 mg/kg-day) but with much less uncertainty reflected in their values. All three latter chemicals have large data sets with reproducible effects, and dose estimated based on physiologically based pharmacokinetic models (for acrylamide and dichloromethane) or have available human health effect data (for benzene). Thus, a chemical with a low RfD may reflect high uncertainty in the value and not necessarily be the most toxic.

Although only federal RfVs are considered in this hazard evaluation, eight of these chemicals also have federal OSFs. These include acrylamide, benzyl chloride, 1,4-dioxane, 1,3-dichloropropene, benzene, epichlorohydrin, aniline, and dichloromethane. Of these chemicals, acrylamide is the most potent carcinogen. Acrylamide has an OSF of 0.5 per mg/kg-day and is classified as a likely human carcinogen in IRIS (U.S. EPA, 2010). Benzene is the only chemical listed as a known human carcinogen and has a calculated OSF of 0.015 mg/kg-day (U.S. EPA, 2002b). The OSF values for each of these chemicals can be found in Appendix G.

Table 9-6. Toxicological properties of the 37 chemicals used in hydraulic fracturing fluid that were identified for hazard evaluation and MCDA analysis.

Chemicals are ranked, from low to high, based on their respective federal chronic RfVs.

Chemical	CASRN	Point of departure (mg/kg-day)	Total uncertainty factor	RfV Chronic RfD (mg/kg-day)	Noncancer effect	Source
(E)-Crotonaldehyde	123-73-9	3.4	3000	0.001	Forestomach lesions	PPRTV
Benzyl chloride	100-44-7	6.4	3000	0.002	Cardiotoxicity	PPRTV
Propargyl alcohol	107-19-7	5	3000	0.002	Renal and hepatotoxicity	IRIS
Acrylamide	79-06-1	0.053	30	0.002	Degenerative nerve changes	IRIS
Benzene	71-43-2	1.2	300	0.004	Decreased lymphocyte count in humans	IRIS
Epichlorohydrin	106-89-8	6.25	1000	0.006	Decreased fertility	PPRTV

Chemical	CASRN	Point of departure (mg/kg-day)	Total uncertainty factor	RfV Chronic RfD (mg/kg-day)	Noncancer effect	Source
Dichloromethane	75-09-2	0.19	30	0.006	Hepatic effects	IRIS
Aniline	62-53-3	7	1000	0.007	Splenic effects	PPRTV
2-(Thiocyano methylthio)benzo thiazole	21564-17-0	3.8	300	0.01	Decreased body weight gain; decreased white blood cells (WBC) and plasma alanine aminotransferase (ALT)	HHBP
Furfural	98-01-1	30	3000	0.01	Liver pathology	HHBP
Naphthalene	91-20-3	71	3000	0.02	Decreased mean terminal body weight > 10%	IRIS
2-(2-Butoxyethoxy) ethanol	112-34-5	81	3000	0.03	Changes in red blood cells (RBC)	PPRTV
1,4-Dioxane	123-91-1	9.6	300	0.03	Liver and kidney toxicity	IRIS
Bisphenol A	80-05-7	50	1000	0.05	Reduced mean body weight	IRIS
1,3-Dichloropropene	542-75-6	3.4	100	0.03	Chronic irritation	IRIS
Toluene	108-88-3	238	3000	0.08	Increased absolute kidney weight	IRIS
Ethylenediamine	107-15-3	9	100	0.09	Liver and kidney toxicity	PPRTV
Ethylbenzene	100-41-4	97.1	1000	0.1	Liver and kidney toxicity; histopathology	IRIS
2-Butoxyethanol (EGBE)	111-76-2	1.4	10	0.1	Hemosiderin deposition in liver (inhalation study)	IRIS
Acetophenone	98-86-2	423	3000	0.1	General toxicity; NO LOAEL identified	IRIS
Didecyldimethyl ammonium chloride	7173-51-5	10	100	0.1	Clinical signs; decreased total cholesterol levels	HHBP

Chemical	CASRN	Point of departure (mg/kg-day)	Total uncertainty factor	RfV Chronic RfD (mg/kg-day)	Noncancer effect	Source
Cumene	98-82-8	110	1000	0.1	Increased average kidney weight in female rats	IRIS
N,N-Dimethylformamide	68-12-2	96	1000	0.1	Increase in ALT and liver weight	PPRTV
1-Butanol	71-36-3	125	1000	0.1	Hypoactivity and ataxia	IRIS
Xylenes	1330-20-7	179	1000	0.2	Decreased body weight; increased mortality	IRIS
Formaldehyde	50-00-0	15	100	0.2	Decreased weight gain	IRIS
Phenol	108-95-2	93	300	0.3	Decreased maternal weight gain; developmental toxicity	IRIS
2-Methyl-1-propanol (Isobutanol)	78-83-1	316	1000	0.3	Hypoactivity and ataxia	IRIS
Acetone	67-64-1	900	1000	0.9	Nephropathy	IRIS
Ethyl acetate	141-78-6	900	1000	0.9	Mortality and body weight loss	IRIS
Formic acid	64-18-6	277	300	0.9	Reproductive effects	PPRTV
Dodecylbenzenesulfonic acid	27176-87-0	50	100	0.5	Decreased pup weight; kidney pathology	HHBP
Ethylene glycol	107-21-1	200	100	2	Kidney toxicity; chronic nephritis	IRIS
Hexanedioic acid	124-04-9	470	300	2	Decreased body weight	PPRTV
Methanol	67-56-1	43.1 mg/L[a]	100	2	Extra cervical ribs; developmental toxicity	IRIS
Benzoic acid	65-85-0	4.4	1	4	No adverse effects observed in humans	IRIS
1,2-Propylene glycol	57-55-6	5200	300	20	Reduced red blood cell counts and hyperglycemia	PPRTV

Chemical	CASRN	Point of departure (mg/kg-day)	Total uncertainty factor	RfV Chronic RfD (mg/kg-day)	Noncancer effect	Source

[a] POD based on internal methanol blood concentration using a PBPK model.

9.5.3.2. MCDA Results: Chemical Used in Hydraulic Fracturing Fluid

The hazard potential scores of the selected 37 chemicals used in hydraulic fracturing fluid are presented in Table 9-7.

Table 9-7. MCDA results for 37 chemicals used in hydraulic fracturing fluid.

Chemicals are ranked, from high to low, based on total hazard potential score. See section 9.5.2 for details on the calculation.

Chemical	CASRN	Physicochemical properties score	Occurrence score	Toxicity score	Total hazard potential score
Propargyl alcohol	107-19-7	1.00	1.00	1.00	**3.00**
2-Butoxyethanol (EGBE)	111-76-2	1.00	1.00	0.67	**2.67**
N,N-Dimethylformamide	68-12-2	1.00	1.00	0.67	**2.67**
Acrylamide	79-06-1	1.00	0.67	1.00	**2.67**
Formaldehyde	50-00-0	1.00	1.00	0.33	**2.33**
Naphthalene	91-20-3	0.67	1.00	0.67	**2.33**
Benzyl chloride	100-44-7	0.67	0.67	1.00	**2.33**
1-Butanol	71-36-3	1.00	0.67	0.67	**2.33**
Epichlorohydrin	106-89-8	0.67	0.67	1.00	**2.33**
2-(2-Butoxyethoxy)ethanol	112-34-5	1.00	0.67	0.67	**2.33**
Methanol	67-56-1	1.00	1.00	0.00	**2.00**
Ethylene glycol	107-21-1	1.00	1.00	0.00	**2.00**
Formic acid	64-18-6	1.00	1.00	0.00	**2.00**
Didecyldimethylammonium chloride	7173-51-5	0.33	1.00	0.67	**2.00**
1,4-Dioxane	123-91-1	1.00	0.33	0.67	**2.00**
(E)-Crotonaldehyde	123-73-9	0.67	0.33	1.00	**2.00**
Aniline	62-53-3	1.00	0.00	1.00	**2.00**
Furfural	98-01-1	1.00	0.00	1.00	**2.00**

Chemical	CASRN	Physicochemical properties score	Occurrence score	Toxicity score	Total hazard potential score
1,2-Propylene glycol	57-55-6	1.00	0.67	0.00	**1.67**
Hexanedioic acid	124-04-9	1.00	0.67	0.00	**1.67**
Toluene	108-88-3	0.33	0.67	0.67	**1.67**
Phenol	108-95-2	1.00	0.33	0.33	**1.67**
2-Methyl-1-propanol (Isobutanol)	78-83-1	1.00	0.33	0.33	**1.67**
Dichloromethane	75-09-2	0.67	0.00	1.00	**1.67**
Ethylenediamine	107-15-3	1.00	0.00	0.67	**1.67**
Bisphenol A	80-05-7	1.00	0.00	0.67	**1.67**
2-(Thiocyanomethylthio) benzothiazole	21564-17-0	0.67	0.00	1.00	**1.67**
Benzene	71-43-2	0.67	0.00	1.00	**1.67**
Dodecylbenzenesulfonic acid	27176-87-0	0.33	1.00	0.00	**1.33**
Xylenes	1330-20-7	0.33	0.67	0.33	**1.33**
Ethylbenzene	100-41-4	0.33	0.33	0.67	**1.33**
Benzoic acid	65-85-0	1.00	0.33	0.00	**1.33**
Acetophenone	98-86-2	0.67	0.00	0.67	**1.33**
1,3-Dichloropropene	542-75-6	0.67	0.00	0.67	**1.33**
Cumene	98-82-8	0.00	0.33	0.67	**1.00**
Ethyl acetate	141-78-6	0.67	0.33	0.00	**1.00**
Acetone	67-64-1	0.67	0.33	0.00	**1.00**

Of the chemicals in hydraulic fracturing fluid that were considered in this hazard evaluation, propargyl alcohol received the highest overall hazard potential score. Propargyl alcohol was used in 33% of wells in the FracFocus database, making it one of the most widely used chemicals that was considered in this analysis, and it also had one of the lowest RfVs, with an RfD of 0.002 mg/kg-day. It is also hydrophilic and has relatively low volatility, indicating that it is likely to be readily transported in water. Given these properties, propargyl alcohol received the highest overall ranking across all of the metrics that were considered in the hazard evaluation.

The other chemicals that fell in the upper quartile in terms of frequency of use received lower hazard potential scores relative to propargyl alcohol, due to lower estimated toxicity and/or physicochemical properties that are less conducive to transport in water. Naphthalene, used in 19% of wells on the FracFocus database, has an RfD of 0.02 mg/kg-day, and is expected to have somewhat lower transport in water relative to other chemicals because it is moderately hydrophobic and moderately volatile. Methanol (RfD of 2 mg/kg-day), ethylene glycol (RfD of 2

mg/kg-day), 2-butoxyethanol (RfD of 0.1 mg/kg-day), formic acid (RfD of 0.9 mg/kg-day), N,N-dimethylformamide (RfD of 0.1 mg/kg-day), and formaldehyde (RfD of 0.2 mg/kg-day)—which were used in 73%, 47%, 23%, 11%, 9%, and 7% of wells in the FracFocus database, respectively—are all expected to be highly mobile in water and have low volatility, but have higher RfVs compared to many of the other chemicals in the assessment. Didecyldimethylammonium chloride (RfD of 0.1 mg/kg-day), used in 8% of wells, is expected to have reduced mobility in water due to its more hydrophobic properties.

In addition to propargyl alcohol, the other most toxic chemicals (occurring in the lowest quartile of RfVs) received moderate to high hazard potential scores overall. Acrylamide (RfD of 0.002 mg/kg-day) is used in only 1% of wells, but has physicochemical properties that are very conducive to transport in water, and therefore received one of the highest overall hazard potential scores. Benzyl chloride (RfD of 0.002 mg/kg-day) and epichlorohydrin (RfD of 0.006 mg/kg-day) are used in 6% and 1% of wells, respectively, but scored slightly lower than acrylamide with regards to their physicochemical properties. Other chemicals, including (E)-crotonaldehyde (RfD of 0.001 mg/kg-day), benzene (RfD of 0.004 mg/kg-day), dichloromethane (RfD of 0.006 mg/kg-day), aniline (RfD of 0.007 mg/kg-day), furfural (RfD of 0.01 mg/kg-day), and 2-(Thiocyanomethylthio)benzothiazole (RfD of 0.01 mg/kg-day), received lower overall scores because they are used more infrequently (each in less than 0.1% of wells in the FracFocus database).

9.5.3.3. Hazard Identification: Chemicals Detected in Flowback and Produced Water

As discussed above, a total of 23 chemicals detected in flowback and produced water were identified for hazard evaluation using the selection criteria described in Section 9.5.1. Of these 23 chemicals, 10 chemicals overlap with the hazard evaluation of chemicals used in hydraulic fracturing fluids. Because of this overlap, many of the effects noted in each hazard evaluation are similar.

These chemicals, along with their POD, total products of uncertainty factors applied, federal chronic RfVs, and the health effect bases for the RfVs, are shown in Table 9-8. As seen in Table 9-8, all of these chemicals had RfDs available from IRIS, PPRTV, or HHBP. These chemicals 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 RfD values within this suite of chemicals range from 0.001−0.9 mg/kg-day, with pyridine having the lowest RfD and acetone having the highest RfD. For this subset of chemicals, 88% have an RfD within 2 orders of magnitude of each other and 78% have RfDs within a factor of 10 (range of 0.01−0.1 mg/kg-day). Some of these chemicals include chloroform, naphthalene, 1,4-dioxane, toluene, cumene, and ethylbenzene.

Although only federal RfVs are considered in this hazard evaluation, 2 of these chemicals—benzene and 1-4-dioxane—also have federal OSFs . These chemicals are also included in the hazard evaluation of chemicals used in hydraulic fracturing fluids, discussed above. 1,4-dioxane is a more potent carcinogen compared to benzene. The OSF for 1,4-dioxane is 0.1 per mg/kg-day and is classified as likely to be a human carcinogen by IRIS (U.S. EPA, 2013f).

Table 9-8. Toxicological properties of the 23 chemicals detected in flowback and produced water that were identified for hazard evaluation and MCDA analysis.

Chemicals are ranked, from low to high, based on their respective federal chronic RfVs. Chemicals in *italics* are also included in the hazard evaluation of chemicals used in hydraulic fracturing fluids.

Chemical	CASRN	Point of departure (mg/kg-day)	Total un-certainty factors	RfV Chronic RfD (mg/kg-day)	Non-cancer effect	Source
Pyridine	110-86-1	1	1000	0.001	Increased liver weight	IRIS
2-Methylnaphthalene	91-57-6	3.5	1000	0.004	Pulmonary alveolar proteinosis	IRIS
Benzene	71-43-2	1.2	300	0.004	Decreased lymphocyte count in humans	IRIS
Chloroform	67-66-3	12.9	1000	0.01	Fatty cyst formation in the liver; elevated SGPT(or ALT)	IRIS
Naphthalene	91-20-3	71	3,000	0.02	Decreased mean terminal body weight > 10%	IRIS
Di(2-ethylhexyl) phthalate	117-81-7	19	1000	0.02	Increased relative liver weight	IRIS
2,4-Dimethylphenol	105-67-9	50	3000	0.02	Clinical signs; hematological changes	IRIS
Pyrene	129-00-0	75	3000	0.03	Kidney effects	IRIS
1,4-Dioxane	123-91-1	9.6	300	0.03	Liver and kidney toxicity	IRIS
Fluorene	86-73-7	125	3000	0.04	Decreased RBC, packed cell volume and hemoglobin	IRIS
Fluoranthene	206-44-0	125	3000	0.04	Nephropathy; increased liver weights; hematological alterations	IRIS
2-Methylphenol (o-Cresol)	95-48-7	50	1000	0.05	Decreased body weights and neurotoxicity	IRIS
Toluene	108-88-3	238	3000	0.08	Increased absolute kidney weight	IRIS
Carbon disulfide	75-15-0	11	100	0.1	Fetal toxicity and malformations	IRIS

Chemical	CASRN	Point of departure (mg/kg-day)	Total un-certainty factors	RfV Chronic RfD (mg/kg-day)	Non-cancer effect	Source
Cumene	98-82-8	110	1000	0.1	increased average kidney weight in female rats	IRIS
Benzyl alcohol	100-51-6	143	1000	0.1	Effects on survival, growth, and tissue histopathology	PPRTV
Dibutyl phthalate	84-74-2	125	1000	0.1	Increased mortality	IRIS
Ethylbenzene	100-41-4	97.1	1000	0.1	liver and kidney toxicity; histopathology	IRIS
Acetophenone	98-86-2	423	3000	0.1	General toxicity; no LOAEL identified	IRIS
Diphenylamine	122-39-4	10	100	0.1	Alterations in clinical chemistry; increased kidney. liver, and spleen weights	HHBP
Xylenes	1330-20-7	179	1000	0.2	Decreased body weight; increased mortality	IRIS
Phenol	108-95-2	93	300	0.3	Decreased maternal weight gain; developmental toxicity	IRIS
Acetone	67-64-1	900	1000	0.9	Nephropathy	IRIS

9.5.3.4. MCDA Results: Flowback and Produced Water

The hazard potential scores of the selected 23 chemicals detected in flowback and produced water are presented in Table 9-9.

Table 9-9. MCDA results for 23 chemicals in hydraulic fracturing flowback and produced water.

Chemicals are ranked, from high to low, based on total hazard potential score. See Section 9.5.2 for details on the calculation.

Chemical	CASRN	Physicochemical properties score	Occurrence score	Toxicity score	Total hazard potential score
Benzene	71-43-2	0.75	1.00	1.00	**2.75**
Pyridine	110-86-1	0.75	1.00	1.00	**2.75**
Naphthalene	91-20-3	0.75	0.67	1.00	**2.42**

Chemical	CASRN	Physicochemical properties score	Occurrence score	Toxicity score	Total hazard potential score
2,4-Dimethylphenol	105-67-9	1.00	0.33	1.00	**2.33**
2-Methylnaphthalene	91-57-6	0.25	1.00	1.00	**2.25**
Chloroform	67-66-3	0.75	0.33	1.00	**2.08**
2-Methylphenol	95-48-7	1.00	0.33	0.67	**2.00**
Benzyl alcohol	100-51-6	1.00	0.67	0.33	**2.00**
Bis(2-Ethylhexyl) Phthalate	117-81-7	0.25	0.67	1.00	**1.92**
Carbon Disulfide	75-15-0	0.50	1.00	0.33	**1.83**
Toluene	108-88-3	0.50	1.00	0.33	**1.83**
Acetone	67-64-1	0.75	0.67	0.00	**1.42**
Pyrene	129-00-0	0.75	0.00	0.67	**1.42**
Di-n-butyl Phthalate	84-74-2	0.75	0.33	0.33	**1.42**
1,4-Dioxane	123-91-1	1.00	0.00	0.67	**1.67**
Fluoranthene	206-44-0	1.00	0.00	0.67	**1.67**
Xylenes	1330-20-7	0.50	1.00	0.00	**1.50**
Ethylbenzene	100-41-4	0.50	0.33	0.33	**1.17**
Phenol	108-95-2	1.00	0.67	0.00	**1.67**
Diphenylamine	122-39-4	1.00	0.00	0.33	**1.33**
Isopropylbenzene	98-82-8	0.25	0.67	0.33	**1.25**
Acetophenone	98-86-2	0.75	0.00	0.33	**1.08**
Fluorene	86-73-7	0.00	0.00	0.67	**0.67**

The highest total hazard potential scores for chemicals in flowback and produced water went to benzene and pyridine, followed closely by naphthalene. These three chemicals all have RfVs that fell in the lowest (most toxic) quartile relative to other chemicals in the hazard evaluation (RfDs of 0.004, 0.001, and 0.02 mg/kg-day, respectively). Benzene fell in the upper quartile of observed chemical concentrations (with a maximum reported average concentration of 680 µg/l; Barnett shale produced water, Table E-9), while pyridine and naphthalene fell in the second highest quartile (with maximum reported average concentrations of 413 and 238 µg/l, respectively; Barnett shale produced water, Table E-10). These three chemicals only scored moderately in terms of their physicochemical properties, however, as all three are expected to have somewhat lower transport in water compared to other chemicals in the assessment. 2-Methylnaphthalene also fell in the lowest quartile in terms of toxicity (RfD of 0.004 mg/kg-day) and the highest quartile in terms of concentration (average of 1,362 µg/l; Barnett shale produced water, Table E-10), but received a slightly lower score than these chemicals with regards to physiochemical properties.

Other chemicals occurring in the upper quartile of flowback and produced water concentrations include toluene (average of 760 µg/l; Barnett shale produced water, Table E-9), xylenes (average of 360 µg/l; Barnett shale produced water, Table E-9), and carbon disulfide (median of 400 µg/l; Marcellus shale produced water, Table E-10). These chemicals all received moderate hazard potential scores, as all have higher RfDs (lower toxicity) 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.

Other chemicals with RfVs that fell in the lowest (most toxic) quartile in flowback and produced water include chloroform (RfD of 0.01 mg/kg-day), di(2-ethylhexyl)phthalate (RfD of 0.02 mg/kg-day), and 2,4,-dimethylphenol (RfD of 0.02 mg/kg-day). Of these, di(2-ethylhexyl)phthalate was detected at moderately high concentrations relative to other chemicals in the assessment (average of 210 µg/l; Barnett shale produced water, Table E-10), but is expected to have reduced mobility in water due primarily to its more hydrophobic properties. The rest are expected to have moderate to high transport in water, but were detected at relatively lower average concentrations compared to other chemicals in the assessment.

9.5.4. Summary of Chemicals Detected in Multiple Stages of the Hydraulic Fracturing Water Cycle

A number of chemicals with federal chronic RfVs that are used in hydraulic fracturing fluids were also found to be present in flowback and produced water stages of the hydraulic fracturing water cycle. The use of a chemical in hydraulic fracturing fluids, and subsequent presence in later stages of the hydraulic fracturing water cycle, is of particular interest in demonstrating which chemicals in this dataset may be mixed, injected, and then detected downstream in the water cycle. This section focuses on that group of chemicals.

Based on the available information in our datasets, 23 chemicals overall had federal chronic RfVs and were identified as being used in hydraulic fracturing fluids and detected in the flowback/produced water stage of the hydraulic fracturing water cycle. These chemicals are shown in Table 9-10. 10 of these chemicals were included in both the hazard evaluation of hydraulic fracturing fluids (see Table 9-6 and Table 9-7) and the flowback and produced water hazard evaluation (see Table 9-8 and Table 9-9). This means that these 10 chemicals had both frequency of use data from FracFocus and a reported measured concentration in flowback and produced water from Chapter 7 (Appendix E). These 10 chemicals included all of the BTEX chemicals, as well as naphthalene, 1,4 dioxane, acetone, acetophenone, cumene, and phenol. The chemicals of this group with the lowest chronic oral RfVs were benzene, naphthalene, and 1,4-dioxane. These chemicals all have RfDs within an order of magnitude of each other and are known or likely human carcinogens. The next chemical of this group—toluene—has an RfD 20 times greater than benzene. Overall, benzene was the most toxic of the chemicals listed in Table 9-10.

Table 9-10. List of the 23 chemicals with federal chronic RfVs identified to be used in hydraulic fracturing fluids and detected in the flowback/produced water stage of the hydraulic fracturing water cycle.

Chemical	CASRN	Used in hydraulic fracturing fluids?	FracFocus frequency of use data?	Detected in flowback or produced water?	Physicochemical properties data available?	In hazard evaluation?[a]
1,4-Dioxane	123-91-1	Y	Y	Y	Y	FF+FB
Acetone	67-64-1	Y	Y	Y	Y	FF+FB
Acetophenone	98-86-2	Y	Y	Y	Y	FF+FB
Benzene	71-43-2	Y	Y	Y	Y	FF+FB
Cumene	98-82-8	Y	Y	Y	Y	FF+FB
Ethylbenzene	100-41-4	Y	Y	Y	Y	FF+FB
Naphthalene	91-20-3	Y	Y	Y	Y	FF+FB
Phenol	108-95-2	Y	Y	Y	Y	FF+FB
Toluene	108-88-3	Y	Y	Y	Y	FF+FB
Xylenes	1330-20-7	Y	Y	Y	Y	FF+FB
1,2-Propylene glycol	57-55-6	Y	Y	Y	Y	FF
Dichloromethane	75-09-2	Y	Y	Y	Y	FF
Ethylene glycol	107-21-1	Y	Y	Y	Y	FF
Formic acid	64-18-6	Y	Y	Y	Y	FF
Methanol	67-56-1	Y	Y	Y	Y	FF
Aluminum	7429-90-5	Y	Y	Y	--	No
Iron	7439-89-6	Y	Y	Y	--	No
Di(2-ethylhexyl) phthalate	117-81-7	Y	--	Y	Y	FB
Acrolein	107-02-8	Y	--	Y	Y	No
Arsenic	7440-38-2	Y	--	Y	--	No
Chlorine	7782-50-5	Y	--	Y	--	No
Chromium (III)	16065-83-1	Y	--	Y	--	No
Chromium (VI)	18540-29-9	Y	--	Y	--	No
Zinc	7440-66-6	Y	--	Y	--	No

[a] FF+FB: chemical in both the hydraulic fracturing fluid and flowback/produced water hazard evaluations; FF or FB: chemical in either the hydraulic fracturing fluid or flowback/produced water hazard evaluations. A dash indicates data for chemical not available.

An additional 6 chemicals were included in either the hazard evaluation of hydraulic fracturing fluids (see Table 9-6 and Table 9-7) or the flowback and produced water hazard evaluation (see Table 9-8 and Table 9-9), but not both. These chemicals were reported to be have been used in hydraulic fracturing fluids and detected in flowback/produced water, but lacked the occurrence data (frequency of use or a measured concentration) to support inclusion in both of these hazard evaluations. The remaining 8 chemicals reported to have been used in hydraulic fracturing fluids or detected in flowback/produced water were not included in either of the hazard evaluations presented above because they lacked one or more of the inclusion criteria. These chemicals include acrolein as well as several metals. Arsenic and acrolein have the lowest RfDs by an order of magnitude and arsenic is classified as a known human carcinogen by the EPA, IARC, and NTP. Chromium (VI) is also classified as a known human carcinogen by IARC and NTP.

9.6. 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 hazard of these chemicals to drinking water resources. Toward this end, the EPA developed a comprehensive list of 1,173 chemicals with reported occurrence in the hydraulic fracturing water cycle, separating them into subsets based on whether they were reported to have been used in hydraulic fracturing fluids or detected in flowback and produced water. First, for each of these chemicals, RfVs and OSFs from selected federal, state, and international sources were collected when available. Second, for subsets of chemicals that were identified as being of interest in previous chapters of this report, federal chronic RfVs were used to conduct an initial identification of the potential human health hazards inherent to these chemicals. Finally, for other subsets of chemicals that had data available, an approach for a more data-informed hazard evaluation was illustrated by integrating data on federal chronic RfVs, occurrence, and physicochemical properties using an MCDA framework.

9.6.1. Summary of Findings

Across the industrial landscape, thousands of chemicals are used commercially that lack toxicity data (Judson et al., 2009). Similarly, major knowledge gaps exist regarding the toxicity of most chemicals used in hydraulic fracturing fluids or detected in flowback/produced water, impeding the assessment of human health risks associated with drinking water resources affected by hydraulic fracturing.

Of the 1,076 chemicals used in hydraulic fracturing fluids, chronic RfVs and/or OSFs from all of the selected federal, state, or international sources were available for 90 chemicals (8.4%). From the federal sources alone, chronic oral RfVs were available for 73 chemicals (6.8%), and OSFs were available for 15 (1.4%). Potential hazards associated with 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.

Of the 134 chemicals that are reported to have been detected in hydraulic fracturing flowback or produced water, chronic RfVs and/or OSFs from all of the selected federal, state, or international

sources were available for 83 chemicals (62%). From the federal sources alone, chronic RfVs were available for 70 chemicals (52%), and OSFs were available for 20 (15%). Potential hazards associated with these chemicals include carcinogenesis, immune system effects, changes in body weight, changes in blood chemistry, pulmonary toxicity, neurotoxicity, liver and kidney toxicity, and reproductive and developmental toxicity.

Of the chemicals included in the hazard evaluations, benzene is the only one of these chemicals with an OSF that is classified as a known human carcinogen, while acrylamide was found to be the most potent likely human carcinogen. Several other chemicals, including 1,4-dioxane, dichloromethane, naphthalene, and ethylbenzene are also classified as possible, probable, or likely human carcinogens.

Toxicity information spans a wide range with respect to extent, quality and reliability. The sources of RfVs and OSFs selected for the purposes of this chapter are based on criteria developed specifically for this report. For the total 1,173 chemicals identified on the EPA's list, federal, state, and international chronic RfVs and/or OSFs that met stringent selection criteria were available for 147 (13%) of the chemicals. Several of the RfVs from selected sources were derived using UFs of up to several orders of magnitude, indicating uncertainty when comparing chemicals for potential toxicity and identifying the chemicals that may be more likely to present a human health hazard. For many of the chemicals used in hydraulic fracturing or found in flowback or produced water there may be relevant information, including cancer and noncancer-related information, from one or more sources that were not evaluated in this chapter. In instances where toxicity data is not available from selected sources, risk assessors may need to draw from alternative sources of hazard information. The chapter discusses two available resources for consideration when RfVs and/or OSFs are not available: QSAR-predicted toxicity data, and toxicity data from the EPA's ACToR database. Oral toxicity data was available on ACToR for 642 (55%) of the chemicals. The information available in the ACToR data warehouse ranges from the federal RfVs discussed in Section 9.3.1, which have undergone extensive peer review, to RfVs and study and test results 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. The majority of chemicals identified in this report lacked the necessary data to conduct such an assessment. However, integrating data on toxicity, occurrence, and physicochemical properties using an MCDA framework enabled a more data-informed hazard evaluation on some chemicals. This analysis highlighted several chemicals that may be more likely than others to reach drinking water and create a toxicological hazard. In hydraulic fracturing fluid, an example is propargyl alcohol. It was among the chemicals with the lowest RfVs considered in this hazard evaluation, was used in 33% of wells in the FracFocus database, and is water soluble with low volatility. In flowback and produced water, examples of such chemicals include benzene, pyridine, and naphthalene. These chemicals were also among those with the lowest RfVs considered in this hazard evaluation, are expected to be relatively mobile in water, and were present at relatively high average concentrations in flowback.

9.6.2. Factors Affecting the Frequency or Severity of Impacts

When assessing chemical hazards, there are multiple pieces of information that could be taken into account. This includes knowledge of the chemicals used at a given well site, the toxicological and physicochemical properties of these chemicals, the amount of fluid being used and recovered, the likelihood of well integrity failures, and the likelihood of spills and other unintentional releases. These topics were previously discussed in Chapters 5 through 8 of this report. Because of the large volumes of fluid being injected, even chemicals representing a small percentage of the total fluid by mass may pose a potential for exposure in the event of a spill or leak.

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 company's preferences. Therefore, potential hazard and risk considerations are best made on a site-specific, well-specific basis. While the MCDA results in this chapter illustrate an approach to evaluate the relative hazards of these chemicals at the national level, a site-specific hazard evaluation would be necessary in order to identify chemicals of concern at the local level.

For example, consider (E)-crotonaldehyde, which is one of the more toxic chemicals considered in the hazard evaluation of hydraulic fracturing fluids. (E)-crotonaldehyde is reportedly used in only 0.06% of wells in the FracFocus database, based on the EPA's analysis. If the FracFocus database represents a fair sample of all of the wells across the country, then the likelihood of (E)-crotonaldehyde contamination on a nationwide scale is limited. However, this in no way diminishes the likelihood of (E)-crotonaldehyde contamination at well sites where this chemical is used. Therefore, potential exposures to more toxic but infrequently used chemicals are more of a local issue, rather than a national one.

This is in contrast with methanol, which was reported in 73% of wells in the FracFocus database. Methanol is soluble and relatively mobile in water, but has a higher RfV relative to other chemicals in the hazard evaluation. Therefore, when considering chemical usage on a nationwide basis, methanol may be expected to have a higher exposure potential compared to other chemicals, with a moderate overall hazard potential due to its relatively high RfV.

9.6.3. Uncertainties

There are several notable uncertainties in the chemical and toxicological data that limit a comprehensive assessment of the potential health impacts of hydraulic fracturing on drinking water resources.

For the purposes of this chapter, the lack of RfVs and OSFs from the sources meeting stringent selection criteria is the most significant data gap. For instance, of the 32 chemicals (excluding water, quartz, and sodium chloride) that are used in ≥10% of wells nationwide according to FracFocus, federal chronic RfVs were only available for 7 chemicals. Without these reliable and peer reviewed data, 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, flowback, or produced water is limited. Consequently, potential impacts on drinking water resources and human health may not be assessed adequately.

Another major uncertainty lies in the total list of chemicals that was compiled for this chapter. As discussed in Section 5.1.3, information is lacking on the chemicals that are used in hydraulic fracturing fluid formulation. CBI chemicals, which were present in approximately 70% of well records on the FracFocus database, were excluded from the EPA's analysis. The analysis also excluded ingredient records that were not able to be assigned standardized chemical names, which resulted in approximately 35% of FracFocus ingredient records being excluded from the report. This lack of data limits the ability to more completely assess the impact of chemicals that are potentially used with great frequency. Moreover, there may be a regional bias in the EPA's analysis of FracFocus, as 78% of chemical disclosures in the FracFocus database came from five states, and 47% were from Texas. Despite these limitations, the FracFocus database 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 1,076 chemicals are currently used in abundance. Consequently, 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 flowback and produced water chemicals identified in this chapter is almost certainly incomplete. Few studies to date have examined the chemical composition of flowback and produced water, and the hazard evaluation in this chapter relied on data from the relatively small number of studies that are presented in Appendix E of this assessment. As discussed in Chapter 7, chemicals and their metabolites may go undetected simply because they were not included in the analytical methodology. Additionally, chemical analysis of flowback and produced water may be challenging, because high levels of dissolved solids in flowback and wastewater can interfere with chemical detection. As a result, it is likely that there are chemicals of concern in flowback and produced water that have not been detected or reported.

Finally, when considering the MCDA framework that was used to illustrate an approach for hazard evaluation, it should be noted that the physicochemical variables were chosen specifically to reflect chemical mobility and persistence in water. While this framework draws attention towards those chemicals that are most likely to be carried in water, it does not attempt to address the numerous other physicochemical variables that may affect chemical exposure. For instance, as discussed in Chapter 5, hydrophobic chemicals may act as long-term sources of pollution by sorbing to soils or sediments. Additionally, volatile chemicals that dissipate into the air have the potential to pose air pollution hazards, which are not considered in this drinking water assessment; or could potentially be deposited in bodies of water that are distant from the hydraulic fracturing site. Furthermore, as discussed in Chapter 5, chemical fate and transport will be influenced by environmental and site-specific conditions. The fate of a chemical in a chemical mixture will be also influenced by the other

chemicals that are present in the mixture, and the relative concentrations of each. Although the assessment of these various scenarios is outside the scope of this report, the potential hazards associated with hydrophobic or volatile chemicals should not be discounted when interpreting the results of this hazard evaluation. It should be emphasized that the MCDA framework illustrated in this chapter 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.

9.6.4. Conclusions

The EPA has identified 1,173 chemicals used or detected in the hydraulic fracturing water cycle. Toxicity-based chronic RfVs and/or OSFs from sources meeting selection criteria are not available for the large majority (87%) of these chemicals. In addition, 56% of these chemicals do not have physicochemical property data. Furthermore, 36% of the chemicals used in hydraulic fracturing fluids lack data on their nationwide frequency of use, and very few studies have analyzed the chemical composition of flowback and produced water. 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 hydraulic fracturing wells nationwide, this missing chemical information represents a significant data gap. Because of these large data gaps for drinking water resources, it remains challenging to fully understand the toxicity and potential health impacts for single chemicals as well as mixtures of chemicals associated with hydraulic fracturing processes. This chapter provides an initial overall assessment of the potential human health effects associated with hydraulic fracturing on a nationwide basis. It also provides tools that may support risk assessment and risk management decision making at the local and regional level.

The toxicological data, occurrence data, and physicochemical data compiled in this report provide a resource for assessing the potential hazards associated with chemicals in the hydraulic fracturing water cycle. Additionally, the MCDA framework presented herein illustrates one method for integrating these data for hazard evaluation. While the analysis in this chapter is constrained to the assessment of chemicals on a nationwide 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. Agencies 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. A summary of the findings related to the overall objective of this chapter and the research questions is presented in Text Box 9-1.

Text Box 9-1. Research Questions Revisited.

What are the toxicological properties of hydraulic fracturing fluid chemical additives?

- In a nationwide assessment, the EPA identified 1,076 chemicals that are used in hydraulic fracturing fluids. This does not include chemicals classified as CBI, which the FracFocus database indicates are used in more than 70% of wells. Chronic RfVs and/or OSFs from selected federal, state, and international sources were available for 90 (8.4%) of these chemicals. From the federal sources alone, chronic RfVs were available for 73 chemicals (6.8%), and OSFs were available for 15 chemicals (1.4%). RfVs and OSFs were not available for the majority of chemicals that are used in hydraulic fracturing fluid, representing a significant data gap with regards to hazard identification. Of the chemicals that have selected RfVs, health effects include the potential for carcinogenesis, immune system effects, changes in body weight, changes in blood chemistry, cardiotoxicity, neurotoxicity, liver and kidney toxicity, and reproductive and developmental toxicity.

- When considering the hazard evaluation of these chemicals on a nationwide scale, chemicals such as propargyl alcohol stand out for their relatively lower RfVs, high frequency of use, and expected transport and mobility in water. However, the FracFocus database indicates that most chemicals are used infrequently on a nationwide scale; therefore, potential exposures to the majority of these chemicals are more likely to be a local issue, rather than a national one. Accordingly, potential hazard and risk considerations for hydraulic fracturing fluid chemical additives are best made on a site-specific, well-specific basis.

What are the toxicological properties of hydraulic fracturing wastewater constituents?

- This assessment identified 134 chemicals that are reported to have been detected in hydraulic fracturing flowback or produced water. These include chemicals that are added to hydraulic fracturing fluids during the chemical mixing stage, as well as naturally occurring organic chemicals, metals, naturally occurring radioactive material, and other subterranean chemicals that may be mobilized by the hydraulic fracturing process. Chronic RfVs and/or OSFs from selected federal, state, and international sources were available for 83 (62%) of these chemicals. From the federal sources alone, chronic RfVs were available for 70 chemicals (52%), and OSFs were available for 20 chemicals (15%). Of the chemicals that had selected RfVs, health effects include the potential for carcinogenesis, immune system effects, changes in body weight, changes in blood chemistry, pulmonary toxicity, neurotoxicity, liver and kidney toxicity, and reproductive and developmental toxicity.

- In a hazard evaluation of flowback and produced water data, chemicals such as benzene, pyridine, and naphthalene stood out for their relatively lower RfVs, high average concentrations, and expected transport and mobility in water. However, the chemicals present in flowback and produced water are likely to vary on a regional and well-specific basis as a result of geological differences as well as differences between hydraulic fracturing fluid formulations. Therefore, potential hazard and risk considerations are best made on a site-specific basis.

9.7. References for Chapter 9

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9.8. Annex

9.8.1. Calculation of Physicochemical Property Scores (MCDA Hazard Evaluation)

Section 9.5.2 describes how physicochemical properties scores were based on three subcriteria: mobility, volatility, and persistence. These subcriteria scores were calculated as follows:

Mobility score: Chemical mobility in water was assessed based upon three physicochemical properties: the octanol-water partition coefficient (K_{ow}), the organic carbon-water partition coefficient (K_{oc}), and aqueous solubility. K_{ow} and aqueous solubility were previously discussed in Section 5.8.3. K_{oc} is a partitioning coefficient that measures the amount of chemical that is adsorbed onto soil organic carbon per the amount of chemical that is dissolved in water. Like K_{ow}, K_{oc} is typically reported as a base-10 logarithm (log K_{oc}). From EPI Suite™, K_{oc} was estimated using the MCl Method. Chemicals with low K_{ow} and K_{oc} values are hydrophilic, and thus are more likely to move with water rather than sorbing to soils or sediments. Chemicals with high aqueous solubility are also more likely to move with water. Therefore, chemicals with low K_{ow}, low K_{oc}, or high aqueous solubility were ranked as having greater potential to affect drinking water resources. Using the thresholds designated in Table 9-5, each of these properties was assigned a score of 1-4. The highest of these three scores was designated as the mobility score for each chemical.

Volatility score: Chemical volatility was assessed based on the Henry's law constant, which was previously discussed in Section 5.8.3. Chemicals with low Henry's law constants are less likely to leave water via volatilization, and were therefore ranked as having greater potential to impact drinking water. Using the thresholds designated in Table 9-5, 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.

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. From EPI Suite™, half-life in water was estimated using the Level III Fugacity model. Chemicals with longer half-lives are more persistent, and were therefore ranked as having greater potential to affect drinking water. Using the thresholds designated in Table 9-5, the half-life of each chemical was assigned a score of 1-4. This value was designated as the persistence score for each chemical.

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 score. The total scores were then standardized by scaling to the highest and lowest scores observed in the subset of chemicals, using the equation described in Section 9.5.2.4.

9.8.2. Example of MCDA Score Calculation

For an example of how the MCDA scores were calculated, consider benzene. This demonstrates how the MCDA score was calculated for benzene in the hazard evaluation of chemicals used in hydraulic fracturing fluids:

- With regards to toxicity (Appendix G), benzene was found to have a federal RfD of 0.004 mg/kg-day (source: IRIS). Within the entire set of chemicals in this hazard evaluation, federal RfDs ranged from 0.001 mg/kg-day [(E)-crotonaldehyde] to 20 mg/kg-day (1,2-propylene glycol). The RfD of benzene fell in the lowest (most toxic) quartile of these scores, and therefore was given a toxicity score of 4. When the results were standardized to the highest score (4) and lowest score (1) within the set of chemicals, benzene was calculated to have a toxicity score of 1, as follows:

$$1 = (4 - 1) / (4 - 1)$$

- Benzene was used in 0.0056% of wells nationwide (U.S. EPA, 2015a). This usage frequency falls in the lowest quartile of chemicals, and therefore benzene was given an occurrence score of 1. When the results were standardized to the highest score (4) and lowest score (1) within the set of chemicals, benzene was calculated to have an occurrence score of 0, as follows:

$$0 = (1 - 1) / (4 - 1)$$

- Based on physicochemical properties, 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). These scores sum to a total physicochemical properties score of 8. Within the entire set of chemicals in this hazard evaluation, several chemicals received total scores of 9, which was the highest observed score. Cumene received a total score of 6, which was the lowest observed score. When the results were standardized to the high score (9) and low score (6) using the equation above, benzene was calculated to have a physicochemical properties score of 0.67 as follows:

$$0.67 = (8 - 6) / (9 - 6)$$

To calculate the total hazard potential score for benzene, the physicochemical properties score, toxicity score, and occurrence score were summed for a total of 1.67. These results can be seen in Table 9-7, which shows the MCDA results for chemicals used in hydraulic fracturing fluid.

Chapter 10

Synthesis

10. Synthesis

In this assessment, we examined the potential for hydraulic fracturing for oil and natural gas to change the quality or quantity of drinking water resources, and identified factors that affect the frequency or severity of potential impacts. Drinking water resources are defined broadly in this report as any body of ground water or surface water that now serves, or in the future could serve, as a source of drinking water for public or private use. We assessed potential effects on drinking water resources from both routine operations and potential accidents. Impacts were defined as any change in the quality or quantity of drinking water resources. Where possible, we identified the mechanisms responsible or potentially responsible for any impacts. For example, a spill of hydraulic fracturing fluid is a mechanism by which drinking water resources could be impacted.

We did this by following water through the hydraulic fracturing water cycle: (1) the withdrawal of ground or surface water needed for hydraulic fracturing fluids; (2) the mixing of water, chemicals, and proppant on the well pad to create the hydraulic fracturing fluid; (3) the injection of hydraulic fracturing fluids into the well to fracture the geologic formation; (4) the management of flowback and produced water, both on the well pad and in transit for reuse, treatment, or disposal; and (5) the reuse, treatment and discharge, or disposal of hydraulic fracturing wastewater.

In this chapter, we summarize major findings of the assessment, organized by each stage of the hydraulic fracturing water cycle (Section 10.1); highlight key uncertainties related to these major findings (Section 10.2); and discuss the assessment's overall conclusions (Section 10.3) and potential uses (Section 10.4).

10.1. Major Findings

From our assessment, we conclude there are above and below ground mechanisms by which hydraulic fracturing activities have the potential to impact drinking water resources. These mechanisms include water withdrawals in times of, or in areas with, low water availability; spills of hydraulic fracturing fluids and produced water; fracturing directly into underground drinking water resources; below ground migration of liquids and gases; and inadequate treatment and discharge of wastewater.

We did not find evidence that these mechanisms have led to widespread, systemic impacts on drinking water resources in the United States. Of the potential mechanisms identified in this report, we found specific instances where one or more mechanisms led to impacts on drinking water resources, including contamination of drinking water wells. The number of identified cases, however, was small compared to the number of hydraulically fractured wells.

This finding could reflect a rarity of effects on drinking water resources, but may also be due to other limiting factors. These factors include: insufficient pre- and post-fracturing data on the quality of drinking water resources; the paucity of long-term systematic studies; the presence of other sources of contamination precluding a definitive link between hydraulic fracturing activities and an impact; and the inaccessibility of some information on hydraulic fracturing activities and potential impacts.

Below, we provide a synopsis of the assessment's key findings, organized according to each stage of the hydraulic fracturing water cycle. We provide answers to the research questions presented in the Study Plan and Chapter 1. Results from Chapter 9 (Hazard Evaluation and Identification of Chemicals across the Hydraulic Fracturing Water Cycle) are included in the Chemical Mixing and the Flowback and Produced Water sections. While some citations are provided here, individual chapters can be consulted for additional detail and citations.

10.1.1. Water Acquisition (Chapter 4)

Water is a major component of nearly all hydraulic fracturing operations. It typically makes up almost 90% or more of the fluid injected into a well, and each hydraulically fractured well requires thousands to millions of gallons of water. Cumulatively, hydraulic fracturing activities in the United States used on average 44 billion gal of water a year in 2011 and 2012, according to the EPA's analysis of FracFocus 1.0 disclosures. Although this represents less than 1% of total annual water use and consumption at this scale, water withdrawals could potentially impact the quantity and quality of drinking water resources at more local scales.

Research Questions: Water Acquisition

- ***What are the types of water used for hydraulic fracturing?***

Water for hydraulic fracturing typically comes from surface water, ground water, or reused hydraulic fracturing wastewater. Hydraulic fracturing operations in the eastern United States generally rely on surface water, while operations in the more semi-arid to arid western states generally use mixed supplies of surface and ground water. In the Marcellus Shale in Pennsylvania, for example, most water used for hydraulic fracturing originates from surface water, whereas surface and ground water are used in approximately equal proportions in the Barnett Shale in Texas (see Figure 10-1a,b). In areas that lack available surface water (e.g., western Texas), ground water supplies most of the water needed for hydraulic fracturing.

Across the United States, the vast majority of water used in hydraulic fracturing is fresh, although operators also make use of lower-quality water, including reused hydraulic fracturing wastewater. Based on available data, the median reuse of hydraulic fracturing wastewater as a percentage of injected volumes is 5% nationally, with the percentage varying by location.[1] Available data on reuse trends indicate increased reuse of wastewater over time in both Pennsylvania and West Virginia. Reuse as a percentage of injected volumes is lower in other areas, including regions with more water stress, likely because of the availability of disposal wells. For example, reused wastewater is approximately 18% of injected volumes in the Marcellus Shale in Pennsylvania's Susquehanna River Basin, whereas it is approximately 5% in the Barnett Shale in Texas (see Figure 10-1a,b).

[1] Reused wastewater as a percentage of injected volumes differs from the percentage of wastewater that is managed through reuse, as opposed to other wastewater management options. For example, in the Marcellus Shale in Pennsylvania, approximately 18% of injected water is reused produced water, while approximately 70% or more of wastewater is managed through reuse (see Figure 10-1a).

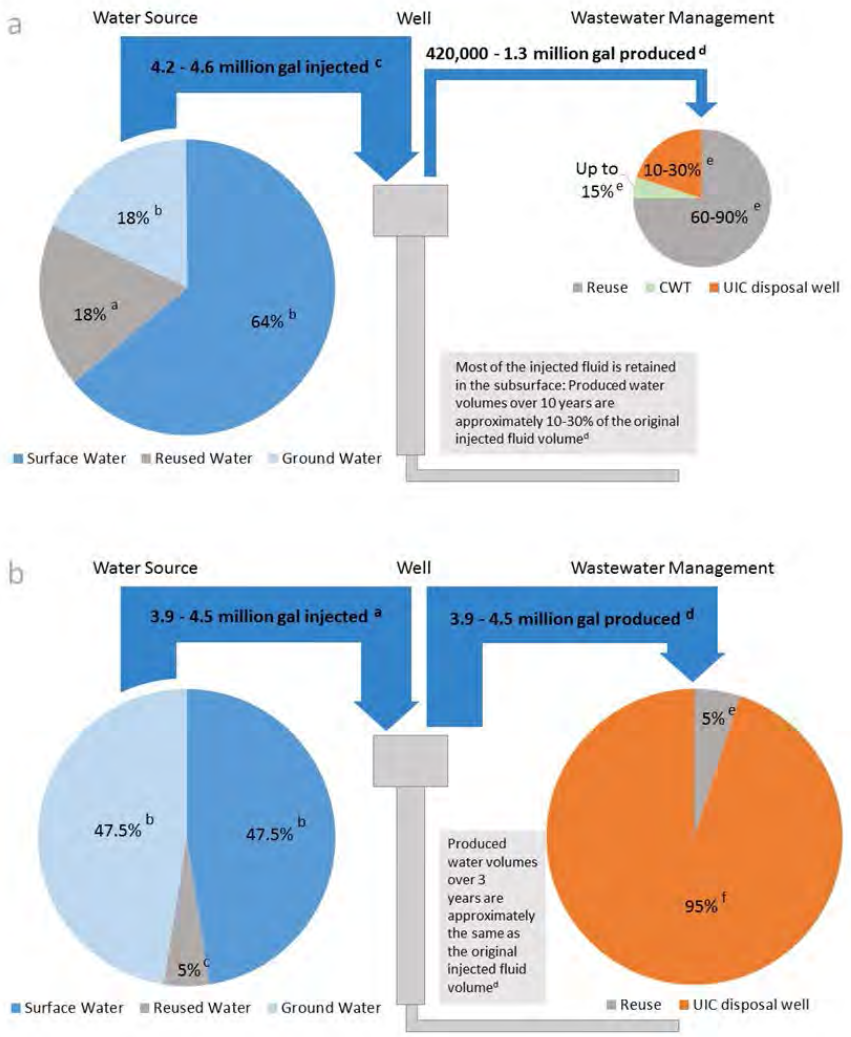

Figure 10-1. Water budgets representative of practices in the Marcellus Shale in the Susquehanna River Basin in Pennsylvania (a) and the Barnett Shale in Texas (b).

Pie size and arrow thickness represent the relative volume of water as it flows through the hydraulic fracturing water cycle. Wastewater going to a centralized waste treatment (CWT) facility may be either discharged to surface water or reused. Wastewater going to an underground injection control (UIC) well is disposed of below ground. These examples represent typical water management practices as depicted for the most recent time period reviewed by this assessment. They do not represent any specific well. Sources for 10-1a: (a) Table 4-1 (Hansen et al., 2013); (b) Table 4-3 (U.S. EPA, 2015c); (c) Appendix Table B-5 (Hansen et al., 2013); (d) Table 7-2 (Ziemkiewicz et al., 2014)—Note: produced water value from the West Virginia portion of the Marcellus; it provided the longest-term measurement of produced water volumes; (e) Figure 8-4 (PA DEP, 2015a) and Table 8-5 (Ma et al., 2014; Shaffer et al., 2013). Sources for 10-1b: (a) Appendix Table B-5 (U.S. EPA, 2015a; Nicot et al., 2012; Nicot et al., 2011); (b) Table 4-3 (Nicot et al., 2014); (c) Table 4-1 (Nicot et al., 2012); d: Table 7-2 (Nicot et al., 2014); (e) Table 8-5 (Nicot et al., 2012); (f) Calculated by subtracting reuse values from 100% (see Table 8-5).

- ***How much water is used per well?***

The national median volume of water used per hydraulically fractured well is approximately 1.5 million gal (5.7 million L), according to the EPA's analysis of FracFocus 1.0 disclosures. This estimate likely represents a wide variety of fractured well types, including vertical wells that generally use much less water per well than horizontal wells. Thus, published estimates for horizontal shale gas wells are typically higher (e.g., approximately 4 million gal (Vengosh et al., 2014)). There is also wide variation within and among states and basins in the median water volumes used per well, from more than 5 million gal (19 million L) in Arkansas, Louisiana and West Virginia to less than 1 million gal (3.8 million L) in California, New Mexico, and Utah, among others. This variation results from several factors, including well length, formation geology, and fracturing fluid formulation.

- ***How might cumulative water withdrawals for hydraulic fracturing affect drinking water quantity?***

Cumulatively, hydraulic fracturing uses billions of gallons of water each year at the national and state scales, and even in some counties. As noted above, hydraulic fracturing water use and consumption are generally less than 1% of total annual water use and consumption at these scales. However, there are a few counties in the United States where these percentages are higher. For 2011 and 2012, annual hydraulic fracturing water use was 10% or more compared to 2010 total annual water use in 6.5% of counties with FracFocus 1.0 disclosures analyzed by the EPA, 30% or more in 2.2% of counties, and 50% or more in 1.0% of counties. Consumption estimates followed the same general pattern. For these counties, hydraulic fracturing is a relatively large user and consumer of water.

High fracturing water use or consumption alone does not necessarily result in impacts to drinking water resources. Rather, impacts result from the combination of water use/consumption and water availability at local scales. In our survey of published literature, we did not find a case where hydraulic fracturing water use or consumption alone caused a drinking water well or stream to run dry. This could indicate an absence of effects or a lack of documentation in the literature we reviewed. Additionally, water availability is rarely impacted by just one use or factor alone. In Louisiana, for example, the state requested hydraulic fracturing operations switch from ground to surface water, due to concerns that ground water withdrawals for fracturing could, in combination with other uses, adversely affect drinking water supplies.

The potential for impacts to drinking water resources from hydraulic fracturing water withdrawals is highest in areas with relatively high fracturing water use and low water availability. Southern and western Texas are two locations where hydraulic fracturing water use, low water availability, drought, and reliance on declining ground water has the potential to affect the quantity of drinking water resources. Any impacts are likely to be realized locally within these areas. In a detailed case study of southern Texas, Scanlon et al. (2014) observed generally adequate water supplies for hydraulic fracturing, except in specific locations. They found excessive drawdown of local ground water in a small proportion (approximately 6% of the area) of the Eagle Ford Shale. They suggested

water management, particularly a shift towards brackish water use, could minimize potential future impacts to fresh water resources.

The potential for impacts to drinking water quantity due to hydraulic fracturing water use appears to be lower—but not eliminated—in other areas of the United States. Future problems could arise if hydraulic fracturing increases substantially in areas with low water availability, or in times of water shortages. In detailed case studies in western Colorado and northeastern Pennsylvania, the EPA did not find current impacts, but did conclude that streams could be vulnerable to water withdrawals from hydraulic fracturing. In northeast Pennsylvania, water management, such as minimum stream flow requirements, limits the potential for impacts, especially in small streams. In western North Dakota, ground water is limited, but the industry may have sufficient supplies of surface water from the Missouri River system. These location-specific examples emphasize the need to focus on regional and local dynamics when considering potential impacts of hydraulic fracturing water acquisition on drinking water resources.

- ***What are the possible impacts of water withdrawals for hydraulic fracturing on water quality?***

Water withdrawals for hydraulic fracturing, similar to all water withdrawals, have the potential to alter the quality of drinking water resources. Ground water withdrawals exceeding natural recharge rates decrease water storage in aquifers, potentially mobilizing contaminants or allowing the infiltration of lower quality water from the land surface or adjacent formations. Withdrawals could also decrease ground water discharge to streams, potentially affecting surface water quality. Areas with large amounts of sustained ground water pumping are most likely to experience impacts, particularly drought-prone regions with limited ground water recharge.

Surface water withdrawals also have the potential to affect water quality. Withdrawals may lower water levels and alter stream flow, potentially decreasing a stream's capacity to dilute contaminants. Case studies by the EPA show that streams can be vulnerable to changes in water quality due to water withdrawals, particularly smaller streams and during periods of low flow. Management of the rate and timing of surface water withdrawals has been shown to help mitigate potential impacts of hydraulic fracturing withdrawals on water quality.

10.1.2. Chemical Mixing (Chapter 5)

Hydraulic fracturing fluids are developed to perform specific functions, including: create and extend fractures, transport proppant, and place proppant in the fractures. The fluid generally consists of three parts: (1) the base fluid, which is the largest constituent by volume and is typically water; (2) the additives, which can be a single chemical or a mixture of chemicals; and (3) the proppant. Additives are chosen to serve a specific purpose (e.g., adjust pH, increase viscosity, limit bacterial growth). Chemicals generally comprise a small percentage (typically 2% or less) of the overall injected fluid volume. Because over one million gallons of fluid are typically injected per well, thousands of gallons of chemicals can be potentially stored on-site and used during hydraulic fracturing activities.

On-site storage, mixing, and pumping of chemicals and hydraulic fracturing fluids have the potential to result in accidental releases, such as spills or leaks. Potential impacts to drinking water resources

from spills of hydraulic fracturing fluids and chemicals depend on the characteristics of the spills, and the fate, transport, and the toxicity of chemicals spilled.

Research Questions: Chemical Mixing

- ***What is currently known about the frequency, severity, and causes of spills of hydraulic fracturing fluids and additives?***

The frequency of on-site spills from hydraulic fracturing could be estimated for two states, but not for operations nationally or for other areas. Frequency estimates from data and literature ranged from one spill for every 100 wells in Colorado to between approximately 0.4 and 12.2 spills for every 100 wells in Pennsylvania.[1] These estimates include spills of hydraulic fracturing fluids and chemicals, and produced water reported in state databases. Available data generally precluded estimates of hydraulic fracturing fluid and/or chemical spill rates separately from estimates of an overall spill frequency. It is unknown whether these spill estimates are representative of national occurrences. If the estimates are representative, the number of spills nationally could range from approximately 100 to 3,700 spills annually, assuming 25,000 to 30,000 new wells are fractured per year.

The EPA characterized volumes and causes of hydraulic fracturing-related spills identified from selected state and industry data sources. The spills occurred between January 2006 and April 2012 in 11 states and included 151 cases in which fracturing fluids or chemicals spilled on or near a well pad. Due to the methods used for the EPA's characterization of spills, these cases were likely a subset of all fracturing fluid and chemical spills during the study's time period. The reported volume of fracturing fluids or chemicals spilled ranged from 5 gal to more than 19,000 gal (19 to 72,000 L), with a median volume of 420 gal (1,600 L) per spill. Spill causes included equipment failure, human error, failure of container integrity, and other causes (e.g., weather and vandalism). The most common cause was equipment failure, specifically blowout preventer failure, corrosion, and failed valves. More than 30% of the 151 fracturing fluid or chemical spills were from fluid storage units (e.g., tanks, totes, and trailers).

- ***What are the identities and volumes of chemicals used in hydraulic fracturing fluids, and how might this composition vary at a given site and across the country?***

In this assessment, we identified a list of 1,076 chemicals used in hydraulic fracturing fluids. This is a cumulative list over multiple wells and years. These chemicals include acids, alcohols, aromatic hydrocarbons, bases, hydrocarbon mixtures, polysaccharides, and surfactants. According to the EPA's analysis of disclosures to FracFocus 1.0, the number of unique chemicals per well ranged from 4 to 28, with a median of 14 unique chemicals per well.

Our analysis indicates that chemical use varies and that no single chemical is used at all well sites across the country, although several chemicals are widely used. Methanol, hydrotreated light

[1] Spill frequency estimates are for a given number of wells over a given period of time. These are not annual estimates nor are they for the lifetime of a well.

petroleum distillates, and hydrochloric acid were reported as used in 65% or more of wells, according to FracFocus 1.0 disclosures analyzed by the EPA. Only 32 chemicals, excluding water, quartz, and sodium chloride, were used in more than 10% of wells according to the EPA's analysis of FracFocus disclosures. The composition of hydraulic fracturing fluids varies by state, by well, and within the same service company and geologic formation. This variability likely results from several factors, including the geology of the formation, the availability and cost of different chemicals, and operator preference.

Estimates from the EPA's database developed from FracFocus 1.0 suggest median volumes of individual chemicals injected per well range from a few gallons to thousands of gallons, with an overall median of 650 gal (2,500 L) per chemical per well. Based on this overall median and assuming 14 unique chemicals are used per well, an estimated 9,100 gal (34,000 L) of chemicals may be injected per well. Given that the number of chemicals per well ranges from 4 to 28, the estimated volume of chemicals injected per well may range from approximately 2,600 to 18,000 gal (9,800 to 69,000 L).

- ***What are the chemical, physical, and toxicological properties of hydraulic fracturing chemical additives?***

Measured or estimated physicochemical properties were obtained for 453 chemicals of the toal 1,076 chemicals reported in hydraulic fracturing fluids. We could not estimate physicochemical properties for the inorganic chemicals or mixtures. The 453 chemicals have a wide range of physicochemical properties.

Properties affecting the likelihood of a spilled chemical reaching and impacting a drinking water resource, include: mobility, solubility, and volatility. Of the 453 chemicals for which physicochemical properties were available, 18 of the top 20 most mobile ones were reported in the EPA's FracFocus 1.0 database for 2% or less of wells. Choline chloride and tetrakis (hydroxymethyl) phosphonium were exceptions and were reported in 14% and 11% of wells, respectively. These two chemicals appear to be relatively more common, and, if spilled, would move quickly through the environment with the flow of water. The majority of the 453 chemicals associate strongly with soils and organic materials, suggesting the potential for these chemicals to persist in the environment as long-term contaminants. Many of the 453 chemicals fully dissolve in water, but their aqueous solubility varies greatly. Few of the chemicals volatilize, and thus a large proportion of most hydraulic fracturing chemicals tend to remain in water.

Oral reference values and oral slope factors meeting the criteria used in this assessment were not available for the majority of chemicals used in hydraulic fracturing fluids, representing a significant data gap for hazard identification.[1,2] Reference values and oral slope factors are important for

[1] A reference value is an estimate of an exposure to the human population (including susceptible subgroups) for a given duration that is likely to be without an appreciable risk of adverse health effects over a lifetime. Reference value is a generic term not specific to a given route of exposure.
[2] An oral slope factor is an upper-bound, approximating 95% confidence limit, on the increased cancer risk from a lifetime oral exposure to an agent.

understanding the potential human health effects resulting from exposure to a chemical. Chronic oral reference values and/or oral slope factors from selected federal, state, and international sources were available for 90 (8%) of the 1,076 chemicals used in hydraulic fracturing fluids. From U.S. federal sources alone, chronic oral reference values were available for 73 chemicals (7%) of the 1,076 chemicals, and oral slope factors were available for 15 chemicals (1%). Of the 32 chemicals reported as used in at least 10% of wells in the EPA's FracFocus database (excluding water, quartz, and sodium chloride), seven (21%) have a federal chronic oral reference value. Oral reference values and oral slope factors are a key component of the risk assessment process, although comprehensive risk assessments that characterize the health risk associated with exposure to these chemicals are not available.

Of the chemicals that had values available, the health endpoints associated with those values include the potential for carcinogenesis, immune system effects, changes in body weight, changes in blood chemistry, cardiotoxicity, neurotoxicity, liver and kidney toxicity, and reproductive and developmental toxicity. However, it is important to note that evaluating any potential risk to human populations would require knowledge of the specific chemicals that are present at a particular site, whether or not humans are exposed to those chemicals and, if so, at what levels and for what duration, and the toxicity of the chemicals. Since most chemicals are used infrequently on a nationwide basis, potential exposure is likely to be a local or regional issue, rather than a national issue. Accordingly, consideration of hazards and risks associated with these chemical additives would be most useful on a site-specific basis and is beyond the scope of this assessment.

- ***If spills occur, how might hydraulic fracturing chemical additives contaminate drinking water resources?***

There are several mechanisms by which a spill can potentially contaminate drinking water resources. These include overland flow to nearby surface water, soil contamination and eventual transport to surface water, and infiltration and contamination of underlying ground water. Of the 151 spills characterized by the EPA, fluids reached surface water in 13 (9% of 151) cases and soil in 97 (64%) cases. None of the spills of hydraulic fracturing fluid were reported to have reached ground water. This could be due to an absence of impact; however, it can take several years for spilled fluids to infiltrate soil and leach into ground water. Thus, it may not be immediately apparent whether a spill has reached ground water or not.

Based on the relative importance of each of these mechanisms, impacts have the potential to occur quickly, be delayed short or long periods, or have a continual effect over time. In Kentucky, for example, a spill impacted a surface water body relatively quickly when hydraulic fracturing fluid entered a creek, significantly reducing the water's pH and increasing its conductivity (Papoulias and Velasco, 2013).

10.1.3. Well Injection (Chapter 6)

Hydraulic fracturing fluids are injected into oil or gas wells under high pressures. The fluids flow through the well (commonly thousands of feet below the surface) into the production zone (i.e., the

geologic formation being fractured) where the fluid injection pressures are sufficient to create fractures in the rock.

There are two major subsurface mechanisms by which the injection of fluid and the creation and propagation of fractures can lead to contamination of drinking water resources: (1) the unintended movement of liquids or gases out of the production well or along the outside of the production well into a drinking water resource via deficiencies in the well's casing or cement, and (2) the unintended movement of liquids or gases from the production zone through subsurface geologic formations into a drinking water resource. Combinations of these two mechanisms are also possible.

Research Questions: Well Injection

- ***How effective are current well construction practices at containing fluids- both liquids and gases - before, during, and after fracturing?***

Production wells are constructed to access and convey hydrocarbons from the formations in which they are found to the surface, and to isolate fluid-bearing zones (containing oil, gas, or water) from each other. Typically, multiple casings are emplaced and cemented along the wellbore to protect and isolate the oil and/or natural gas from the formations it must travel through to reach the surface.

Below ground drinking water resources are often separated from the production well using casing and cement. Cemented surface casing, in particular, is an important well construction feature for isolating drinking water resources from liquids and gases that may move through the subsurface. A limited risk modeling study of selected injection wells in the Williston Basin in North Dakota suggests that the risk of aquifer contamination from leaks inside the well to the drinking water resource decreases by a factor of approximately one thousand when surface casing extends below the bottom of the drinking water resource (Michie and Koch, 1991). Most wells used in hydraulic fracturing operations have casing and a layer of cement to protect drinking water resources, but there are exceptions: a survey conducted by the EPA of oil and gas production wells hydraulically fractured by nine oil and gas service companies in 2009 and 2010 estimated that at least 3% of the wells (600 out of 23,000 wells) did not have cement across a portion of the casing installed through the protected ground water resource identified by well operators. The absence of cement does not in and of itself lead to an impact. However, it does reduce the overall number of casing and cement barriers fluids must travel through to reach ground water resources.

Impacts to drinking water resources from subsurface liquid and gas movement may occur if casing or cement are inadequately designed or constructed, or fail. There are several examples of these occurrences in hydraulically fractured wells that have or may have resulted in impacts to drinking water resources. In one example, an inner string of casing burst during hydraulic fracturing, which resulted in a release of fluids on the land surface and possibly into the aquifer near Killdeer, North Dakota. The EPA found that, based on the data analysis performed for the study, the only potential source consistent with conditions observed in two impacted monitoring wells was the blowout that

occurred during hydraulic fracturing (U.S. EPA, 2015j). In other examples, inadequately cemented casing has contributed to impacts to drinking water resources. In Bainbridge, Ohio, inadequately cemented casing in a hydraulically fractured well contributed to the buildup of natural gas and high pressures along the outside of a production well. This ultimately resulted in movement of natural gas into local drinking water aquifers (Bair et al., 2010; ODNR, 2008). In the Mamm Creek gas field in Colorado, inadequate cement placement in a production well allowed methane and benzene to migrate along the production well and through natural faults and fractures to drinking water resources (Science Based Solutions LLC, 2014; Crescent, 2011; COGCC, 2004). These cases illustrate how construction issues, sustained casing pressure, and the presence of natural faults and fractures can work together to create pathways for fluids to migrate toward drinking water resources.

Fracturing older wells may also increase the potential for impacts to drinking water resources via movement of liquids and gases from the inside of the production well or along the outside of the production well to ground water resources. The EPA estimated that 6% of 23,000 oil and gas production wells were drilled more than 10 years before being hydraulically fractured in 2009 or 2010. Although new wells can be designed to withstand the stresses associated with hydraulic fracturing operations, older wells may not have been built or tested to the same specifications and their reuse for this purpose could be of concern. Moreover, aging and use of the well can contribute to casing degradation, which can be accelerated by exposure to corrosive chemicals such as hydrogen sulfide, carbonic acid, and brines.

- ***Can subsurface migration of fluids- both liquids and gases- to drinking water resources occur, and what local geologic or artificial features might allow this?***

Physical separation between the production zone and drinking water resources can help protect drinking water. Many hydraulic fracturing operations target deep formations such as the Marcellus Shale or the Haynesville Shale (Louisiana/Texas), where the vertical distance between the base of drinking water resources and the top of the shale formation may be a mile or greater. Numerical modeling and microseismic studies based on a Marcellus Shale-like environment suggest that fractures created during hydraulic fracturing are unlikely to extend upward from these deep formations into shallow drinking water aquifers.

Not all hydraulic fracturing is performed in zones that are deep below drinking water resources. For example, operations in the Antrim Shale (Michigan) and the New Albany Shale (Illinois/Indiana/Kentucky) take place at shallower depths (100 to 1,900 ft or 30 to 579 m), with less vertical separation between the formation and drinking water resources (NETL, 2013; GWPC and ALL Consulting, 2009). The EPA's survey of oil and gas production wells hydraulically fractured by nine service companies in 2009 and 2010 estimated that 20% of 23,000 wells had less than 2,000 ft (610 m) of measured distance between the point of shallowest hydraulic fracturing and the base of the protected ground water resources reported by well operators.

There are also places in the subsurface where oil and gas resources and drinking water resources co-exist in the same formation. Evidence indicates that hydraulic fracturing occurs within these formations. This results in the introduction of fracturing fluids into formations that may currently serve, or in the future could serve, as a source of drinking water for public or private use. According

to the data examined, the overall frequency of occurrence of this practice appears to be low, with the activity generally concentrated in some areas in the western United States. The practice of injecting fracturing fluids into a formation that also contains a drinking water resource directly affects the quality of that water, since some of the fluid likely remains in the formation following hydraulic fracturing. Hydraulic fracturing in a drinking water resource is a concern in the short-term (should there be people currently using these zones as a drinking water supply) and the long-term (if drought or other conditions necessitate the future use of these zones for drinking water).

Liquid and gas movement from the production zone to underground drinking water resources may also occur via other production wells or injection wells near hydraulic fracturing operations. Fractures created during hydraulic fracturing can intersect nearby wells or their fracture networks, resulting in the flow of fluids into those wells. These well communications, or "frac hits," are more likely to occur if wells are close to each other or on the same well pad. In the Woodford Shale in Oklahoma, the likelihood of well communication was less than 10% between wells more than 4,000 ft (1,219 m) apart, but rose to nearly 50% between wells less than 1,000 ft (305 m) apart (Ajani and Kelkar, 2012). If an offset well is not able to withstand the stresses applied during the hydraulic fracturing of a neighboring well, well components may fail, which could result in a release of fluids at the surface from the offset well. The EPA identified incidents in which surface spills of hydraulic fracturing-related fluids were attributed to well communication events.

Older or inactive wells—including oil and gas wells, injection wells, or drinking water wells—near the hydraulic fracturing operation may pose an even greater potential for impacts. A study in Oklahoma found that older wells were more likely to be negatively affected by the stresses applied by hydraulic fracturing in neighboring wells (Ajani and Kelkar, 2012). In some cases, inactive wells in the vicinity of hydraulic fracturing activities may not have been plugged properly—many wells plugged before the 1950s were done so with little or no cement. The Interstate Oil and Gas Compact Commission estimates that over one million wells may have been drilled in the United States prior to a formal regulatory system being in place, and the status and location of many of these wells are unknown (IOGCC, 2008). State programs exist to plug identified inactive wells, and work is on-going to identify and address such wells.

10.1.4. Flowback and Produced Water (Chapter 7)

Water, of variable quality, is a byproduct of oil and gas production. After hydraulic fracturing, the injection pressure is released and water flows back from the well. Initially this water is similar to the hydraulic fracturing fluid, but as time goes on the composition is affected by the characteristics of the formation and possible reactions between the formation and the fracturing fluid. Water initially produced from the well after hydraulic fracturing is sometimes called flowback in the literature, and the term appears in this assessment. However, hydraulic fracturing fluids and any formation water returning to the surface are often referred to collectively as produced water. This definition of produced water is used in this assessment.

The amount of produced water varies, but typically averages 10% to 25% of injected volumes, depending upon the amount of time since fracturing and the particular well (see Figure 10-1a). However, there are exceptions to this, such as in the Barnett Shale in Texas where the total volume

of produced water can equal or exceed the injected volume of hydraulic fracturing fluid (see Figure 10-1b). Flow rates are generally high initially, and then decrease over time throughout oil or gas production.

Impacts on drinking water resources have the potential to occur if produced water is spilled and enters surface water or ground water. Environmental transport of chemical constituents in produced water depends on the characteristics of the spill (e.g., volume and duration), the composition of spilled fluids, and the characteristics of the surrounding environment.

Research Questions: Flowback and Produced Water

- ***What is currently known about the frequency, severity, and causes of spills of flowback and produced water?***

Surface spills of produced water from hydraulically fractured wells have occurred. As noted in the Chemical Mixing section above, the frequency of on-site spills from hydraulic fracturing activities could be estimated for two states, but not nationally. Estimates of spill frequencies at hydraulic fracturing sites in Colorado and Pennsylvania, including spills of produced water, ranged from approximately 0.4 to 12.2 spills per 100 wells. Available data generally precluded estimates of produced water spill rates separately from estimates of overall spill frequency. Away from the well, produced water spills from pipelines and truck transport also have the potential to impact drinking water resources.

The EPA characterized spill volumes and causes for 225 cases in which produced water spilled on or near a well pad. These spills occurred between January 2006 and April 2012 in 11 states. The median reported volume per produced water spill was 990 gallons (3,750 L), more than double that for spills of hydraulic fracturing fluids and chemicals. The causes of produced water spills were reported as human error, equipment failure, container integrity failure, miscellaneous causes (e.g., well communication), and unknown causes. Most of the total volume spilled (74%) for all 225 cases combined was caused by a failure of container integrity.

- ***What is the composition of hydraulic fracturing flowback and produced water, and what factors might influence this composition?***

A combination of factors influence the composition of produced water, including: the composition of injected hydraulic fracturing fluids, the type of formation fractured, subsurface processes, and residence time. The initial chemical composition of produced water primarily reflects the chemistry of the injected fluids. At later times, the chemical composition of produced water reflects the geochemistry of the fractured formation.

Produced water varies in quality from fresh to highly saline, and can contain high levels of major anions and cations, metals, organics, and naturally occurring radionuclides. Produced water from shale and tight gas formations typically contains high levels of total dissolved solids (TDS) and ionic constituents (e.g., bromide, calcium, chloride, iron, potassium, manganese, magnesium, and sodium). Produced water also may contain metals (e.g., barium, cadmium, chromium, lead, and

mercury), and organic compounds such as benzene. Produced water from coalbed methane typically has much lower TDS levels compared to other produced water types, particularly if the coalbed was deposited under fresh water conditions.

We identified 134 chemicals that have been detected in hydraulic fracturing produced water. These include chemicals added during the chemical mixing stage, as well as naturally occurring organic chemicals and radionuclides, metals, and other constituents of subsurface rock formations mobilized by the hydraulic fracturing process. Data on measured chemical concentrations in produced water were available for 75 of these 134 chemicals.

Most of the available data on produced water content are for shale and coalbed methane formations, while less data are available for tight formations, such as sandstones. The composition of produced water must be determined through sampling and analysis, both of which have limitations—the former due to challenges in accessing production equipment, and the latter due to difficulties identifying target analytes before analysis and the lack of appropriate analytical methods. Most current data are for inorganic chemicals, while less data exist for organic chemicals. Many more organic chemicals were reported as used in hydraulic fracturing fluid than have been identified in produced water. The difference may be due to analytical limitations, limited study scopes, and undocumented subsurface reactions.

- ***What are the chemical, physical, and toxicological properties of hydraulic fracturing flowback and produced water constituents?***

The identified constituents of produced water include inorganic chemicals (cations and anions, i.e., metals, metalloids, non-metals, and radioactive materials), organic chemicals and compounds, and unidentified materials measured as total organic carbon and dissolved organic carbon. Some constituents are readily transported with water (i.e., chloride and bromide), while others depend strongly on the geochemical conditions in the receiving water body (i.e., radium and barium), and assessment of their transport is based on site-specific factors. We were able to obtain actual or estimated physicochemical properties for 86 (64%) of the 134 chemicals identified in produced water.

As in the case of chemicals in hydraulic fracturing fluid, chemical properties that affect the likelihood of an organic chemical in produced water reaching and impacting drinking water resources include: mobility, solubility, and volatility. In general, physicochemical properties suggest that organic chemicals in produced water tend to be less mobile in the environment. Consequently, if spilled, these chemicals may remain in soils or sediments near spill sites. Low mobility may result in smaller dissolved contaminant plumes in ground water, although these chemicals can be transported with sediments in surface water or small particles in ground water. Organic chemical properties vary with salinity, and effects depend on the nature of the chemical.

Oral reference values and/or oral slope factors from selected federal, state, and international sources were available for 83 (62%) of the 134 chemicals detected in produced water. From U.S. federal sources alone, chronic oral reference values were available for 70 (52%) of the 134 chemicals, and oral slope factors were available for 20 chemicals (15%). Of the chemicals that had

values available, noted health effects include the potential for carcinogenesis, immune system effects, changes in body weight, changes in blood chemistry, pulmonary toxicity, neurotoxicity, liver and kidney toxicity, and reproductive and developmental toxicity. As noted above, evaluating any potential risk to human populations would require knowledge of the specific chemicals that are present at a particular site, whether or not humans are exposed to those chemicals and, if so, at what levels and for what duration, and the toxicity of the chemicals. The chemicals present in produced water can vary based on the formation and specific well, due to differences in fracturing fluid formulation and formation geology. Accordingly, consideration of hazards and risks associated with these chemicals would be most useful on a site-specific basis and is beyond the scope of this assessment. .

- ***If spills occur, how might hydraulic fracturing flowback and produced water contaminate drinking water resources?***

Impacts to drinking water resources from spills or releases of produced water depend on the volume, timing, and composition of the produced water. Impacts are more likely the greater the volume of the spill, the longer the duration of the release, and the higher the concentration of produced water constituents (i.e., salts, naturally occurring radioactive material, and metals).

The EPA characterization of hydraulic fracturing-related spills found that 8% of the 225 produced water spills included in the study reached surface water or ground water. These spills tended to be of greater volume than spills that did not reach a water body. A well blowout in Bradford County, Pennsylvania spilled an estimated 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 and ground water.

Chronic releases can and do occur from produced water disposed in unlined pits or impoundments, and can have long-term impacts. Ground water impacts may persist longer than surface water impacts because of lower flow rates and decreased mixing. Plumes from unlined pits used for produced water have been shown to persist for long periods and extend to nearby surface water bodies.

10.1.5. Wastewater Management and Waste Disposal (Chapter 8)

Hydraulic fracturing generates large volumes of produced water that require management. In this section we refer to produced water and any other waters generated onsite by the single term "wastewater." Clark and Veil (2009) estimated that in 2007 approximately one million active oil and gas wells in the United States generated 2.4 billion gal per day (9.1 billion L per day) of wastewater. There is currently no reliable way to estimate what fraction of this total volume can be attributed to hydraulically fractured wells. Wastewater volumes in a region can increase sharply as hydraulic fracturing activity increases.

Wastewater management and disposal could affect drinking water resources through multiple mechanisms including: inadequate treatment of wastewater prior to discharge to a receiving water, accidental releases during transport or leakage from wastewater storage pits, unpermitted

discharges, migration of constituents in wastewaters following land application, inappropriate management of residual materials from treatment, or accumulation of wastewater constituents in sediments near outfalls of centralized waste treatment facilities (CWTs) or publicly owned treatment works (POTWs) that have treated hydraulic fracturing wastewater. The scope of this assessment excludes potential impacts to drinking water from the disposal of hydraulic fracturing wastewater in underground injection control (UIC) wells.

Research Questions: Wastewater Management and Waste Disposal

- ***What are the common treatment and disposal methods for hydraulic fracturing wastewater, and where are these methods practiced?***

Hydraulic fracturing wastewater is managed using several options including disposal in UIC wells (also called disposal wells); through evaporation ponds; treatment at CWTs, followed by reuse or by discharge to either surface waters or POTWs; reuse with minimal or no treatment; and land application or road spreading. Treatment of hydraulic fracturing wastewater by POTWs was used in the past in Pennsylvania. This decreased sharply following new state-level requirements and a request by the Pennsylvania Department of Environmental Protection (PA DEP) for well operators to stop sending Marcellus Shale wastewater to POTWs (and 15 CWTs) discharging to surface waters.

Wastewater management decisions are generally based on the availability and associated costs (including transportation) of disposal or treatment facilities. A survey of state agencies found that, in 2007, more than 98% of produced water from the oil and gas industry was managed via underground injection (Clark and Veil, 2009). Available information suggests that disposal wells are also the primary management practice for hydraulic fracturing wastewater in most regions in the United States (e.g., the Barnett Shale; see Figure 10-1b). The Marcellus Shale region is a notable exception, where most wastewater is reused because of the small number of disposal wells in Pennsylvania (see Figure 10-1a). Although this assessment does not address potential effects on drinking water resources from the use of disposal wells, any changes in cost of disposal or availability of disposal wells would likely influence wastewater management decisions.

Wastewater from some hydraulic fracturing operations is sent to CWTs, which may discharge treated wastewater to surface waters, POTWs, or back to well operators for reuse in other hydraulic fracturing operations. Available data indicate that the use of CWTs for treating hydraulic fracturing wastewater is greater in the Marcellus Shale region than other parts of the country. Most of the CWTs accepting hydraulic fracturing wastewater in Pennsylvania cannot significantly reduce TDS, and many of these facilities provide treated wastewater to well operators for reuse and do not currently discharge treated wastewater to surface water.

Reuse of wastewater for subsequent hydraulic fracturing operations may require no treatment, minimal treatment, or more extensive treatment. Operators reuse a substantial amount (ca. 70–90%) of Marcellus Shale wastewater in Pennsylvania (see Figure 10-1a). Lesser amounts of reuse

occur in other areas (e.g., the Barnett Shale; see Figure 10-1b). In certain formations, such as the Bakken Shale in North Dakota, there is currently no indication of appreciable reuse.

In some cases, wastewater is used for land applications such as irrigation or road spreading for deicing or dust suppression. Land application has the potential to introduce wastewater constituents to surface water and ground water due to runoff and migration of brines. Studies of road spreading of conventional oil and gas brines have found elevated levels of metals in soils and chloride in ground water.

- ***How effective are conventional POTWs and commercial treatment systems in removing organic and inorganic contaminants of concern in hydraulic fracturing wastewater?***

Publicly owned treatment works using basic treatment processes are not designed to effectively reduce TDS concentrations in highly saline hydraulic fracturing wastewater—although specific constituents or constituents groups can be removed (e.g., metals, oil, and grease by chemical precipitation or other processes). In some cases, wastewater treated at CWTs may be sent to a POTW for additional treatment and discharge. It is blended with POTW influent to prevent detrimental effects on biological processes in the POTW that aid in the treatment of wastewater.

Centralized waste treatment facilities with advanced wastewater treatment options, such as reverse osmosis, thermal distillation, or mechanical vapor recompression, reduce TDS concentrations and can treat contaminants currently known to be in hydraulic fracturing wastewater. However, there are limited data on the composition of hydraulic fracturing wastewater, particularly for organic constituents. It is unknown whether advanced treatment systems are effective at removing constituents that are generally not tested for.

- ***What are the potential impacts from surface water disposal of treated hydraulic fracturing wastewater on drinking water treatment facilities?***

Potential impacts to drinking water resources may occur if hydraulic fracturing wastewater is inadequately treated and discharged to surface water. Inadequately treated hydraulic fracturing wastewater may increase concentrations of TDS, bromide, chloride, and iodide in receiving waters. In particular, bromide and iodide are precursors of disinfection byproducts (DBPs) that can form in the presence of organic carbon in drinking water treatment plants or wastewater treatment plants. Drinking water treatment plants are required to monitor for certain types of DBPs, because some are toxic and can cause cancer.

Radionuclides can also be found in inadequately treated hydraulic fracturing wastewater from certain shales, such as the Marcellus. A recent study by the PA DEP (2015b) found elevated radium concentrations in the tens to thousands of picocuries per liter and gross alpha and gross beta in the hundreds to thousands of picocuries per liter in effluent samples from some CWTs receiving oil and gas wastewater. Radium, gross alpha, and gross beta were also detected in effluents from POTWs receiving oil and gas wastewater (mainly as effluent from CWTs), though at lower concentrations than from the CWTs. Research in Pennsylvania also indicates the accumulation of radium in sediments and soils affected by the outfalls of some treatment plants that have handled oil and gas wastewater, including Marcellus Shale wastewater, and other wastewaters (PA DEP, 2015b;

Warner et al., 2013a). Mobilization of radium from sediments and potential impacts on downstream water quality depend upon how strongly the radium has sorbed to sediments. Impacts may also occur if sediment is resuspended (e.g., following storm events). There is no evidence of radionuclide contamination in drinking water intakes due to inadequately treated hydraulic fracturing wastewater.

Hydraulic fracturing wastewaters contain other constituents such as barium, boron, and heavy metals. Barium in particular has been documented in some shale gas produced waters. Little data exist on metal and organic compound concentrations in untreated and treated wastewaters in order to evaluate whether treatment is effective, and whether there are potential downstream effects on drinking water resources when wastewater is treated and discharged.

10.2.Key Data Limitations and Uncertainties

This assessment used available data and literature to examine the potential impacts of hydraulic fracturing for oil and gas on drinking water resources nationally. As part of this effort, we identified data limitations and uncertainties associated with current information on hydraulic fracturing and its potential to affect drinking water resources. In particular, data limitations preclude a determination of the frequency of impacts with any certainty. There is a high degree of uncertainty about whether the relatively few instances of impacts noted in this report are the result of a rarity of effects or a lack of data. These limitations and uncertainties are discussed in brief below.

10.2.1. Limitations in monitoring data and chemical information

While many activities conducted as part of the hydraulic fracturing water cycle take place above ground, hydraulic fracturing itself occurs below ground and is not directly observable. Additionally, potential mechanisms identified in this assessment may result in impacts to drinking water resources that are below ground (e.g., spilled fluids leaching into ground water). Because of this, monitoring data are needed before, during, and after hydraulic fracturing to characterize the status of the well being fractured and the presence, migration, or transformation of chemicals in the subsurface. These data can include results from mechanical integrity tests performed on hydraulically fractured oil and gas production wells and data on local water quality collected pre- and post-hydraulic fracturing. In particular, baseline data on local water quality is needed to quantify changes to drinking water resources and to provide insights into whether nearby hydraulic fracturing activities may have caused any detected changes. The limited amount of data collected before and during hydraulic fracturing activities reduces the ability to determine whether hydraulic fracturing affected drinking water resources in cases of alleged contamination.

Water quality testing for hydraulic fracturing-related chemicals is routinely conducted for a small subset of chemicals reportedly used in hydraulic fracturing fluids or detected in produced water. Public water systems regularly test for selected contaminants under the National Primary Drinking Water Regulations. Approximately 6% of the 1,173 chemicals in Table A-2 and Table A-4 are

routinely tested for under these regulations.[1] Private water wells are usually tested less often and for fewer potential contaminants than public water supplies (USGS, 2014c). Since chemical use varies widely across the country, testing for any particular chemical may or may not be appropriate for detecting potential impacts on a drinking water resource from a nearby hydraulic fracturing operation. Furthermore, the concentration, mobility, and detectability (as determined by the lowest concentration that an analytical method is able to determine a chemical's presence) of chemicals used in or produced by hydraulic fracturing operations will affect whether or not it would be identified in a drinking water resource in the event of its release into the environment.

Information (identity, frequency of use, physicochemical and toxicological properties, etc.) on the chemicals associated with the hydraulic fracturing water cycle is not complete and limits understanding of potential impacts on drinking water resources. Well operators identified one or more chemicals as confidential in approximately 70% of wells reported to FracFocus 1.0 and analyzed by the EPA (U.S. EPA, 2015a). Additionally, chemicals found in flowback and produced water (see Table A-4) were identified for a limited number of geographic locations and formations. These characterization studies are constrained by available methods for detecting organic and inorganic compounds in flowback and produced water. The identity of hydraulic fracturing-related chemicals is necessary to understand their chemical, physical, and toxicological properties, which determine how they might move through the environment to drinking water resources and any resulting effects. Knowing their identities would also help inform what chemicals to test for in the event of suspected drinking water impacts and, in the case of wastewater, may help predict whether current treatment systems are effective at removing them.

Peer reviewed toxicity data for known hydraulic fracturing-related chemicals is very limited. Of the 1,173 hydraulic fracturing-related chemicals identified in Appendix A, 147 have chronic oral reference values and/or oral slope factors from the sources that met the selection criteria for inclusion in this assessment. Because the majority of chemicals identified in this report do not have chronic oral reference values and/or oral slope factors, risk assessors at the local and regional level may need to use alternative sources of toxicity information that could introduce greater uncertainties. It also makes an assessment of potential cumulative effects of exposure to chemical mixtures in hydraulic fracturing fluid, flowback, or produced water difficult.

[1] We identified 73 chemicals that are reported to be used in hydraulic fracturing fluids (see Table A-2) or that have been detected in produced water (see Table A-4) that are tested for as part of the contaminant monitoring conducted for 40 different drinking water standards under the National Primary Drinking Water Regulations (NPDWR). For inorganic chemicals regulated under the NPDWR, we identified the chemical or element itself, its regulated ion (as applicable), or other more complex forms on the list of hydraulic fracturing-related chemicals. For regulated organic chemicals, we identified only the chemical itself on the list of hydraulic fracturing-related chemicals with three exceptions: (1) we identified all four trihalomethanes that comprise total trihalomethanes, (2) we identified two of the five regulated chlorinated/brominated haloacetic acids as their sodium salts, and (3) we identified a subset of polychlorinated biphenyls (PCBs) as Aroclor 1248. Although various forms of petroleum distillates are used in hydraulic fracturing fluids and may contain BTEX or benzo(a)pyrene (the regulated entities that can occur naturally in petroleum distillates), we did not include them in our count of 73 chemicals.

10.2.2. Other Contributing Limitations

We found other limitations that hamper our ability to assess the potential impacts of hydraulic fracturing on drinking water resources nationally. These include the number and location of hydraulically fractured wells, the location of drinking water resources, and information on industry practices and any changes that may take place in practices in the coming years. Our estimates of the number of fractured wells are based on an evaluation of several commercial and public sources and a number of assumptions. This lack of a definitive well count particularly contributes to uncertainties regarding total water use or total wastewater volume estimates, and would limit any kind of cumulative impact assessment.

There are also some fundamental gaps in our understanding of drinking water resources, including where they are located in relation to hydraulic fracturing operations and which might be most vulnerable to impacts from hydraulic fracturing activities. Improving our assessment of potential drinking water impacts requires better information, particularly about private drinking water well locations and the depths of drinking water resources in relation to the hydraulically fractured formations and well construction features (e.g., casing and cement). This information would allow us to better assess whether subsurface drinking water resources are isolated from hydraulically fractured oil and gas production wells.

Finally, this assessment summarizes available information on industry practices with respect to the hydraulic fracturing water cycle. While some information on hydraulic fracturing activities is available for many areas of the United States, specific data on water withdrawals for hydraulic fracturing, volumes of flowback and produced water generated, and the disposal or reuse of wastewaters is needed to better characterize potential impacts of hydraulic fracturing on drinking water resources. Additionally, industry practices are rapidly changing (e.g., the number of wells fractured, the location of activities, and the chemicals used), and it is unclear how changes in industry practices could affect potential drinking water impacts in the future. Consideration of future development scenarios was not a part of this assessment, but such an evaluation could help establish potential short- and long-term impacts to drinking water resources and how to assess them.

10.3.Conclusions

Through this national-level assessment, we have identified potential mechanisms by which hydraulic fracturing could affect drinking water resources. Above ground mechanisms can affect surface and ground water resources and include water withdrawals at times or in locations of low water availability, spills of hydraulic fracturing fluid and chemicals or produced water, and inadequate treatment and discharge of hydraulic fracturing wastewater. Below ground mechanisms include movement of liquids and gases via the production well into underground drinking water resources and movement of liquids and gases from the fracture zone to these resources via pathways in subsurface rock formations.

We did not find evidence that these mechanisms have led to widespread, systemic impacts on drinking water resources in the United States. Of the potential mechanisms identified in this report,

we found specific instances where one or more of these mechanisms led to impacts on drinking water resources, including contamination of drinking water wells. The cases occurred during both routine activities and accidents and have resulted in impacts to surface or ground water. Spills of hydraulic fracturing fluid and produced water in certain cases have reached drinking water resources, both surface and ground water. Discharge of treated hydraulic fracturing wastewater has increased contaminant concentrations in receiving surface waters. Below ground movement of fluids, including gas, most likely via the production well, have contaminated drinking water resources. In some cases, hydraulic fracturing fluids have also been directly injected into drinking water resources, as defined in this assessment, to produce oil or gas that co-exists in those formations.

The number of identified cases where drinking water resources were impacted are small relative to the number of hydraulically fractured wells. This could reflect a rarity of effects on drinking water resources, or may be an underestimate as a result of several factors. There is insufficient pre- and post-hydraulic fracturing data on the quality of drinking water resources. This inhibits a determination of the frequency of impacts. Other limiting factors include the presence of other causes of contamination, the short duration of existing studies, and inaccessible information related to hydraulic fracturing activities.

10.4. Use of the Assessment

The practice of hydraulic fracturing is simultaneously expanding and changing rapidly. Over 60% of new oil and gas wells are likely to be hydraulically fractured, and this percentage may be over 90% in some locations. Economic forces are likely to cause short term volatility in the number of wells drilled and fractured, yet hydraulic fracturing is expected to continue to expand and drive an increase in domestic oil and gas production in coming decades (EIA, 2014a).[1] As a result, hydraulic fracturing will likely increase in existing locations, while also potentially expanding to new areas.

This state-of-the-science assessment contributes to the understanding of the potential impacts of hydraulic fracturing on drinking water resources and the factors that may influence those impacts. The findings in this assessment can be used by federal, state, tribal, and local officials; industry; and the public to better understand and address any vulnerabilities of drinking water resources to hydraulic fracturing activities. This assessment can also be used to help facilitate and inform dialogue among interested stakeholders, and support future efforts, including: providing context to site-specific exposure or risk assessments, local and regional public health assessments, and to assessments of cumulative impacts of hydraulic fracturing on drinking water resources over time or over defined geographic areas of interest.

We hope the identification of limitations and uncertainties will promote greater attention to these areas through pre- and post- hydraulic fracturing monitoring programs and by researchers. We also

[1] In their reference case projections, the U.S. Energy Information Administration (EIA) forecasts that U.S. gas production by 2035 will have increased 50% over 2012 levels. Crude oil production is projected to increase almost 40% above current levels by 2025, before declining in subsequent decades (EIA, 2014a).

hope it will lead to greater dissemination of data in forms accessible by a wide-range of researchers and audiences.

Finally, and most importantly, this assessment advances the scientific basis for 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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Assessment of the Potential Impacts of Hydraulic Fracturing for Oil and Gas on Drinking Water Resources

(Appendices A – J)

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Appendix A

Chemicals Identified in Hydraulic Fracturing Fluids and/or Flowback and Produced Water

Appendix A. Chemicals Identified in Hydraulic Fracturing Fluids and/or Flowback and Produced Water

A.1. Supplemental Tables and Information

The EPA identified authoritative sources for information on hydraulic fracturing chemicals and, to the extent possible, verified the chemicals used in hydraulic fracturing fluids and detected in flowback and produced water of hydraulically fractured wells. The EPA used 10 sources to identify the chemicals used in hydraulic fracturing fluids or detected in flowback or produced water. Seven sources are government entities (Congressional, federal, or state) that obtained the data directly from industry. The remaining three represent collaborations between state, non-profit, academic, and industry groups. FracFocus is the result of a collaboration between the Ground Water Protection Council (a non-profit coalition of state ground water protection agencies) and the Interstate Oil and Gas Compact Commission (a multi-state government agency). The Marcellus Shale Coalition is a drilling industry trade group. Colborn et al. (2011) is a peer-reviewed journal article. Most of the listed chemicals were cited by multiple sources.

Seven of the ten sources obtained information about the chemicals used in hydraulic fracturing fluids from material safety data sheets (MSDSs) provided by chemical manufacturers for the products they sell, as required by the Occupational Safety and Health Administration (OSHA). The MSDSs must list all hazardous ingredients if they comprise at least 1% of the product; for carcinogens, the reporting threshold is 0.1%. However, chemical manufacturers may withhold information (e.g., chemical name, concentration of the substance in a mixture) about a hazardous substance from MSDSs if it is claimed as confidential business information (CBI), provided that certain conditions are met (OSHA, 2013).

Table A-1. Description of sources used to create lists of chemicals used in fracturing fluids or detected in flowback or produced water.

The number next to each citation in the reference column corresponds to numbers in the reference columns found in Table A-2, Table A-3, and Table A-4.

Description / Content	Reference
Chemicals and other components used by 14 hydraulic fracturing service companies from 2005 to 2009 as reported to the House Committee on Energy and Commerce. For each hydraulic fracturing product reported, companies also provided an MSDS with information about the product's chemical components.	House of Representatives (2011)[a] (1)

Description / Content	Reference
Chemicals used during natural gas operations with some potential health effects. The list of chemicals was compiled from MSDSs from several sources, including the Bureau of Land Management, U.S. Forest Service, state agencies, and industry.	Colborn et al. (2011)[a] (2)
Chemicals used or proposed for use in hydraulic fracturing in the Marcellus Shale in New York based on product composition disclosures and MSDSs submitted to the New York State Department of Environmental Conservation (NYSDEC). Also includes data provided separately to NYSDEC by well operators on analytical results of flowback water samples from Marcellus Shale operations in Pennsylvania and West Virginia.	NYSDEC (2011)[a,b] (3)
Chemicals reported to be used by nine hydraulic fracturing service companies from 2005 to 2010. Companies provided the chemical names in MSDSs, product bulletins, and formulation sheets.	U.S. EPA (2013a)[a] (4)
MSDSs provided to the EPA during on-site visits to hydraulically fractured oil and gas wells in Oklahoma and Colorado.	Sheets
Characteristics of undiluted chemicals found in hydraulic fracturing fluids associated with coalbed methane production, based on MSDSs, literature searches, reviews of relevant MSDSs provided by service companies, and discussions with field engineers, service company chemists, and state and federal employees.	U.S. EPA (2004)[a] (6)
Chemicals used in Pennsylvania for hydraulic fracturing activities based on MSDSs provided by industry.	PA DEP (2010)[a] (7)
Chemical records entered in FracFocus by oil and gas operators for individual wells from January 1, 2011, through February 28, 2013. FracFocus is a publicly accessible hydraulic fracturing chemical registry developed by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission. Chemicals claimed as confidential business information (CBI) do not have to be reported in FracFocus.	U.S. EPA (2015c)[a] (8)
Chemicals detected in flowback from 19 hydraulically fractured shale gas wells in Pennsylvania and West Virginia, based on analyses conducted by 17 Marcellus Shale Coalition member companies.	Hayes (2009)[b] (9)
Chemicals reportedly detected in flowback and produced water from 81 wells provided to the EPA by nine well operating companies.	U.S. EPA (2011b)[b] (10)

[a] Sources used to identify chemicals used in hydraulic fracturing fluids.

[b] Sources used to identify chemicals detected in flowback and produced water.

Once it had identified chemicals used in hydraulic fracturing fluids and chemicals detected in flowback/produced water, the EPA conducted an initial review of the chemicals for preliminary validation of provided chemical name and Chemical Abstracts Service Registry Number (CASRN) combinations. A CASRN is a unique numeric identifier assigned by the Chemical Abstracts Service (CAS) to a chemical substance when it enters the CAS Registry Database. The EPA Office of Research

and Development's National Center for Computational Toxicology (NCCT) provided the final formal validation and verification of the listed chemicals.

The EPA first compared the hydraulic fracturing chemical CASRNs and names with chemicals listed in NCCT's Distributed Structure-Searchable Toxicity Database network (DSSTox) database (U.S. EPA, 2013b). For the CASRNs and chemical names that did not appear in the DSSTox database, the EPA's Substance Registry Services database and the U.S. National Library of Medicine ChemID database were used to verify accurate chemical name and CASRN pairing (NLM, 2014; U.S. EPA, 2014c). The EPA also identified cases where CASRN/name combinations could not be verified by use of selected public sources and flagged those cases for resolution by NCCT.

NCCT then verified all of the CASRN and chemical names for the chemical lists generated by the EPA in accordance with NCCT DSSTox Chemical Information Quality Review Procedures (http://www.epa.gov/ncct/dsstox/ChemicalInfQAProcedures.html). The process included QA/QC on the identification and validation of CASRN/chemical name combinations and resolution of inconsistencies and problems including duplications, CASRN errors, and CASRN/chemical name mismatches.

The general methodology for resolving conflicts between CASRN/chemical name combinations and other chemical identification issues differed slightly depending on the data provided by each source. To resolve chemical/CASRN conflict in data provided by the nine service companies, the EPA worked with each company to verify the CASRN/chemical combinations proposed by NCCT. In cases of CASRN/chemical name mismatches in data provided by FracFocus, chemical names were considered primary to the CASRN (i.e., the name overrode the CASRN). When the chemical name was non-specific and the CASRN was valid, then the CASRN was considered primary to the chemical name, and the correct specific chemical name from DSSTox was assigned to the CASRN. For all other sources, the CASRN was considered primary unless it was invalid or missing. In such cases, the chemical name was primary. All Toxic Substance Control Act (TSCA) CBI chemical lists were managed in accordance with TSCA CBI procedures.

Chemicals with verified CASRNs that are used in hydraulic fracturing fluids are presented in Table A-2. Generic chemicals used in hydraulic fracturing fluids are presented in Table A-3. Chemicals with verified CASRNs that have been detected in flowback or produced water are presented in Table A-4. Chemicals found in both fracturing fluids (see Table A-2) and flowback and produced water (see Table A-4) are italicized in each table.

Table A-2. Chemicals reported to be used in hydraulic fracturing fluids.

An "X" indicates the availability of physicochemical properties from EPI Suite™ (see Appendix C) and selected toxicity reference values (see Appendix G). An empty cell indicates no information was available from the sources we consulted. Reference number corresponds to the citations in Table A-1. Italicized chemicals are found in both fracturing fluids and flowback/produced water.

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
(13Z)-N,N-bis(2-hydroxyethyl)-N-methyldocos-13-en-1-aminium chloride	120086-58-0	X		1
(2,3-dihydroxypropyl)trimethylammonium chloride	34004-36-9	X		8
(E)-Crotonaldehyde	123-73-9	X	X	1, 4
[Nitrilotris(methylene)]tris-phosphonic acid pentasodium salt	2235-43-0	X		1
1-(1-Naphthylmethyl)quinolinium chloride	65322-65-8	X		1
1-(Alkyl* amino)-3-aminopropane *(42%C12, 26%C18, 15%C14, 8%C16, 5%C10, 4%C8)	68155-37-3	X		8
1-(Phenylmethyl)pyridinium Et Me derivs., chlorides	68909-18-2	X		1, 2, 3, 4, 6, 8
1,2,3-Trimethylbenzene	526-73-8	X		1, 4
1,2,4-Trimethylbenzene	*95-63-6*	X		*1, 2, 3, 4, 5*
1,2-Benzisothiazolin-3-one	2634-33-5	X		1, 3, 4
1,2-Dibromo-2,4-dicyanobutane	35691-65-7	X		1, 4
1,2-Dimethylbenzene	95-47-6	X		4
1,2-Ethanediamine, polymer with 2-methyloxirane	25214-63-5			8
1,2-Ethanediaminium, N,N'-bis[2-[bis(2-hydroxyethyl)methylammonio]ethyl]-N,N'-bis(2-hydroxyethyl)-N,N'-dimethyl-, tetrachloride	138879-94-4	X		1, 4
1,2-Propylene glycol	*57-55-6*	X	X	*1, 2, 3, 4, 8*
1,2-Propylene oxide	75-56-9	X	X	1, 4
1,3,5-Triazine	290-87-9	X		8
1,3,5-Triazine-1,3,5(2H,4H,6H)-triethanol	4719-04-4	X		1, 4
1,3,5-Trimethylbenzene	*108-67-8*	X		*1, 4*
1,3-Butadiene	106-99-0	X	X	8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
1,3-Dichloropropene	542-75-6	X	X	8
1,4-Dioxane	123-91-1	X	X	2, 3, 4
1,4-Dioxane-2,5-dione, 3,6-dimethyl-, (3R,6R)-, polymer with (3S,6S)-3,6-dimethyl-1,4-dioxane-2,5-dione and (3R,6S)-rel-3,6-dimethyl-1,4-dioxane-2,5-dione	9051-89-2			1, 4, 8
1,6-Hexanediamine	124-09-4	X		1, 2
1,6-Hexanediamine dihydrochloride	6055-52-3	X		1
1-[2-(2-Methoxy-1-methylethoxy)-1-methylethoxy]-2-propanol	20324-33-8	X		4
1-Amino-2-propanol	78-96-6	X		8
1-Benzylquinolinium chloride	15619-48-4	X		1, 3, 4
1-Butanol	71-36-3	X	X	1, 2, 3, 4, 7
1-Butoxy-2-propanol	5131-66-8	X		8
1-Decanol	112-30-1	X		1, 4
1-Dodecyl-2-pyrrolidinone	2687-96-9	X		1, 4
1-Eicosene	3452-07-1	X		3
1-Ethyl-2-methylbenzene	611-14-3	X		4
1-Hexadecene	629-73-2	X		3
1-Hexanol	111-27-3	X		1, 4, 8
1-Hexanol, 2-ethyl-, manuf. of, by products from, distn. residues	68909-68-7			4
1H-Imidazole-1-ethanamine, 4,5-dihydro-, 2-nortall-oil alkyl derivs.	68442-97-7			2, 4
1-Methoxy-2-propanol	107-98-2	X		1, 2, 3, 4
1-Octadecanamine, acetate (1:1)	2190-04-7	X		8
1-Octadecanamine, N,N-dimethyl-	124-28-7	X		1, 3, 4
1-Octadecene	112-88-9	X		3
1-Octanol	111-87-5	X		1, 4
1-Pentanol	71-41-0	X		8
1-Propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-, N-coco acyl derivs., chlorides, sodium salts	61789-39-7			1

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
1-Propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-, N-coco acyl derivs., inner salts	61789-40-0			1, 2, 3, 4
1-Propanaminium, 3-chloro-2-hydroxy-N,N,N-trimethyl-, chloride	3327-22-8	X		8
1-Propanaminium, N-(3-aminopropyl)-2-hydroxy-N,N-dimethyl-3-sulfo-, N-coco acyl derivs., inner salts	68139-30-0			1, 3, 4
1-Propanaminium, N-(carboxymethyl)-N,N-dimethyl-3-[(1-oxooctyl)amino]-, inner salt	73772-46-0			8
1-Propanesulfonic acid	5284-66-2	X		3
1-Propanol	71-23-8	X		1, 2, 4, 5
1-Propanol, zirconium(4+) salt	23519-77-9			1, 4, 8
1-Propene	115-07-1	X		2
1-tert-Butoxy-2-propanol	57018-52-7	X		8
1-Tetradecene	1120-36-1	X		3
1-Tridecanol	112-70-9	X		1, 4
1-Undecanol	112-42-5	X		2
2-(2-Butoxyethoxy)ethanol	112-34-5	X	X	2, 4
2-(2-Ethoxyethoxy)ethanol	111-90-0	X	X	1, 4
2-(2-Ethoxyethoxy)ethyl acetate	112-15-2	X		1, 4
2-(Dibutylamino)ethanol	102-81-8	X		1, 4
2-(Hydroxymethylamino)ethanol	34375-28-5	X		1, 4
2-(Thiocyanomethylthio)benzothiazole	21564-17-0	X	X	2
2,2'-(diazene-1,2-diyldiethane-1,1-diyl)bis-4,5-dihydro-1H-imidazole dihydrochloride	27776-21-2	X		3
2,2'-(Octadecylimino)diethanol	10213-78-2	X		1
2,2'-[Ethane-1,2-diylbis(oxy)]diethanamine	929-59-9	X		1, 4
2,2'-Azobis(2-amidinopropane) dihydrochloride	2997-92-4	X		1, 4
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	X		1, 2, 3, 4, 6, 7, 8
2,2-Dibromopropanediamide	73003-80-2	X		3
2,4-Hexadienoic acid, potassium salt, (2E,4E)-	24634-61-5	X		3

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
2,6,8-Trimethyl-4-nonanol	123-17-1	X		8
2-Acrylamide - 2-propanesulfonic acid and N,N-dimethylacrylamide copolymer	NOCAS_51252			2
2-Acrylamido -2-methylpropanesulfonic acid copolymer	NOCAS_51255			8
2-Acrylamido-2-methyl-1-propanesulfonic acid	15214-89-8	X		1, 3
2-Amino-2-methylpropan-1-ol	124-68-5	X		8
2-Aminoethanol ester with boric acid (H3BO3) (1:1)	10377-81-8			8
2-Aminoethanol hydrochloride	2002-24-6	X		4, 8
2-Bromo-3-nitrilopropionamide	1113-55-9	X		1, 2, 3, 4, 5
2-Butanone oxime	96-29-7	X		1
2-Butenediamide, (2E)-, N,N'-bis[2-(4,5-dihydro-2-nortall-oil alkyl-1H-imidazol-1-yl)ethyl] derivs.	68442-77-3			3, 8
2-Butoxy-1-propanol	15821-83-7	X		8
2-Butoxyethanol	111-76-2	X	X	1, 2, 3, 4, 6, 7, 8
2-Dodecylbenzenesulfonic acid- n-(2-aminoethyl)ethane-1,2-diamine(1:1)	40139-72-8	X		8
2-Ethoxyethanol	110-80-5	X	X	6
2-Ethoxynaphthalene	93-18-5	X		3
2-Ethyl-1-hexanol	104-76-7	X		1, 2, 3, 4, 5
2-Ethyl-2-hexenal	645-62-5	X		2
2-Ethylhexyl benzoate	5444-75-7	X		4
2-Hydroxyethyl acrylate	818-61-1	X		1, 4
2-Hydroxyethylammonium hydrogen sulphite	13427-63-9	X		1
2-Hydroxy-N,N-bis(2-hydroxyethyl)-N-methylethanaminium chloride	7006-59-9	X		8
2-Mercaptoethanol	60-24-2	X		1, 4
2-Methoxyethanol	109-86-4	X	X	4
2-Methyl-1-propanol	78-83-1	X	X	1, 2, 4
2-Methyl-2,4-pentanediol	107-41-5	X		1, 2, 4

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
2-Methyl-3(2H)-isothiazolone	2682-20-4	X		1, 2, 4
2-Methyl-3-butyn-2-ol	115-19-5	X		3
2-Methylbutane	78-78-4	X		2
2-Methylquinoline hydrochloride	62763-89-7	X		3
2-Phosphono-1,2,4-butanetricarboxylic acid	37971-36-1	X		1, 4
2-Phosphonobutane-1,2,4-tricarboxylic acid, potassium salt (1:x)	93858-78-7	X		1
2-Propanol, aluminum salt	555-31-7			1
2-Propen-1-aminium, N,N-dimethyl-N-2-propenyl-, chloride, homopolymer	26062-79-3			3
2-Propenamide, homopolymer	25038-45-3			8
2-Propenoic acid, 2-(2-hydroxyethoxy)ethyl ester	13533-05-6	X		4
2-Propenoic acid, 2-ethylhexyl ester, polymer with 2-hydroxyethyl 2-propenoate	36089-45-9			8
2-Propenoic acid, 2-methyl-, polymer with 2-propenoic acid, sodium salt	28205-96-1			8
2-Propenoic acid, 2-methyl-, polymer with sodium 2-methyl-2-[(1-oxo-2-propen-1-yl)amino]-1-propanesulfonate (1:1)	136793-29-8			8
2-Propenoic acid, ethyl ester, polymer with ethenyl acetate and 2,5-furandione, hydrolyzed	113221-69-5			4, 8
2-Propenoic acid, ethyl ester, polymer with ethenyl acetate and 2,5-furandione, hydrolyzed, sodium salt	111560-38-4			8
2-Propenoic acid, polymer with 2-propenamide, sodium salt	25987-30-8			3, 4, 8
2-Propenoic acid, polymer with ethene, zinc salt	28208-80-2			8
2-Propenoic acid, polymer with ethenylbenzene	25085-34-1			8
2-Propenoic acid, polymer with sodium ethanesulfonate, peroxydisulfuric acid, disodium salt- initiated, reaction products with tetrasodium ethenylidenebis (phosphonata)	397256-50-7			8
2-Propenoic acid, polymer with sodium phosphinate (1:1), sodium salt	129898-01-7			8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
2-Propenoic acid, sodium salt (1:1), polymer with sodium 2-methyl-2-((1-oxo-2-propen-1-yl)amino)-1-propanesulfonate (1:1)	37350-42-8			1
2-Propenoic acid, telomer with sodium 4-ethenylbenzenesulfonate (1:1), sodium 2-methyl-2-[(1-oxo-2-propen-1-yl)amino]-1-propanesulfonate (1:1) and sodium sulfite (1:1), sodium salt	151006-66-5			4
2-Propenoic, polymer with sodium phosphinate	71050-62-9			3, 4
3-(Dimethylamino)propylamine	109-55-7	**X**		8
3,4,4-Trimethyloxazolidine	75673-43-7	**X**		8
3,5,7-Triazatricyclo(3.3.1.13,7)decane, 1-(3-chloro-2-propenyl)-, chloride, (Z)-	51229-78-8	**X**		3
3,7-Dimethyl-2,6-octadienal	5392-40-5	**X**		3
3-Hydroxybutanal	107-89-1	**X**		1, 2, 4
3-Methoxypropylamine	5332-73-0	**X**		8
3-Phenylprop-2-enal	104-55-2	**X**		1, 2, 3, 4, 7
4,4-Dimethyloxazolidine	51200-87-4	**X**		8
4,6-Dimethyl-2-heptanone	19549-80-5	**X**		8
4-[Abieta-8,11,13-trien-18-yl(3-oxo-3-phenylpropyl)amino]butan-2-one hydrochloride	143106-84-7	**X**		1, 4
4-Ethyloct-1-yn-3-ol	5877-42-9	**X**		1, 2, 3, 4
4-Hydroxy-3-methoxybenzaldehyde	121-33-5	**X**		3
4-Methoxybenzyl formate	122-91-8	**X**		3
4-Methoxyphenol	150-76-5	**X**		4
4-Methyl-2-pentanol	108-11-2	**X**		1, 4
4-Methyl-2-pentanone	108-10-1	**X**		5
4-Nonylphenol	104-40-5	**X**		8
4-Nonylphenol polyethoxylate	68412-54-4			2, 3, 4
5-Chloro-2-methyl-3(2H)-isothiazolone	26172-55-4	**X**		1, 2, 4
Acetaldehyde	75-07-0	**X**		1, 4
Acetic acid	*64-19-7*	**X**		*1, 2, 3, 4, 5, 6, 7, 8*

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Acetic acid ethenyl ester, polymer with ethenol	25213-24-5			1, 4
Acetic acid, C6-8-branched alkyl esters	90438-79-2	**X**		4
Acetic acid, hydroxy-, reaction products with triethanolamine	68442-62-6	**X**		3
Acetic acid, mercapto-, monoammonium salt	5421-46-5	**X**		2, 8
Acetic anhydride	108-24-7	**X**		1, 2, 3, 4, 7
Acetone	*67-64-1*	**X**	**X**	*1, 3, 4, 6*
Acetonitrile, 2,2',2''-nitrilotris-	7327-60-8	**X**		1, 4
Acetophenone	*98-86-2*	**X**	**X**	*1*
Acetyltriethyl citrate	77-89-4	**X**		1, 4
Acrolein	*107-02-8*	**X**	**X**	*2*
Acrylamide	79-06-1	**X**	**X**	1, 2, 3, 4
Acrylamide/ sodium acrylate copolymer	25085-02-3			1, 2, 3, 4, 8
Acrylamide-sodium-2-acrylamido-2-methlypropane sulfonate copolymer	38193-60-1			1, 2, 3, 4
Acrylic acid	79-10-7	**X**	**X**	2, 4
Acrylic acid, with sodium-2-acrylamido-2-methyl-1-propanesulfonate and sodium phosphinate	110224-99-2	**X**		8
Alcohols (C13-C15), ethoxylated	64425-86-1			8
Alcohols, C10-12, ethoxylated	67254-71-1	**X**		3
Alcohols, C10-14, ethoxylated	66455-15-0			3
Alcohols, C11-14-iso-, C13-rich	68526-86-3	**X**		3
Alcohols, C11-14-iso-, C13-rich, butoxylated ethoxylated	228414-35-5			1
Alcohols, C11-14-iso-, C13-rich, ethoxylated	78330-21-9	**X**		3, 4, 8
Alcohols, C12-13, ethoxylated	66455-14-9	**X**		4
Alcohols, C12-14, ethoxylated	68439-50-9			2, 3, 4, 8
Alcohols, C12-14, ethoxylated propoxylated	68439-51-0	**X**		1, 3, 4, 8
Alcohols, C12-14-secondary	126950-60-5	**X**		1, 3, 4
Alcohols, C12-14-secondary, ethoxylated	84133-50-6			3, 4, 8
Alcohols, C12-15, ethoxylated	68131-39-5			3, 4

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Alcohols, C12-16, ethoxylated	68551-12-2	**X**		3, 4, 8
Alcohols, C14-15, ethoxylated	68951-67-7	**X**		3, 4, 8
Alcohols, C6-12, ethoxylated	68439-45-2	**X**		3, 4, 8
Alcohols, C7-9-iso-, C8-rich, ethoxylated	78330-19-5	**X**		2, 4, 8
Alcohols, C8-10, ethoxylated propoxylated	68603-25-8			3
Alcohols, C9-11, ethoxylated	68439-46-3	**X**		3, 4
Alcohols, C9-11-iso-, C10-rich, ethoxylated	78330-20-8	**X**		1, 2, 4, 8
Alkanes C10-16-branched and linear	90622-52-9			4
Alkanes, C10-14	93924-07-3			1
Alkanes, C12-14-iso-	68551-19-9	**X**		2, 4, 8
Alkanes, C13-16-iso-	68551-20-2	**X**		1, 4
Alkenes, C>10 .alpha.-	64743-02-8	**X**		1, 3, 4, 8
Alkenes, C>8	68411-00-7			1
Alkenes, C24-25 alpha-, polymers with maleic anhydride, docosyl esters	68607-07-8			8
Alkyl quaternary ammonium with bentonite	71011-24-0			4
Alkyl* dimethyl ethylbenzyl ammonium chloride *(50%C12, 30%C14, 17%C16, 3%C18)	85409-23-0_1	**X**		8
Alkyl* dimethyl ethylbenzyl ammonium chloride *(60%C14, 30%C16, 5%C12, 5%C18)	68956-79-6	**X**		8
Alkylbenzenesulfonate, linear	42615-29-2	**X**		1, 4, 6
Almandite and pyrope garnet	1302-62-1			1, 4
alpha-[3.5-dimethyl-1-(2-methylpropyl)hexyl]-omega-hydroxy-poly(oxy-1,2-ethandiyl)	60828-78-6			3
alpha-Amylase	9000-90-2			4
alpha-Lactose monohydrate	5989-81-1	**X**		8
alpha-Terpineol	98-55-5	**X**		3
Alumina	1344-28-1			1, 2, 4
Aluminatesilicate	1327-36-2			8
Aluminum	*7429-90-5*		**X**	*1, 4, 6*
Aluminum calcium oxide (Al2CaO4)	12042-68-1			2

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Aluminum chloride	7446-70-0			1, 4
Aluminum chloride hydroxide sulfate	39290-78-3			8
Aluminum chloride, basic	1327-41-9			3, 4
Aluminum oxide (Al2O3)	90669-62-8			8
Aluminum oxide silicate	12068-56-3			1, 2, 4
Aluminum silicate	12141-46-7			1, 2, 4
Aluminum sulfate	10043-01-3			1, 4
Amaranth	915-67-3	**X**		4
Amides, C8-18 and C18-unsatd., N,N-bis(hydroxyethyl)	68155-07-7			3
Amides, coco, N-[3-(dimethylamino)propyl]	68140-01-2			1, 4
Amides, coco, N-[3-(dimethylamino)propyl], alkylation products with chloroacetic acid, sodium salts	70851-07-9			1, 4
Amides, coco, N-[3-(dimethylamino)propyl], alkylation products with sodium 3-chloro-2-hydroxypropanesulfonate	70851-08-0			8
Amides, coco, N-[3-(dimethylamino)propyl], N-oxides	68155-09-9			1, 3, 4
Amides, from C16-22 fatty acids and diethylenetriamine	68876-82-4			3
Amides, tall-oil fatty, N,N-bis(hydroxyethyl)	68155-20-4			3, 4
Amides, tallow, N-[3-(dimethylamino)propyl],N-oxides	68647-77-8			1, 4
Amine oxides, cocoalkyldimethyl	61788-90-7			8
Amines, C14-18; C16-18-unsaturated, alkyl, ethoxylated	68155-39-5			1
Amines, C8-18 and C18-unsatd. alkyl	68037-94-5			5
Amines, coco alkyl	61788-46-3			4
Amines, coco alkyl, acetates	61790-57-6			1, 4
Amines, coco alkyl, ethoxylated	61791-14-8			8
Amines, coco alkyldimethyl	61788-93-0			8
Amines, dicoco alkyl	61789-76-2			8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Amines, dicoco alkylmethyl	61788-62-3			8
Amines, ditallow alkyl, acetates	71011-03-5			8
Amines, hydrogenated tallow alkyl, acetates	61790-59-8			4
Amines, N-tallow alkyltrimethylenedi-, ethoxylated	61790-85-0			8
Amines, polyethylenepoly-, ethoxylated, phosphonomethylated	68966-36-9			1, 4
Amines, polyethylenepoly-, reaction products with benzyl chloride	68603-67-8			1
Amines, tallow alkyl	61790-33-8			8
Amines, tallow alkyl, ethoxylated, acetates (salts)	68551-33-7			1, 3, 4
Amines, tallow alkyl, ethoxylated, phosphates	68308-48-5			4
Aminotrimethylene phosphonic acid	6419-19-8	**X**		1, 4, 8
Ammonia	*7664-41-7*			*1, 2, 3, 4, 7*
Ammonium (lauryloxypolyethoxy)ethyl sulfate	32612-48-9			4
Ammonium acetate	631-61-8	**X**		1, 3, 4, 5, 8
Ammonium acrylate	10604-69-0	**X**		8
Ammonium acrylate-acrylamide polymer	26100-47-0			2, 4, 8
Ammonium bisulfate	7803-63-6			2
Ammonium bisulfite	10192-30-0			1, 2, 3, 4, 7
Ammonium chloride	12125-02-9			1, 2, 3, 4, 5, 6, 8
Ammonium citrate (1:1)	7632-50-0	**X**		3
Ammonium citrate (2:1)	3012-65-5	**X**		8
Ammonium dodecyl sulfate	2235-54-3	**X**		1
Ammonium fluoride	12125-01-8			1, 4
Ammonium hydrogen carbonate	1066-33-7	**X**		1, 4
Ammonium hydrogen difluoride	1341-49-7			1, 3, 4, 7
Ammonium hydrogen phosphonate	13446-12-3			4
Ammonium hydroxide	1336-21-6			1, 3, 4
Ammonium lactate	515-98-0	**X**		8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Ammonium ligninsulfonate	8061-53-8			2
Ammonium nitrate	6484-52-2			1, 2, 3
Ammonium phosphate	7722-76-1		**X**	1, 4
Ammonium sulfate	7783-20-2			1, 2, 3, 4, 6
Ammonium thiosulfate	7783-18-8			8
Amorphous silica	99439-28-8			1, 7
Anethole	104-46-1	**X**		3
Aniline	62-53-3	**X**	**X**	2, 4
Antimony pentoxide	1314-60-9			1, 4
Antimony trichloride	10025-91-9		**X**	1, 4
Antimony trioxide	1309-64-4		**X**	8
Arsenic	*7440-38-2*		**X**	*4*
Ashes, residues	68131-74-8			4
Asphalt, sulfonated, sodium salt	68201-32-1			2
Attapulgite	12174-11-7			2, 3
Aziridine, polymer with 2-methyloxirane	31974-35-3			4, 8
Barium sulfate	7727-43-7			1, 2, 4
Bauxite	1318-16-7			1, 2, 4
Benactyzine hydrochloride	57-37-4	**X**		8
Bentonite	1302-78-9			1, 2, 4, 6
Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex	121888-68-4			3, 4
Benzamorf	12068-08-5	**X**		1, 4
Benzene	*71-43-2*	**X**	**X**	*1, 3, 4*
Benzene, 1,1'-oxybis-, sec-hexyl derivs., sulfonated, sodium salts	147732-60-3			8
Benzene, 1,1'-oxybis-, tetrapropylene derivs., sulfonated	119345-03-8			8
Benzene, 1,1'-oxybis-, tetrapropylene derivs., sulfonated, sodium salts	119345-04-9			3, 4, 8
Benzene, C10-16-alkyl derivs.	68648-87-3	**X**		1

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Benzene, ethenyl-, polymer with 2-methyl-1,3-butadiene, hydrogenated	68648-89-5			8
Benzenemethanaminium, N,N-dimethyl-N-(2-((1-oxo-2-propen-1-yl)oxy)ethyl)-, chloride (1:1), polymer with 2-propenamide	74153-51-8			3
Benzenesulfonic acid	98-11-3	**X**		2
Benzenesulfonic acid, (1-methylethyl)-,	37953-05-2	**X**		4
Benzenesulfonic acid, (1-methylethyl)-, ammonium salt	37475-88-0	**X**		3, 4
Benzenesulfonic acid, (1-methylethyl)-, sodium salt	28348-53-0	**X**		8
Benzenesulfonic acid, C10-16-alkyl derivs.	68584-22-5		**X**	1, 4
Benzenesulfonic acid, C10-16-alkyl derivs., compds. with cyclohexylamine	255043-08-4	**X**		1
Benzenesulfonic acid, C10-16-alkyl derivs., compds. with triethanolamine	68584-25-8	**X**		8
Benzenesulfonic acid, C10-16-alkyl derivs., potassium salts	68584-27-0	**X**		1, 4, 8
Benzenesulfonic acid, dodecyl-, branched, compds. with 2-propanamine	90218-35-2	**X**		4
Benzenesulfonic acid, mono-C10-16 alkyl derivs., compds. with 2-propanamine	68648-81-7			1, 4
Benzenesulfonic acid, mono-C10-16-alkyl derivs., sodium salts	68081-81-2	**X**		8
Benzoic acid	65-85-0	**X**	**X**	1, 4, 7
Benzyl chloride	100-44-7	**X**	**X**	1, 2, 4, 8
Benzyldimethyldodecylammonium chloride	139-07-1	**X**		2, 8
Benzylhexadecyldimethylammonium chloride	122-18-9	**X**		8
Benzyltrimethylammonium chloride	56-93-9	**X**		8
Bicine	150-25-4	**X**		1, 4
Bio-Perge	55965-84-9			8
Bis(1-methylethyl)naphthalenesulfonic acid, cyclohexylamine salt	68425-61-6	**X**		1
Bis(2-chloroethyl) ether	*111-44-4*	**X**	**X**	*8*

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Bisphenol A	80-05-7	X	X	4
Bisphenol A/ Epichlorohydrin resin	25068-38-6			1, 2, 4
Bisphenol A/ Novolac epoxy resin	28906-96-9			1, 4
Blast furnace slag	65996-69-2			2, 3
Borax	1303-96-4			1, 2, 3, 4, 6
Boric acid	10043-35-3			1, 2, 3, 4, 6, 7
Boric acid (H3BO3), compd. with 2-aminoethanol (1:x)	26038-87-9			8
Boric oxide	1303-86-2			1, 2, 3, 4
Boron potassium oxide (B4K2O7)	1332-77-0			8
Boron potassium oxide (B4K2O7), tetrahydrate	12045-78-2			8
Boron potassium oxide (B5KO8)	11128-29-3			1
Boron sodium oxide	1330-43-4			1, 2, 4
Boron sodium oxide pentahydrate	12179-04-3			8
Bronopol	52-51-7	X		1, 2, 3, 4, 6
Butane	106-97-8	X		2, 5
Butanedioic acid, sulfo-, 1,4-bis(1,3-dimethylbutyl) ester, sodium salt	2373-38-8	X		1
Butene	25167-67-3	X		8
Butyl glycidyl ether	2426-08-6	X		1, 4
Butyl lactate	138-22-7	X		1, 4
Butyryl trihexyl citrate	82469-79-2	X		8
C.I. Acid Red 1	3734-67-6	X		4
C.I. Acid violet 12, disodium salt	6625-46-3	X		4
C.I. Pigment Red 5	6410-41-9	X		4
C.I. Solvent Red 26	4477-79-6	X		4
C10-16-Alkyldimethylamines oxides	70592-80-2	X		4
C10-C16 ethoxylated alcohol	68002-97-1	X		1, 2, 3, 4, 8
C11-15-Secondary alcohols ethoxylated	68131-40-8			1, 2, 8
C12-14 tert-alkyl ethoxylated amines	73138-27-9	X		3
C8-10 Alcohols	85566-12-7			8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Calcined bauxite	66402-68-4			2, 8
Calcium aluminate	12042-78-3			2
Calcium bromide	7789-41-5			4
Calcium carbide (CaC2)	75-20-7			8
Calcium chloride	10043-52-4			1, 2, 3, 4, 7
Calcium dichloride dihydrate	10035-04-8			1, 4
Calcium dodecylbenzene sulfonate	26264-06-2	X		4
Calcium fluoride	7789-75-5			1, 4
Calcium hydroxide	1305-62-0			1, 2, 3, 4
Calcium hypochlorite	7778-54-3			1, 2, 4
Calcium magnesium hydroxide oxide	58398-71-3			4
Calcium oxide	1305-78-8			1, 2, 4, 7
Calcium peroxide	1305-79-9			1, 3, 4, 8
Calcium sulfate	7778-18-9			1, 2, 4
Calcium sulfate dihydrate	10101-41-4			2
Camphor	76-22-2	X		3
Canola oil	120962-03-0			8
Carbon black	1333-86-4			1, 2, 4
Carbon dioxide	*124-38-9*	X		*1, 3, 4, 6*
Carbonic acid calcium salt (1:1)	471-34-1			1, 2, 4
Carbonic acid, dipotassium salt	584-08-7	X		1, 2, 3, 4, 8
Carboxymethyl guar gum, sodium salt	39346-76-4			1, 2, 4
Castor oil	8001-79-4			8
Cedarwood oil	8000-27-9			3
Cellophane	9005-81-6			1, 4
Cellulose	9004-34-6			1, 2, 3, 4
Chloride	*16887-00-6*			*4, 8*
Chlorine	*7782-50-5*		X	*2*
Chlorine dioxide	10049-04-4		X	1, 2, 3, 4, 8
Choline bicarbonate	78-73-9	X		3, 8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Choline chloride	67-48-1	X		1, 3, 4, 7, 8
Chromium (III)	*16065-83-1*		X	*2, 6*
Chromium (VI)	*18540-29-9*		X	*6*
Chromium acetate, basic	39430-51-8			2
Chromium(III) acetate	1066-30-4			1, 2
Citric acid	77-92-9	X		1, 2, 3, 4, 7
Citronella oil	8000-29-1			3
Citronellol	106-22-9	X		3
Citrus extract	94266-47-4			1, 3, 4, 8
Coal, granular	50815-10-6			1, 2, 4
Cobalt(II) acetate	71-48-7			1, 4
Coco-betaine	68424-94-2			3
Coconut oil	8001-31-8			8
Coconut oil acid/Diethanolamine condensate (2:1)	68603-42-9			1
Coconut trimethylammonium chloride	61789-18-2	X		1, 8
Copper	*7440-50-8*		X	*1, 4*
Copper sulfate	7758-98-7			1, 4, 8
Copper(I) chloride	7758-89-6			1, 4
Copper(I) iodide	7681-65-4		X	1, 2, 4, 6
Copper(II) chloride	7447-39-4			1, 3, 4
Copper(II) sulfate, pentahydrate	7758-99-8			8
Corn flour	68525-86-0			4
Corn sugar gum	11138-66-2			1, 2, 4
Corundum (Aluminum oxide)	1302-74-5			4, 8
Cottonseed, flour	68308-87-2			2, 4
Coumarin	91-64-5	X		3
Cremophor(R) EL	61791-12-6			1, 3
Cristobalite	14464-46-1			1, 2, 4
Crystalline silica, tridymite	15468-32-3			1, 2, 4

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Cumene	*98-82-8*	**X**	**X**	*1, 2, 3, 4*
Cupric chloride dihydrate	10125-13-0			1, 4, 7
Cyclohexane	110-82-7	**X**		1, 7
Cyclohexanol	108-93-0	**X**		8
Cyclohexanone	108-94-1	**X**	**X**	1, 4
Cyclohexylamine sulfate	19834-02-7	**X**		8
D&C Red 28	18472-87-2	**X**		4
D&C Red No. 33	3567-66-6	**X**		8
Daidzein	486-66-8	**X**		8
Dapsone	80-08-0	**X**		1, 4
Dazomet	533-74-4	**X**		1, 2, 3, 4, 7, 8
Decamethylcyclopentasiloxane	541-02-6			8
Decyldimethylamine	1120-24-7	**X**		3, 4
Deuterium oxide	7789-20-0			8
D-Glucitol	50-70-4	**X**		1, 3, 4
D-Gluconic acid	526-95-4	**X**		1, 4
D-Glucopyranoside, methyl	3149-68-6	**X**		2
D-Glucose	50-99-7	**X**		1, 4
Di(2-ethylhexyl) phthalate	*117-81-7*	**X**	**X**	*1, 4*
Diammonium peroxydisulfate	7727-54-0			1, 2, 3, 4, 6, 7, 8
Diatomaceous earth	68855-54-9			2, 4
Diatomaceous earth, calcined	91053-39-3			1, 2, 4
Dibromoacetonitrile	3252-43-5	**X**		1, 2, 3, 4, 8
Dicalcium silicate	10034-77-2			1, 2, 4
Dichloromethane	*75-09-2*	**X**	**X**	*8*
Didecyldimethylammonium chloride	7173-51-5	**X**	**X**	1, 2, 4, 8
Diethanolamine	111-42-2	**X**		1, 2, 3, 4, 6
Diethylbenzene	25340-17-4	**X**		1, 3, 4
Diethylene glycol	111-46-6	**X**		1, 2, 3, 4, 7

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Diethylene glycol monomethyl ether	111-77-3	X		1, 2, 4
Diethylenetriamine	111-40-0	X		1, 2, 4, 5
Diethylenetriamine reaction product with fatty acid dimers	68647-57-4			2
Diisobutyl ketone	108-83-8	X		8
Diisopropanolamine	110-97-4	X		8
Diisopropylnaphthalene	38640-62-9	X		3, 4
Dimethyl adipate	627-93-0	X		8
Dimethyl glutarate	1119-40-0	X		1, 4
Dimethyl polysiloxane	63148-62-9			1, 2, 4
Dimethyl succinate	106-65-0	X		8
Dimethylaminoethanol	108-01-0	X		2, 4
Dimethyldiallylammonium chloride	7398-69-8	X		3, 4
Diphenyl oxide	101-84-8	X		3
Dipotassium monohydrogen phosphate	7758-11-4			5
Dipropylene glycol	25265-71-8	X		1, 3, 4
Di-sec-butylphenol	31291-60-8	X		1
Disodium dodecyl(sulphonatophenoxy) benzenesulphonate	28519-02-0	X		1
Disodium ethylenediaminediacetate	38011-25-5	X		1, 4
Disodium ethylenediaminetetraacetate dihydrate	6381-92-6	X		1
Disodium octaborate	12008-41-2			4, 8
Disodium octaborate tetrahydrate	12280-03-4			1, 4
Disodium sulfide	1313-82-2			8
Distillates, petroleum, catalytic reformer fractionator residue, low-boiling	68477-31-6			1, 4
Distillates, petroleum, heavy arom.	67891-79-6			1, 4
Distillates, petroleum, hydrodesulfurized light catalytic cracked	68333-25-5			1
Distillates, petroleum, hydrodesulfurized middle	64742-80-9			1

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Distillates, petroleum, hydrotreated heavy naphthenic	64742-52-5			1, 2, 3, 4
Distillates, petroleum, hydrotreated heavy paraffinic	64742-54-7			1, 2, 4
Distillates, petroleum, hydrotreated light	64742-47-8			1, 2, 3, 4, 5, 7, 8
Distillates, petroleum, hydrotreated light naphthenic	64742-53-6			1, 2, 8
Distillates, petroleum, hydrotreated light paraffinic	64742-55-8			8
Distillates, petroleum, hydrotreated middle	64742-46-7			1, 2, 3, 4, 8
Distillates, petroleum, light catalytic cracked	64741-59-9			1, 4
Distillates, petroleum, light hydrocracked	64741-77-1			3
Distillates, petroleum, solvent-dewaxed heavy paraffinic	64742-65-0			1
Distillates, petroleum, solvent-refined heavy naphthenic	64741-96-4			1, 4
Distillates, petroleum, steam-cracked	64742-91-2			1, 4
Distillates, petroleum, straight-run middle	64741-44-2			1, 2, 4
Distillates, petroleum, sweetened middle	64741-86-2			1, 4
Ditallow alkyl ethoxylated amines	71011-04-6			3
D-Lactic acid	10326-41-7	X		1, 4
D-Limonene	5989-27-5	X	X	1, 3, 4, 5, 7, 8
Docusate sodium	577-11-7	X		1
Dodecamethylcyclohexasiloxane	540-97-6			8
Dodecane	112-40-3	X		8
Dodecylbenzene	123-01-3	X		3, 4
Dodecylbenzenesulfonic acid	27176-87-0	X	X	2, 3, 4, 8
Dodecylbenzenesulfonic acid, monoethanolamine salt	26836-07-7	X		1, 4
Edifas B	9004-32-4			2, 3, 4
EDTA, copper salt	12276-01-6			1, 5, 6
Endo-1,4-.beta.-mannanase	37288-54-3			3, 8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Epichlorohydrin	106-89-8	X	X	1, 4, 8
Epoxy resin	25085-99-8			1, 4, 8
Erucic amidopropyl dimethyl betaine	149879-98-1			1, 3
Ethanaminium, N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]-, chloride	44992-01-0	X		3
Ethanaminium, N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]-,chloride, polymer with 2-propenamide	69418-26-4			1, 3, 4
Ethanaminium, N,N,N-trimethyl-2-[(2-methyl-1-oxo-2-propen-1-yl)oxy]-, chloride (1:1), polymer with 2-propenamide	35429-19-7			8
Ethanaminium, N,N,N-trimethyl-2-[(2-methyl-1-oxo-2-propenyl)oxy]-, methyl sulfate, homopolymer	27103-90-8			8
Ethane	74-84-0	X		2, 5
Ethanol	64-17-5	X		1, 2, 3, 4, 5, 6, 8
Ethanol, 2,2',2''-nitrilotris-, tris(dihydrogen phosphate) (ester), sodium salt	68171-29-9	X		4
Ethanol, 2,2'-iminobis-, N-coco alkyl derivs., N-oxides	61791-47-7			1
Ethanol, 2,2'-iminobis-, N-tallow alkyl derivs.	61791-44-4			1
Ethanol, 2,2'-oxybis-, reaction products with ammonia, morpholine derivs. residues	68909-77-3			4, 8
Ethanol, 2,2-oxybis-, reaction products with ammonia, morpholine derivs. residues, acetates (salts)	68877-16-7			4
Ethanol, 2,2-oxybis-, reaction products with ammonia, morpholine derivs. residues, reaction products with sulfur dioxide	102424-23-7			4
Ethanol, 2-[2-[2-(tridecyloxy)ethoxy]ethoxy]-, hydrogen sulfate, sodium salt	25446-78-0	X		1, 4
Ethanol, 2-amino-, polymer with formaldehyde	34411-42-2			4
Ethanol, 2-amino-, reaction products with ammonia, by-products from, phosphonomethylated	68649-44-5			4

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Ethanolamine	141-43-5	**X**		1, 2, 3, 4, 6
Ethoxylated dodecyl alcohol	9002-92-0	**X**		4
Ethoxylated hydrogenated tallow alkylamines	61790-82-7			4
Ethoxylated, propoxylated trimethylolpropane	52624-57-4			3
Ethyl acetate	141-78-6	**X**	**X**	1, 4, 7
Ethyl acetoacetate	141-97-9	**X**		1, 4
Ethyl benzoate	93-89-0	**X**		3
Ethyl lactate	97-64-3	**X**		3
Ethyl salicylate	118-61-6	**X**		3
Ethylbenzene	*100-41-4*	**X**	**X**	*1, 2, 3, 4, 7*
Ethylcellulose	9004-57-3			2
Ethylene	74-85-1	**X**		8
Ethylene glycol	*107-21-1*	**X**	**X**	*1, 2, 3, 4, 6, 7, 8*
Ethylene oxide	75-21-8	**X**	**X**	1, 2, 3, 4
Ethylenediamine	107-15-3	**X**	**X**	2, 4
Ethylenediaminetetraacetic acid	60-00-4	**X**		1, 2, 4
Ethylenediaminetetraacetic acid tetrasodium salt	64-02-8	**X**		1, 2, 3, 4
Ethylenediaminetetraacetic acid, diammonium copper salt	67989-88-2			4
Ethylenediaminetetraacetic acid, disodium salt	139-33-3	**X**		1, 3, 4, 8
Ethyne	74-86-2	**X**		7
Fats and Glyceridic oils, vegetable, hydrogenated	68334-28-1			8
Fatty acid, tall oil, hexa esters with sorbitol, ethoxylated	61790-90-7			1, 4
Fatty acids, C 8-18 and C18-unsaturated compounds with diethanolamine	68604-35-3			3
Fatty acids, C14-18 and C16-18-unsatd., distn. residues	70321-73-2			2
Fatty acids, C18-unsatd., dimers	61788-89-4	**X**		2

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Fatty acids, C18-unsatd., dimers, compds. with ethoxylated tall-oil fatty acid-polyethylenepolyamine reaction products	68132-59-2			8
Fatty acids, C18-unsatd., dimers, ethoxylated propoxylated	68308-89-4			8
Fatty acids, coco, ethoxylated	61791-29-5			3
Fatty acids, coco, reaction products with diethylenetriamine and soya fatty acids, ethoxylated, chloromethane-quaternized	68604-75-1			8
Fatty acids, coco, reaction products with ethanolamine, ethoxylated	61791-08-0			3
Fatty acids, tall oil, reaction products with acetophenone, formaldehyde and thiourea	68188-40-9			3
Fatty acids, tall-oil	61790-12-3			1, 2, 3, 4
Fatty acids, tall-oil, reaction products with diethylenetriamine	61790-69-0			1, 4
Fatty acids, tall-oil, reaction products with diethylenetriamine, maleic anhydride, tetraethylenepentamine and triethylenetetramine	68990-47-6			8
Fatty acids, tallow, sodium salts	8052-48-0			1, 3
Fatty acids, vegetable-oil, reaction products with diethylenetriamine	68153-72-0			3
Fatty quaternary ammonium chloride	61789-68-2			1, 4
FD&C Blue no. 1	3844-45-9	**X**		1, 4
FD&C Yellow 5	1934-21-0	**X**		8
FD&C Yellow 6	2783-94-0	**X**		8
Ferric chloride	7705-08-0			1, 3, 4
Ferric sulfate	10028-22-5			1, 4
Ferrous sulfate monohydrate	17375-41-6			2
Ferumoxytol	1309-38-2			8
Fiberglass	65997-17-3			2, 3, 4
Formaldehyde	50-00-0	**X**	**X**	1, 2, 3, 4

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Formaldehyde polymer with 4,1,1-(dimethylethyl)phenol and methyloxirane	29316-47-0			3
Formaldehyde polymer with methyl oxirane, 4-nonylphenol and oxirane	63428-92-2			4, 8
Formaldehyde, polymer with 4-(1,1-dimethylethyl)phenol, 2-methyloxirane and oxirane	30704-64-4			1, 2, 4, 8
Formaldehyde, polymer with 4-(1,1-dimethylethyl)phenol, 2-methyloxirane, 4-nonylphenol and oxirane	68188-99-8			8
Formaldehyde, polymer with 4-nonylphenol and oxirane	30846-35-6			1, 4
Formaldehyde, polymer with 4-nonylphenol and phenol	40404-63-5			8
Formaldehyde, polymer with ammonia and phenol	35297-54-2			1, 4
Formaldehyde, polymer with bisphenol A	25085-75-0			4
Formaldehyde, polymer with N1-(2-aminoethyl)-1,2-ethanediamine, benzylated	70750-07-1			8
Formaldehyde, polymer with nonylphenol and oxirane	55845-06-2			4
Formaldehyde, polymers with branched 4-nonylphenol, oxirane and 2-methyloxirane	153795-76-7			1 3
Formaldehyde/ amine	50-00-0_3			1, 2, 3, 4
Formamide	75-12-7	**X**		1, 2, 3, 4
Formic acid	*64-18-6*	**X**	**X**	*1, 2, 3, 4, 6, 7*
Formic acid, potassium salt	590-29-4	**X**		1, 3, 4
Frits, chemicals	65997-18-4			8
Fuel oil, no. 2	68476-30-2			1, 2
Fuels, diesel	68334-30-5			2
Fuels, diesel, no. 2	68476-34-6			2, 4, 8
Fuller's earth	8031-18-3			2
Fumaric acid	110-17-8	**X**		1, 2, 3, 4, 6
Fumes, silica	69012-64-2			8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Furfural	98-01-1	X	X	1, 4
Furfuryl alcohol	98-00-0	X		1, 4
Galantamine hydrobromide	69353-21-5	X		8
Gas oils, petroleum, straight-run	64741-43-1			1, 4
Gelatin	9000-70-8			1, 4
Gilsonite	12002-43-6			1, 2, 4
Gluconic acid	133-42-6	X		7
Glutaraldehyde	111-30-8	X		1, 2, 3, 4, 7
Glycerides, C14-18 and C16-18-unsatd. mono- and di-	67701-32-0			8
Glycerol	56-81-5	X		1, 2, 3, 4, 5
Glycine, N-(carboxymethyl)-N-(2-hydroxyethyl)-, disodium salt	135-37-5	X		1
Glycine, N-(hydroxymethyl)-, monosodium salt	70161-44-3	X		8
Glycine, N,N-bis(carboxymethyl)-, trisodium salt	5064-31-3	X		1, 2, 3, 4
Glycine, N-[2-[bis(carboxymethyl)amino]ethyl]-N-(2-hydroxyethyl)-, trisodium salt	139-89-9	X		1
Glycolic acid	79-14-1	X		1, 3, 4
Glycolic acid sodium salt	2836-32-0	X		1, 3, 4
Glyoxal	107-22-2	X	X	1, 2, 4
Glyoxylic acid	298-12-4	X		1
Goethite (Fe(OH)O)	1310-14-1			8
Guar gum	9000-30-0			1, 2, 3, 4, 7, 8
Guar gum, carboxymethyl 2-hydroxypropyl ether, sodium salt	68130-15-4			1, 2, 3, 4, 7
Gypsum ($Ca(SO_4).2H_2O$)	13397-24-5			2, 4
Hematite	1317-60-8			1, 2, 4
Hemicellulase	9012-54-8			1, 2, 3, 4, 5
Hemicellulase enzyme concentrate	9025-56-3			3, 4
Heptane	142-82-5	X		1, 2
Heptene, hydroformylation products, high-boiling	68526-88-5			1, 4

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Hexadecyltrimethylammonium bromide	57-09-0	**X**		1
Hexane	110-54-3	**X**	**X**	5
Hexanedioic acid	124-04-9	**X**	**X**	1, 2, 4, 6
Humic acids, commercial grade	1415-93-6			2
Hydrazine	302-01-2		**X**	8
Hydrocarbons, terpene processing by-products	68956-56-9			1, 3, 4
Hydrochloric acid	7647-01-0			1, 2, 3, 4, 5, 6, 7, 8
Hydrogen fluoride	7664-39-3			1, 2, 4
Hydrogen peroxide	7722-84-1			1, 3, 4
Hydrogen sulfide	7783-06-4			1, 2
Hydroxyethylcellulose	9004-62-0			1, 2, 3, 4
Hydroxylamine hydrochloride	5470-11-1			1, 3, 4
Hydroxylamine sulfate (2:1)	10039-54-0			4
Hydroxypropyl cellulose	9004-64-2			2, 4
Hydroxypropyl guar gum	39421-75-5			1, 3, 4, 5, 6, 8
Hydroxyvalerenic acid	1619-16-5	**X**		8
Hypochlorous acid	7790-92-3			8
Illite	12173-60-3			8
Ilmenite ($FeTiO_3$), conc.	98072-94-7			8
Indole	120-72-9	**X**		2
Inulin, carboxymethyl ether, sodium salt	430439-54-6			1, 4
Iridium oxide	12030-49-8			8
Iron	*7439-89-6*		**X**	*2, 4*
Iron oxide	1332-37-2			1, 4
Iron oxide (Fe_3O_4)	1317-61-9			4
Iron(II) sulfate	7720-78-7			2
Iron(II) sulfate heptahydrate	7782-63-0			1, 2, 3, 4
Iron(III) oxide	1309-37-1			1, 2, 4
Isoascorbic acid	89-65-6	**X**		1, 3, 4

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Isobutane	75-28-5	X		2
Isobutene	115-11-7	X		8
Isooctanol	26952-21-6	X		1, 4, 5
Isopentyl alcohol	123-51-3	X		1, 4
Isopropanol	*67-63-0*	X		*1, 2, 3, 4, 6, 7*
Isopropanolamine dodecylbenzene	42504-46-1	X		1, 3, 4
Isopropylamine	75-31-0	X		1, 4
Isoquinoline	119-65-3	X		8
Isoquinoline, reaction products with benzyl chloride and quinoline	68909-80-8	X		3
Isoquinolinium, 2-(phenylmethyl)-, chloride	35674-56-7	X		3
Isotridecanol, ethoxylated	9043-30-5			1, 3, 4, 8
Kaolin	1332-58-7			1, 2, 4
Kerosine, petroleum, hydrodesulfurized	64742-81-0			1, 2, 4
Kieselguhr	61790-53-2			1, 2, 4
Kyanite	1302-76-7			1, 2, 4
Lactic acid	50-21-5	X		1, 4, 8
Lactose	63-42-3	X		3
Latex 2000 TM	9003-55-8			2, 4
Lauryl hydroxysultaine	13197-76-7	X		1
Lavandula hybrida abrial herb oil	8022-15-9			3
L-Dilactide	4511-42-6	X		1, 4
Lead	*7439-92-1*		X	*1, 4*
Lecithin	8002-43-5			4
L-Glutamic acid	56-86-0	X		8
Lignite	129521-66-0			2
Lignosulfuric acid	8062-15-5			2
Ligroine	8032-32-4			8
Limestone	1317-65-3			1, 2, 3, 4
Linseed oil	8001-26-1			8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
L-Lactic acid	79-33-4	**X**		1, 4, 8
Magnesium carbonate (1:1)	7757-69-9			8
Magnesium carbonate (1:x)	546-93-0			1, 3, 4
Magnesium chloride	7786-30-3			1, 2, 4
Magnesium chloride hexahydrate	7791-18-6			4
Magnesium hydroxide	1309-42-8			1, 4
Magnesium iron silicate	19086-72-7			1, 4
Magnesium nitrate	10377-60-3			1, 2, 4
Magnesium oxide	1309-48-4			1, 2, 3, 4
Magnesium peroxide	14452-57-4			1, 4
Magnesium phosphide	12057-74-8			1
Magnesium silicate	1343-88-0			1, 4
Magnesium sulfate	7487-88-9			8
Maleic acid homopolymer	26099-09-2			8
Methanamine-N-methyl polymer with chloromethyl oxirane	25988-97-0			4
Methane	74-82-8	**X**		2, 5
Methanol	*67-56-1*	**X**	**X**	*1, 2, 3, 4, 5, 6, 7, 8*
Methenamine	100-97-0	**X**		1, 2, 4
Methoxyacetic acid	625-45-6	**X**		8
Methyl cellulose	9004-67-5			8
Methyl salicylate	119-36-8	**X**		1, 2, 3, 4, 7
Methyl vinyl ketone	78-94-4	**X**		1, 4
Methylcyclohexane	108-87-2	**X**		1
Methylene bis(thiocyanate)	6317-18-6	**X**		2
Methylenebis(5-methyloxazolidine)	66204-44-2	**X**		2
Methyloxirane polymer with oxirane, mono (nonylphenol) ether, branched	68891-11-2			3
Mica	12001-26-2			1, 2, 4, 6
Mineral oil - includes paraffin oil	8012-95-1		**X**	4, 8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Mineral spirits	64475-85-0			2
Mono- and di- potassium salts of phosphorous acid	13492-26-7			8
Montmorillonite	1318-93-0			2
Morpholine	110-91-8	**X**		1, 2, 4
Morpholinium, 4-ethyl-4-hexadecyl-, ethyl sulfate	78-21-7	**X**		8
MT 6	76-31-3			8
Mullite	1302-93-8			1,2, 4, 8
N-(2-Acryloyloxyethyl)-N-benzyl-N,N-dimethylammonium chloride	46830-22-2	**X**		3
N-(3-Chloroallyl)hexaminium chloride	4080-31-3	**X**		8
N,N,N-Trimethyl-2[1-oxo-2-propenyl]oxy ethanaminimum chloride, homopolymer	54076-97-0			3
N,N,N-Trimethyl-3-((1-oxooctadecyl)amino)-1-propanaminium methyl sulfate	19277-88-4	**X**		1
N,N,N-Trimethyloctadecan-1-aminium chloride	112-03-8	**X**		1, 3, 4
N,N'-Dibutylthiourea	109-46-6	**X**		1, 4
N,N-Dimethyldecylamine oxide	2605-79-0	**X**		1, 3, 4
N,N-Dimethylformamide	68-12-2	**X**	**X**	1, 2, 4, 5, 8
N,N-Dimethylmethanamine hydrochloride	593-81-7	**X**		1, 4, 5, 7
N,N-Dimethyl-methanamine-N-oxide	1184-78-7	**X**		3
N,N-dimethyloctadecylamine hydrochloride	1613-17-8	**X**		1, 4
N,N'-Methylenebisacrylamide	110-26-9	**X**		1, 4
Naphtha, petroleum, heavy catalytic reformed	64741-68-0			1, 2, 3, 4
Naphtha, petroleum, hydrotreated heavy	64742-48-9			1, 2, 3, 4, 8
Naphthalene	*91-20-3*	**X**	**X**	*1, 2, 3, 4, 5, 7*
Naphthalenesulfonic acid, bis(1-methylethyl)-	28757-00-8	**X**		1, 3, 4
Naphthalenesulfonic acid, polymer with formaldehyde, sodium salt	9084-06-4			2
Naphthalenesulphonic acid, bis (1-methylethyl)-methyl derivatives	99811-86-6	**X**		1

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Naphthenic acid ethoxylate	68410-62-8	X		4
Navy fuels JP-5	8008-20-6_2			1, 2, 3, 4, 8
Nickel sulfate	7786-81-4			2
Nickel(II) sulfate hexahydrate	10101-97-0			1, 4
Nitriles, tallow, hydrogenated	61790-29-2			4
Nitrilotriacetamide	4862-18-4	X		1, 4, 7
Nitrilotriacetic acid	139-13-9	X	X	1, 4
Nitrilotriacetic acid trisodium monohydrate	18662-53-8	X	X	1, 4
Nitrogen	7727-37-9			1, 2, 3, 4, 6
N-Methyl-2-pyrrolidone	872-50-4	X	X	1, 4
N-Methyldiethanolamine	105-59-9	X		2, 4, 8
N-Methylethanolamine	109-83-1	X		4
N-Methyl-N-hydroxyethyl-N-hydroxyethoxyethylamine	68213-98-9	X		4
N-Oleyl diethanolamide	13127-82-7	X		1, 4
Nonyl nonoxynol-10	9014-93-1			4
Nonylphenol (mixed)	25154-52-3			1, 4
Octamethylcyclotetrasiloxane	556-67-2			8
Octoxynol-9	9036-19-5			1, 2, 3, 4, 8
Oil of eucalyptus	8000-48-4			3
Oil of lemongrass	8007-02-1			3
Oil of rosemary	8000-25-7			3
Oleic acid	112-80-1	X		2, 4
Olivine-group minerals	1317-71-1			4
Orange terpenes	8028-48-6			4
Oxirane, 2-methyl-, polymer with oxirane, ether with (chloromethyl) oxirane polymer with 4,4`-(1-methylidene) bis[phenol]	68036-95-3			8
Oxirane, 2-methyl-, polymer with oxirane, mono(2-ethylhexyl) ether	64366-70-7			8
Oxirane, 2-methyl-, polymer with oxirane, monodecyl ether	37251-67-5			8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Oxirane, methyl-, polymer with oxirane, mono-C10-16-alkyl ethers, phosphates	68649-29-6			1, 4
Oxygen	7782-44-7			4
Ozone	10028-15-6			8
Paraffin waxes and Hydrocarbon waxes	8002-74-2			1
Paraformaldehyde	30525-89-4			2
PEG-10 Hydrogenated tallow amine	61791-26-2			1, 3
Pentaethylenehexamine	4067-16-7	**X**		4
Pentane	109-66-0	**X**		2, 5
Pentyl acetate	628-63-7	**X**		3
Pentyl butyrate	540-18-1	**X**		3
Peracetic acid	79-21-0	**X**		8
Perboric acid, sodium salt, monohydrate	10332-33-9			1, 8
Perlite	93763-70-3			4
Petrolatum, petroleum, oxidized	64743-01-7			3
Petroleum	8002-05-9			1, 2
Petroleum distillate hydrotreated light	6742-47-8			8
Phenanthrene	*85-01-8*	**X**		*6*
Phenol	*108-95-2*	**X**	**X**	*1, 2, 4*
Phenol, 4,4'-(1-methylethylidene)bis-, polymer with 2-(chloromethyl)oxirane, 2-methyloxirane and oxirane	68123-18-2			8
Phenol-formaldehyde resin	9003-35-4			1, 2, 4, 7
Phosphine	7803-51-2		**X**	1, 4
Phosphonic acid	13598-36-2			1, 4
Phosphonic acid (dimethylamino(methylene))	29712-30-9	**X**		1
Phosphonic acid, (((2-[(2-hydroxyethyl)(phosphonomethyl)amino)ethyl)imino]bis(methylene))bis-, compd. with 2-aminoethanol	129828-36-0	**X**		1
Phosphonic acid, (1-hydroxyethylidene)bis-, potassium salt	67953-76-8	**X**		4

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Phosphonic acid, (1-hydroxyethylidene)bis-, tetrasodium salt	3794-83-0	X		1, 4
Phosphonic acid, [[(phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-	15827-60-8	X		1, 2, 4
Phosphonic acid, [[(phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-, ammonium salt (1:x)	70714-66-8	X		3
Phosphonic acid, [[(phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-, sodium salt	22042-96-2	X		3
Phosphonic acid, [[(phosphonomethyl)imino]bis[6,1-hexanediylnitrilobis(methylene)]]tetrakis-	34690-00-1	X		1, 4, 8
Phosphoric acid	7664-38-2		X	1, 2, 4
Phosphoric acid, aluminium sodium salt	7785-88-8		X	1, 2
Phosphoric acid, ammonium salt (1:3)	10361-65-6			8
Phosphoric acid, diammonium salt	7783-28-0		X	2
Phosphoric acid, mixed decyl and Et and octyl esters	68412-60-2			1
Phosphorous acid	10294-56-1			1
Phthalic anhydride	85-44-9	X	X	1, 4
Pine oils	8002-09-3			1, 2, 4
Pluronic F-127	9003-11-6			1, 3, 4, 8
Policapram (Nylon 6)	25038-54-4			1, 4
Poly (acrylamide-co-acrylic acid), partial sodium salt	62649-23-4			3, 4
Poly(acrylamide-co-acrylic acid)	9003-06-9			4, 8
Poly(lactide)	26680-10-4			1
Poly(oxy-1,2-ethanediyl), .alpha.-(nonylphenyl)-.omega.-hydroxy-, phosphate	51811-79-1			1, 4
Poly(oxy-1,2-ethanediyl), .alpha.-(octylphenyl)-.omega.-hydroxy-, branched	68987-90-6	X		1, 4

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Poly(oxy-1,2-ethanediyl), .alpha.,.alpha.'-[[(9Z)-9-octadecenylimino]di-2,1-ethanediyl]bis[.omega.-hydroxy-	26635-93-8			1, 4
Poly(oxy-1,2-ethanediyl), .alpha.-[(9Z)-1-oxo-9-octadecenyl]-.omega.-hydroxy-	9004-96-0			8
Poly(oxy-1,2-ethanediyl), .alpha.-hydro-.omega.-hydroxy-, mono-C10-14-alkyl ethers, phosphates	68585-36-4			8
Poly(oxy-1,2-ethanediyl), .alpha.-hydro-.omega.-hydroxy-, mono-C8-10-alkyl ethers, phosphates	68130-47-2			8
Poly(oxy-1,2-ethanediyl), .alpha.-isodecyl-.omega.-hydroxy-	61827-42-7			8
Poly(oxy-1,2-ethanediyl), .alpha.-sulfo-.omega.-hydroxy-, C10-16-alkyl ethers, sodium salts	68585-34-2			8
Poly(oxy-1,2-ethanediyl), .alpha.-sulfo-.omega.-hydroxy-, C12-14-alkyl ethers, sodium salts	68891-38-3			1, 4
Poly(oxy-1,2-ethanediyl), alpha-(2,3,4,5-tetramethylnonyl)-omega-hydroxy	68015-67-8			1
Poly(oxy-1,2-ethanediyl), alpha-(nonylphenyl)-omega-hydroxy-,branched, phosphates	68412-53-3			1
Poly(oxy-1,2-ethanediyl), alpha-hexyl-omega-hydroxy	31726-34-8			3, 8
Poly(oxy-1,2-ethanediyl), alpha-hydro-omega-hydroxy-, (9Z)-9-octadecenoate	56449-46-8			3
Poly(oxy-1,2-ethanediyl), alpha-hydro-omega-hydroxy-, ether with alpha-fluoro-omega-(2-hydroxyethyl)poly(difluoromethylene) (1:1)	65545-80-4			1
Poly(oxy-1,2-ethanediyl), alpha-hydro-omega-hydroxy-, ether with D-glucitol (2:1), tetra-(9Z)-9-octadecenoate	61723-83-9			8
Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-(decyloxy)-, ammonium salt (1:1)	52286-19-8			4
Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-(hexyloxy)-, ammonium salt (1:1)	63428-86-4			1, 3, 4
Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-(hexyloxy)-, C6-10-alkyl ethers, ammonium salts	68037-05-8			3, 4

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega--(nonylphenoxy)-	9081-17-8			4
Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-(octyloxy)-, ammonium salt (1:1)	52286-18-7			4
Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-hydroxy-, C10-12-alkyl ethers, ammonium salts	68890-88-0			8
Poly(oxy-1,2-ethanediyl), alpha-tridecyl-omega-hydroxy-	24938-91-8			1, 3, 4
Poly(oxy-1,2-ethanediyl), alpha-undecyl-omega-hydroxy-, branched and linear	127036-24-2			1
Poly-(oxy-1,2-ethanediyl)-alpha-undecyl-omega-hydroxy	34398-01-1			1, 3, 4, 8
Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy branched	127087-87-0			1, 2, 3, 4
Poly(sodium-p-styrenesulfonate)	25704-18-1			1,4
Poly(tetrafluoroethylene)	9002-84-0			8
Poly[imino(1,6-dioxo-1,6-hexanediyl)imino-1,6-hexanediyl]	32131-17-2			2
Polyacrylamide	9003-05-8			1, 2, 4, 6
Polyacrylate/ polyacrylamide blend	NOCAS_51256			2
Polyacrylic acid, sodium bisulfite terminated	66019-18-9			3
Polyethylene glycol	25322-68-3			1, 2, 3, 4, 7, 8
Polyethylene glycol (9Z)-9-octadecenyl ether	9004-98-2			8
Polyethylene glycol ester with tall oil fatty acid	68187-85-9			1
Polyethylene glycol monobutyl ether	9004-77-7			1, 4
Polyethylene glycol mono-C8-10-alkyl ether sulfate ammonium	68891-29-2			1, 3, 4
Polyethylene glycol nonylphenyl ether	9016-45-9			1, 2, 3, 4, 8
Polyethylene glycol tridecyl ether phosphate	9046-01-9			1, 3, 4
Polyethyleneimine	9002-98-6			4
Polyglycerol	25618-55-7			2
Poly-L-aspartic acid sodium salt	34345-47-6			8
Polyoxyethylene sorbitan trioleate	9005-70-3			3

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Polyoxyethylene(10)nonylphenyl ether	26027-38-3			1, 2, 3, 4, 8
Polyoxyl 15 hydroxystearate	70142-34-6			8
Polyoxypropylenediamine	9046-10-0			1
Polyphosphoric acids, esters with triethanolamine, sodium salts	68131-72-6			1
Polyphosphoric acids, sodium salts	68915-31-1		**X**	1, 4
Polypropylene glycol	25322-69-4			1, 2, 4
Polypropylene glycol glycerol triether, epichlorohydrin, bisphenol A polymer	68683-13-6			1
Polyquaternium 5	26006-22-4			1, 4
Polysorbate 20	9005-64-5			8
Polysorbate 60	9005-67-8			3, 4
Polysorbate 80	9005-65-6			3, 4
Polyvinyl acetate copolymer	9003-20-7			2
Polyvinyl acetate, partially hydrolyzed	304443-60-5			8
Polyvinyl alcohol	9002-89-5			1, 2, 4
Polyvinyl alcohol/polyvinyl acetate copolymer	NOCAS_50147			2
Polyvinylidene chloride	9002-85-1			8
Polyvinylpyrrolidone	9003-39-8			8
Portland cement	65997-15-1			2, 4
Potassium acetate	127-08-2	**X**		1, 3, 4
Potassium aluminum silicate	1327-44-2			5
Potassium antimonate	29638-69-5			1, 4
Potassium bisulfate	7646-93-7			8
Potassium borate	12712-38-8			3
Potassium borate (1:x)	20786-60-1			1, 3
Potassium carbonate sesquihydrate	6381-79-9			5
Potassium chloride	7447-40-7			1, 2, 3, 4, 5, 6, 7
Potassium dichromate	7778-50-9			4
Potassium hydroxide	1310-58-3			1, 2, 3, 4, 6

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Potassium iodide	7681-11-0		X	1, 4
Potassium metaborate	13709-94-9			1, 2, 3, 4, 8
Potassium oleate	143-18-0	X		4
Potassium oxide	12136-45-7			1, 4
Potassium persulfate	7727-21-1			1, 2, 4
Potassium phosphate, tribasic	7778-53-2		X	8
Potassium sulfate	7778-80-5			2
Propane	74-98-6	X		2, 5
Propanol, 1(or 2)-(2-methoxymethylethoxy)-	34590-94-8	X		1, 2, 3, 4
Propargyl alcohol	107-19-7	X	X	1, 2, 3, 4, 5, 6, 7, 8
Propylene carbonate	108-32-7	X		1, 4
Propylene pentamer	15220-87-8	X		1
p-Xylene	106-42-3	X		1, 4
Pyridine, alkyl derivs.	68391-11-7			1, 4
Pyridinium, 1-(phenylmethyl)-, alkyl derivs., chlorides	100765-57-9			4, 8
Pyridinium, 1-(phenylmethyl)-, C7-8-alkyl derivs., chlorides	70914-44-2			6
Pyrimidine	289-95-2	X		2
Pyrrole	109-97-7	X		2
Quartz-alpha (SiO2)	14808-60-7			1, 2, 3, 4, 5, 6, 8
Quaternary ammonium compounds (2-ethylhexyl) hydrogenated tallow alkyl)dimethyl, methyl sulfates	308074-31-9			8
Quaternary ammonium compounds, (oxydi-2,1-ethanediyl)bis[coco alkyldimethyl, dichlorides	68607-28-3			2, 3, 4, 8
Quaternary ammonium compounds, benzyl(hydrogenated tallow alkyl)dimethyl, bis(hydrogenated tallow alkyl)dimethylammonium salt with bentonite	71011-25-1			8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Quaternary ammonium compounds, benzylbis(hydrogenated tallow alkyl)methyl, salts with bentonite	68153-30-0			2, 5, 6
Quaternary ammonium compounds, benzyl-C10-16-alkyldimethyl, chlorides	68989-00-4			1, 4
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides	68424-85-1		**X**	1, 2, 4, 8
Quaternary ammonium compounds, benzyl-C12-18-alkyldimethyl, chlorides	68391-01-5			8
Quaternary ammonium compounds, bis(hydrogenated tallow alkyl)dimethyl, salts with bentonite	68953-58-2			2, 3, 4, 8
Quaternary ammonium compounds, bis(hydrogenated tallow alkyl)dimethyl, salts with hectorite	71011-27-3			2
Quaternary ammonium compounds, di-C8-10-alkyldimethyl, chlorides	68424-95-3	**X**		2
Quaternary ammonium compounds, dicoco alkyldimethyl, chlorides	61789-77-3			1
Quaternary ammonium compounds, pentamethyltallow alkyltrimethylenedi-, dichlorides	68607-29-4			4
Quaternary ammonium compounds, trimethyltallow alkyl, chlorides	8030-78-2			1, 4
Quinaldine	91-63-4	**X**		8
Quinoline	91-22-5	**X**	**X**	2, 4
Raffinates (petroleum)	68514-29-4			5
Raffinates, petroleum, sorption process	64741-85-1			1, 2, 4, 8
Residual oils, petroleum, solvent-refined	64742-01-4			5
Residues, petroleum, catalytic reformer fractionator	64741-67-9			1, 4, 8
Rhodamine B	81-88-9	**X**		4
Rosin	8050-09-7			1, 4
Rutile titanium dioxide	1317-80-2			8
Sand	308075-07-2			8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Scandium oxide	12060-08-1			8
Sepiolite	63800-37-3			2
Silane, dichlorodimethyl-, reaction products with silica	68611-44-9			2, 4
Silica	*7631-86-9*			*1, 2, 3, 4, 8*
silica gel, cryst. -free	112926-00-8			3, 4
Silica, amorphous, fumed, cryst.-free	112945-52-5			1, 3, 4
Silica, vitreous	60676-86-0			1, 4, 8
Silicic acid, aluminum potassium sodium salt	12736-96-8			4
Siloxanes (Polysiloxane)	9011-19-2			4
Siloxanes and Silicones, di-Me, 3-hydroxypropyl Me, ethoxylated propoxylated	68937-55-3			8
Siloxanes and Silicones, di-Me, Me hydrogen	68037-59-2			8
Siloxanes and silicones, di-Me, polymers with Me silsesquioxanes	68037-74-1			4
Siloxanes and Silicones, di-Me, reaction products with silica	67762-90-7			4
Siloxanes and silicones, dimethyl,	63148-52-7			4
Silwet L77	27306-78-1			1
Sodium 1-octanesulfonate	5324-84-5	**X**		3
Sodium 2-mercaptobenzothiolate	2492-26-4	**X**		2
Sodium acetate	127-09-3	**X**		1, 3, 4
Sodium aluminate	1302-42-7			2, 4
Sodium benzoate	532-32-1	**X**		3
Sodium bicarbonate	144-55-8	**X**		1, 2, 3, 4, 7
Sodium bis(tridecyl) sulfobutanedioate	2673-22-5	**X**		4
Sodium bisulfite	7631-90-5			1, 3, 4
Sodium borate	1333-73-9			1, 4, 6, 7
Sodium bromate	7789-38-0			1, 2, 4
Sodium bromide	7647-15-6			1, 2, 3, 4, 7
Sodium bromosulfamate	1004542-84-0			8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Sodium C14-16 alpha-olefin sulfonate	68439-57-6	X		1, 3, 4
Sodium caprylamphopropionate	68610-44-6	X		4
Sodium carbonate	497-19-8	X		1, 2, 3, 4, 8
Sodium chlorate	7775-09-9		X	1, 4
Sodium chloride	7647-14-5			1, 2, 3, 4, 5, 8
Sodium chlorite	7758-19-2		X	1, 2, 3, 4, 5, 8
Sodium chloroacetate	3926-62-3	X		3
Sodium cocaminopropionate	68608-68-4			1
Sodium decyl sulfate	142-87-0	X		1
Sodium D-gluconate	527-07-1	X		4
Sodium diacetate	126-96-5	X		1, 4
Sodium dichloroisocyanurate	2893-78-9	X		2
Sodium dl-lactate	72-17-3	X		8
Sodium dodecyl sulfate	151-21-3	X		8
Sodium erythorbate (1:1)	6381-77-7	X		1, 3, 4, 8
Sodium ethasulfate	126-92-1	X		1
Sodium formate	141-53-7	X		2, 8
Sodium hydrogen sulfate	7681-38-1			4
Sodium hydroxide	1310-73-2			1, 2, 3, 4, 7, 8
Sodium hydroxymethanesulfonate	870-72-4	X		8
Sodium hypochlorite	7681-52-9			1, 2, 3, 4, 8
Sodium iodide	7681-82-5		X	4
Sodium ligninsulfonate	8061-51-6			2
Sodium l-lactate	867-56-1	X		8
Sodium maleate (1:x)	18016-19-8	X		8
Sodium metabisulfite	7681-57-4			1
Sodium metaborate	7775-19-1			3, 4
Sodium metaborate dihydrate	16800-11-6			1, 4
Sodium metaborate tetrahydrate	10555-76-7			1, 4, 8
Sodium metasilicate	6834-92-0			1, 2, 4

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Sodium molybdate(VI)	7631-95-0			8
Sodium nitrate	7631-99-4			2
Sodium nitrite	7632-00-0			1, 2, 4
Sodium N-methyl-N-oleoyltaurate	137-20-2	X		4
Sodium octyl sulfate	142-31-4	X		1
Sodium oxide	1313-59-3			1
Sodium perborate	11138-47-9			4
Sodium perborate tetrahydrate	10486-00-7			1, 4, 5, 8
Sodium peroxoborate	7632-04-4			1
Sodium persulfate	7775-27-1			1, 2, 3, 4, 7, 8
Sodium phosphate	7632-05-5			1, 4
Sodium polyacrylate	9003-04-7			1, 2, 3, 4
Sodium pyrophosphate	7758-16-9		X	1, 2, 4
Sodium salicylate	54-21-7	X		1, 4
Sodium sesquicarbonate	533-96-0	X		1, 2
Sodium silicate	1344-09-8			1, 2, 4
Sodium starch glycolate	9063-38-1			2
Sodium sulfate	7757-82-6			1, 2, 3, 4
Sodium sulfite	7757-83-7			2, 4, 8
Sodium thiocyanate	540-72-7	X		1, 4
Sodium thiosulfate	7772-98-7			1, 2, 3, 4
Sodium thiosulfate, pentahydrate	10102-17-7			1, 4
Sodium trichloroacetate	650-51-1	X		1, 4
Sodium trimetaphosphate	7785-84-4		X	8
Sodium xylenesulfonate	1300-72-7	X		1, 3, 4
Sodium zirconium lactate	15529-67-6			8
Sodium zirconium lactic acid (4:4:1)	10377-98-7			1, 4
Solvent naphtha, petroleum, heavy aliph.	64742-96-7			2, 4, 8
Solvent naphtha, petroleum, heavy arom.	64742-94-5			1, 2, 4, 5, 8
Solvent naphtha, petroleum, light aliph.	64742-89-8			8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Solvent naphtha, petroleum, light arom.	64742-95-6			1, 2, 4
Sorbic acid	110-44-1	**X**		8
Sorbitan sesquioleate	8007-43-0	**X**		4
Sorbitan, mono-(9Z)-9-octadecenoate	1338-43-8	**X**		1, 2, 3, 4
Sorbitan, monooctadecanoate	1338-41-6	**X**		8
Sorbitan, tri-(9Z)-9-octadecenoate	26266-58-0	**X**		8
Spirit of ammonia, aromatic	8013-59-0			8
Stannous chloride dihydrate	10025-69-1			1, 4
Starch	9005-25-8			1, 2, 4
Steam cracked distillate, cyclodiene dimer, dicyclopentadiene polymer	68131-87-3			1
Stoddard solvent	8052-41-3			1, 3, 4
Stoddard solvent IIC	64742-88-7			1, 2, 4
Strontium chloride	10476-85-4		**X**	4
Styrene	100-42-5	**X**	**X**	2
Subtilisin	9014-01-1			8
Sucrose	57-50-1	**X**		1, 2, 3, 4
Sulfamic acid	5329-14-6			1, 4
Sulfan blue	129-17-9	**X**		8
Sulfate	*14808-79-8*			*1, 4*
Sulfo NHS Biotin	119616-38-5			8
Sulfomethylated quebracho	68201-64-9			2
Sulfonic acids, C10-16-alkane, sodium salts	68608-21-9			6
Sulfonic acids, petroleum	61789-85-3			1
Sulfonic acids, petroleum, sodium salts	68608-26-4			3
Sulfur dioxide	7446-09-5			2, 4, 8
Sulfuric acid	7664-93-9			1, 2, 4, 7
Sulfuric acid, mono-C12-18-alkyl esters, sodium salts	68955-19-1	**X**		4
Sulfuric acid, mono-C6-10-alkyl esters, ammonium salts	68187-17-7	**X**		1, 4, 8

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Symclosene	87-90-1	X		2
Talc	14807-96-6			1, 3, 4, 6, 7
Tall oil	8002-26-4			4, 8
Tall oil imidazoline	61791-36-4			4
Tall oil, compound with diethanolamine	68092-28-4			1
Tall oil, ethoxylated	65071-95-6			4, 8
Tall-oil pitch	8016-81-7			4
Tallow alkyl amines acetate	61790-60-1			8
Tar bases, quinoline derivatives, benzyl chloride-quaternized	72480-70-7			1, 3, 4
Tegin M	8043-29-6			8
Terpenes and Terpenoids, sweet orange-oil	68647-72-3			1, 3, 4, 8
Terpineol	8000-41-7			1, 3
tert-Butyl hydroperoxide	75-91-2	X		1, 4
tert-Butyl perbenzoate	614-45-9	X		1
Tetra-calcium-alumino-ferrite	12068-35-8			1, 2, 4
Tetradecane	629-59-4	X		8
Tetradecyldimethylbenzylammonium chloride	139-08-2	X		1, 4, 8
Tetraethylene glycol	112-60-7	X		1, 4
Tetraethylenepentamine	112-57-2	X		1, 4
Tetrakis(hydroxymethyl)phosphonium sulfate	55566-30-8	X		1, 2, 3, 4, 7
Tetramethyl orthosilicate	681-84-5			1
Tetramethylammonium chloride	75-57-0	X		1, 2, 3, 4, 7, 8
Tetrasodium pyrophosphate	7722-88-5		X	8
Thiamine hydrochloride	67-03-8	X		8
Thiocyanic acid, ammonium salt	1762-95-4	X		2, 3, 4
Thioglycolic acid	68-11-1	X		1, 2, 3, 4
Thiourea	62-56-6	X	X	1, 2, 3, 4, 6
Thiourea, polymer with formaldehyde and 1-phenylethanone	68527-49-1			1, 4, 8
Thuja plicata donn ex. D. don leaf oil	68917-35-1			3

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Tin(II) chloride	7772-99-8			1
Titanium dioxide	13463-67-7			1, 2, 4
Titanium(4+) 2-[bis(2-hydroxyethyl)amino]ethanolate propan-2-olate (1:2:2)	36673-16-2			1
Titanium, isopropoxy (triethanolaminate)	74665-17-1			1, 4
Toluene	*108-88-3*	**X**	**X**	*1, 3, 4*
Tributyl phosphate	126-73-8	**X**	**X**	1, 2, 4
Tributyltetradecylphosphonium chloride	81741-28-8	**X**		1, 3, 4
Tricalcium phosphate	7758-87-4		**X**	1, 4
Tricalcium silicate	12168-85-3			1, 2, 4
Tridecane	629-50-5	**X**		8
Triethanolamine	102-71-6	**X**		1, 2, 4
Triethanolamine hydrochloride	637-39-8	**X**		8
Triethanolamine hydroxyacetate	68299-02-5	**X**		3
Triethanolamine polyphosphate ester	68131-71-5			1, 4, 8
Triethyl citrate	77-93-0	**X**		1, 4
Triethyl phosphate	78-40-0	**X**		1, 4
Triethylene glycol	112-27-6	**X**		1, 2, 3
Triethylenetetramine	112-24-3	**X**		4
Triisopropanolamine	122-20-3	**X**		1, 4
Trimethanolamine	14002-32-5	**X**		3
Trimethyl borate	121-43-7			8
Trimethylamine	75-50-3	**X**		8
Trimethylamine quaternized polyepichlorohydrin	51838-31-4			1, 2, 3, 4, 5, 8
Trimethylbenzene	25551-13-7			1, 2, 4
Triphosphoric acid, pentasodium salt	7758-29-4		**X**	1, 4
Tripoli	1317-95-9			4
Tripotassium citrate monohydrate	6100-05-6	**X**		4
Tripropylene glycol monomethyl ether	25498-49-1	**X**		2

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Trisodium citrate	68-04-2	**X**		3
Trisodium citrate dihydrate	6132-04-3	**X**		1, 4
Trisodium ethylenediaminetetraacetate	150-38-9	**X**		1, 3
Trisodium ethylenediaminetriacetate	19019-43-3	**X**		1, 4, 8
Trisodium phosphate	7601-54-9		**X**	1, 2, 4
Trisodium phosphate dodecahydrate	10101-89-0			1
Tritan R (X-100)	92046-34-9			8
Triton X-100	9002-93-1			1, 3, 4
Tromethamine	77-86-1	**X**		3, 4
Tryptone	73049-73-7			8
Ulexite	1319-33-1			1, 2, 3, 8
Undecane	1120-21-4	**X**		3, 8
Undecanol, branched and linear	128973-77-3			8
Urea	57-13-6	**X**		1, 2, 4, 8
Vermiculite	1318-00-9			2
Vinyl acetate ethylene copolymer	24937-78-8			1, 4
Vinylidene chloride/methylacrylate copolymer	25038-72-6			4
Water	7732-18-5			2, 4, 8
White mineral oil, petroleum	8042-47-5			1, 2, 4
Xylenes	*1330-20-7*	**X**	**X**	*1, 2, 4*
Yeast extract	8013-01-2			8
Zeolites	1318-02-1			8
Zinc	*7440-66-6*		**X**	*2*
Zinc carbonate	3486-35-9			2
Zinc chloride	7646-85-7			1, 2
Zinc oxide	1314-13-2			1, 4
Zinc sulfate monohydrate	7446-19-7			8
Zirconium nitrate	13746-89-9			2, 6
Zirconium oxide sulfate	62010-10-0			1, 4
Zirconium oxychloride	7699-43-6			1, 2, 4

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Zirconium(IV) chloride tetrahydrofuran complex	21959-01-3			5
Zirconium(IV) sulfate	14644-61-2			2, 6
Zirconium, 1,1'-((2-((2-hydroxyethyl)(2-hydroxypropyl)amino)ethyl)imino)bis(2-propanol) complexes	197980-53-3			4
Zirconium, acetate lactate oxo ammonium complexes	68909-34-2			4, 8
Zirconium, chloro hydroxy lactate oxo sodium complexes	174206-15-6			4
Zirconium, hydroxylactate sodium complexes	113184-20-6			1, 4
Zirconium,tetrakis[2-[bis(2-hydroxyethyl)amino-kN]ethanolato-kO]-	101033-44-7			1, 2, 4, 5

Table A-3. List of generic names of chemicals reportedly used in hydraulic fracturing fluids.

In some cases, the generic chemical name masks a specific chemical name and CASRN provided to the EPA and claimed as CBI by one or more of the nine hydraulic fracturing service companies.

Generic chemical name	Reference
2-Substituted aromatic amine salt	1, 4
Acetylenic alcohol	1
Acrylamide acrylate copolymer	4
Acrylamide copolymer	1, 4
Acrylamide modified polymer	4
Acrylamide-sodium acrylate copolymer	4
Acrylate copolymer	1
Acrylic copolymer	1
Acrylic polymer	1, 4
Acrylic resin	4
Acyclic hydrocarbon blend	1, 4
Acylbenzylpyridinium choride	8
Alcohol alkoxylate	1, 4
Alcohol and fatty acid blend	2

Generic chemical name	Reference
Alcohol ethoxylates	4
Alcohols	1, 4
Alcohols, C9-C22	1, 4
Aldehydes	1, 4, 5
Alfa-alumina	1, 4
Aliphatic acids	1, 2, 3, 4
Aliphatic alcohol	2
Aliphatic alcohol glycol ether	3, 4
Aliphatic alcohols, ethoxylated	2
Aliphatic amine derivative	1
Aliphatic carboxylic acid	4
Alkaline bromide salts	1, 4
Alkaline metal oxide	4
Alkanes/alkenes	4
Alkanolamine derivative	2
Alkanolamine/aldehyde condensate	1, 2, 4
Alkenes	1, 4
Alklaryl sulfonic acid	1, 4
Alkoxylated alcohols	1
Alkoxylated amines	1, 4
Alkyaryl sulfonate	1, 2, 3, 4
Alkyl alkoxylate	1, 4
Alkyl amide	4
Alkyl amine	1, 4
Alkyl amine blend in a metal salt solution	1, 4
Alkyl aryl amine sulfonate	4
Alkyl aryl polyethoxy ethanol	3, 4
Alkyl dimethyl benzyl ammonium chloride	4
Alkyl esters	1, 4
Alkyl ether phosphate	4
Alkyl hexanol	1, 4
Alkyl ortho phosphate ester	1, 4

Generic chemical name	Reference
Alkyl phosphate ester	1, 4
Alkyl phosphonate	4
Alkyl pyridines	2
Alkyl quaternary ammonium chlorides	1, 4
Alkyl quaternary ammonium salt	4
Alkylamine alkylaryl sulfonate	4
Alkylamine salts	2
Alkylaryl sulfonate	1, 4
Alkylated quaternary chloride	1, 2, 4
Alkylated sodium naphthalenesulphonate	2
Alkylbenzenesulfonate	2
Alkylbenzenesulfonic acid	1, 4, 5
Alkylethoammonium sulfates	1
Alkylphenol ethoxylates	1, 4
Alkylpyridinium quaternary	4
Alphatic alcohol polyglycol ether	2
Aluminum oxide	1, 4
Amide	4
Amidoamine	1, 4
Amine	1, 4
Amine compound	4
Amine oxides	1, 4
Amine phosphonate	1, 4
Amine salt	1
Amino compounds	1, 4
Amino methylene phosphonic acid salt	1, 4
Ammonium alcohol ether sulfate	1, 4
Ammonium salt	1, 4
Ammonium salt of ethoxylated alcohol sulfate	1, 4
Amorphous silica	4
Amphoteric surfactant	2
Anionic acrylic polymer	2

Generic chemical name	Reference
Anionic copolymer	1, 4
Anionic polyacrylamide	1, 2, 4
Anionic polyacrylamide copolymer	1, 4, 6
Anionic polymer	1, 3, 4
Anionic surfactants	2, 4, 6
Antifoulant	1, 4
Antimonate salt	1, 4
Aqueous emulsion of diethylpolysiloxane	2
Aromatic alcohol glycol ether	1
Aromatic aldehyde	1, 4
Aromatic hydrocarbons	3, 4
Aromatic ketones	1, 2, 3, 4
Aromatic polyglycol ether	1
Arsenic compounds	4
Ashes, residues	4
Bentone clay	4
Biocide	4
Biocide component	1, 4
Bis-quaternary methacrylamide monomer	4
Blast furnace slag	4
Borate salts	1, 2, 4
Cadmium compounds	4
Carbohydrates	1, 2, 4
Carboxylmethyl hydroxypropyl guar	4
Cationic polyacrylamide	4
Cationic polymer	2, 4
Cedar fiber, processed	2
Cellulase enzyme	1
Cellulose derivative	1, 2, 4
Cellulose ether	2
Cellulosic polymer	2
Ceramic	4

Generic chemical name	Reference
Chlorous ion solution	1
Chromates	1, 4
Chrome-free lignosulfonate compound	2
Citrus rutaceae extract	4
Common white	4
Complex alkylaryl polyo-ester	1
Complex aluminum salt	1, 4
Complex carbohydrate	2
Complex organometallic salt	1
Complex polyamine salt	7
Complex substituted keto-amine	1
Complex substituted keto-amine hydrochloride	1
Copper compounds	6
Coric oxide	4
Cotton dust (raw)	2
Cottonseed hulls	2
Cured acrylic resin	1, 4
Cured resin	1, 4, 5
Cured urethane resin	1, 4
Cyclic alkanes	1, 4
Defoamer	4
Dibasic ester	4
Dicarboxylic acid	1, 4
Diesel	1, 4, 6
Dimethyl silicone	1, 4
Dispersing agent	1
Emulsifier	4
Enzyme	4
Epoxy	4
Epoxy resin	1, 4
Essential oils	1, 4
Ester Salt	2, 4

Generic chemical name	Reference
Esters	2, 4
Ether compound	4
Ether salt	4
Ethoxylated alcohol blend	4
Ethoxylated alcohol/ester mixture	4
Ethoxylated alcohols	1, 2, 4, 5, 7
Ethoxylated alkyl amines	1, 4
Ethoxylated amine blend	4
Ethoxylated amines	1, 4
Ethoxylated fatty acid	4
Ethoxylated fatty acid ester	1, 4
Ethoxylated nonionic surfactant	1, 4
Ethoxylated nonylphenol	1, 2, 4
Ethoxylated sorbitol esters	1, 4
Ethylene oxide-nonylphenol polymer	4
Fatty acid amine salt mixture	4
Fatty acid ester	1, 2, 4
Fatty acid tall oil	1, 4
Fatty acid, ethoxylate	4
Fatty acids	1
Fatty alcohol alkoxylate	1, 4
Fatty alkyl amine salt	1, 4
Fatty amine carboxylates	1, 4
Fatty imidazoline	4
Fluoroaliphatic polymeric esters	1, 4
Formaldehyde polymer	1
Glass fiber	1, 4
Glyceride esters	2
Glycol	4
Glycol blend	2
Glycol ethers	1, 4, 7
Ground cedar	2

Generic chemical name	Reference
Ground paper	2
Guar derivative	1, 4
Guar gum	4
Haloalkyl heteropolycycle salt	1, 4
Hexanes	1
High molecular weight polymer	2
High pH conventional enzymes	2
Hydrocarbons	1
Hydrogen solvent	4
Hydrotreated and hydrocracked base oil	1, 4
Hydrotreated distillate, light C9-16	4
Hydrotreated heavy naphthalene	5
Hydrotreated light distillate	2, 4
Hydrotreated light petroleum distillate	4
Hydroxyalkyl imino carboxylic sodium salt	2
Hydroxycellulose	6
Hydroxyethyl cellulose	1, 2, 4
Imidazolium compound	4
Inner salt of alkyl amines	1, 4
Inorganic borate	1, 4
Inorganic chemical	4
Inorganic particulate	1, 4
Inorganic salt	2, 4
Iso-alkanes/n-alkanes	1, 4
Isomeric aromatic ammonium salt	1, 4
Latex	2, 4
Lead compounds	4
Low toxicity base oils	1, 4
Lubra-Beads course	4
Maghemite	1, 4
Magnetite	1, 4
Metal salt	1

Generic chemical name	Reference
Metal salt solution	1
Mineral	1, 4
Mineral fiber	2
Mineral filler	1
Mineral oil	4
Mixed titanium ortho ester complexes	1, 4
Modified acrylamide copolymer	2, 4
Modified acrylate polymer	4
Modified alkane	1, 4
Modified bentonite	4
Modified cycloaliphatic amine adduct	1, 4
Modified lignosulfonate	2, 4
Naphthalene derivatives	1, 4
Neutralized alkylated napthalene sulfonate	4
Nickel chelate catalyst	4
Nonionic surfactant	1
N-tallowalkyltrimethylenediamines	4
Nuisance particulates	1, 2, 4
Nylon	4
Olefinic sulfonate	1, 4
Olefins	1, 4
Organic acid salt	1, 4
Organic acids	1, 4
Organic alkyl amines	4
Organic chloride	4
Organic modified bentonite clay	4
Organic phosphonate	1, 4
Organic phosphonate salts	1, 4
Organic phosphonic acid salts	1, 4
Organic polymer	4
Organic polyol	4
Organic salt	1, 4

Generic chemical name	Reference
Organic sulfur compound	1, 4
Organic surfactants	1
Organic titanate	1, 4
Organo amino silane	4
Organo phosphonic acid	4
Organo phosphonic acid salt	4
Organometallic ammonium complex	1
Organophilic clay	4
Oxidized tall oil	2
Oxoaliphatic acid	2
Oxyalkylated alcohol	1, 4
Oxyalkylated alkyl alcohol	2, 4
Oxyalkylated alkylphenol	1, 2, 3, 4
Oxyalkylated fatty acid	1, 4
Oxyalkylated fatty alcohol salt	2
Oxyalkylated phenol	1, 4
Oxyalkylated phenolic resin	4
Oxyalkylated polyamine	1
Oxyalkylated tallow diamine	2
Oxyethylated alcohol	2
Oxylated alcohol	1, 4
P/F resin	4
Paraffin inhibitor	4
Paraffinic naphthenic solvent	1
Paraffinic solvent	1, 4
Paraffins	1
Pecan shell	2
Petroleum distallate blend	2, 3, 4
Petroleum gas oils	1
Petroleum hydrocarbons	4
Petroleum solvent	2
Phosphate ester	1, 4

Generic chemical name	Reference
Phosphonate	2
Phosphonic acid	1, 4
Phosphoric acid, mixed polyoxyalkylene aryl and alkyl esters	4
Plasticizer	1, 2
Polyacrylamide copolymer	4
Polyacrylamides	1
Polyacrylate	1, 4
Polyactide resin	4
Polyalkylene esters	4
Polyaminated fatty acid	2
Polyaminated fatty acid surfactants	2
Polyamine	1, 4
Polyamine polymer	4
Polyanionic cellulose	1
Polyaromatic hydrocarbons	6
Polycyclic organic matter	6
Polyelectrolyte	4
Polyether polyol	2
Polyethoxylated alkanol	2, 3, 4
Polyethylene copolymer	4
Polyethylene glycols	4
Polyethylene wax	4
Polyglycerols	2
Polyglycol	2
Polyglycol ether	6
Polylactide resin	4
Polymer	2, 4
Polymeric hydrocarbons	3, 4
Polymerized alcohol	4
Polymethacrylate polymer	4
Polyol phosphate ester	2
Polyoxyalkylene phosphate	2

Generic chemical name	Reference
Polyoxyalkylene sulfate	2
Polyoxyalkylenes	1, 4, 7
Polyphenylene ether	4
Polyphosphate	4
Polypropylene glycols	2
Polyquaternary amine	4
Polysaccaride polymers in suspension	2
Polysaccharide	4
Polysaccharide blend	4
Polyvinylalcohol/polyvinylactetate copolymer	4
Potassium chloride substitute	4
Quarternized heterocyclic amines	4
Quaternary amine	2, 4
Quaternary amine salt	4
Quaternary ammonium chloride	4
Quaternary ammonium compound	1, 2, 4
Quaternary ammonium salts	1, 2, 4
Quaternary compound	1, 4
Quaternary salt	1, 4
Quaternized alkyl nitrogenated compd	4
Red dye	4
Refined mineral oil	2
Resin	4
Salt of amine-carbonyl condensate	3, 4
Salt of fatty acid/polyamine reaction product	3, 4
Salt of phosphate ester	1
Salt of phosphono-methylated diamine	1, 4
Salts	4
Salts of oxyalkylated fatty amines	4
Sand	4
Sand, AZ silica	4
Sand, brown	4

Generic chemical name	Reference
Sand, sacked	4
Sand, white	4
Secondary alcohol	1, 4
Silica sand, 100 mesh, sacked	4
Silicone emulsion	1
Silicone ester	4
Sodium acid pyrophosphate	4
Sodium calcium magnesium polyphosphate	4
Sodium phosphate	4
Sodium salt of aliphatic amine acid	2
Sodium xylene sulfonate	4
Softwood dust	2
Starch blends	6
Substituted alcohol	1, 2, 4
Substituted alkene	1
Substituted alklyamine	1, 4
Substituted alkyne	4
Sulfate	4
Sulfomethylated tannin	2, 5
Sulfonate	4
Sulfonate acids	1
Sulfonate surfactants	1
Sulfonated asphalt	2
Sulfonic acid salts	1, 4
Sulfur compound	1, 4
Sulphonic amphoterics	4
Sulphonic amphoterics blend	4
Surfactant blend	3, 4
Surfactants	1, 2, 4
Synthetic copolymer	2
Synthetic polymer	4
Tallow soap	4

Generic chemical name	Reference
Telomer	4
Terpenes	1, 4
Titanium complex	4
Triethanolamine zirconium chelate	1 4
Triterpanes	4
Vanadium compounds	4
Wall material	1
Walnut hulls	1, 2, 4
Zirconium complex	2, 4
Zirconium salt	4

Table A-4. Chemicals detected in flowback or produced water.

An "X" indicates the availability of physicochemical properties from EPI Suite™ and selected toxicity reference values (see Appendix G). An empty cell indicates no information was available from the sources we consulted. Reference number corresponds to the citations in Table A-1. Italicized chemicals are found in both fracturing fluids and flowback/produced water.

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
1,2,3-Trichlorobenzene	87-61-6	**X**	**X**	3, 9
1,2,4-Trichlorobenzene	120-82-1	**X**	**X**	9
1,2,4-Trimethylbenzene	*95-63-6*	**X**		*3, 9, 10*
1,2-Propylene glycol	*57-55-6*	**X**	**X**	*3, 9*
1,3,5-Trimethylbenzene	*108-67-8*	**X**		*3, 9, 10*
1,4-Dioxane	*123-91-1*	**X**	**X**	*9, 10*
2,4-Dimethylphenol	105-67-9	**X**	**X**	3, 9, 10
2,6-Dichlorophenol	87-65-0	**X**		3, 9
2-Methylnaphthalene	91-57-6	**X**	**X**	3, 9, 10
2-Methylpropanoic acid	79-31-2	**X**		10
2-Methylpyridine	109-06-8	**X**		3, 9
7,12-Dimethylbenz(a)anthracene	57-97-6	**X**	**X**	3, 9
Acetic acid	*64-19-7*	**X**		*3, 9, 10*

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Acetone	*67-64-1*	**X**	**X**	*3, 9, 10*
Acetophenone	*98-86-2*	**X**	**X**	*3, 9*
Acrolein	*107-02-8*	**X**	**X**	*9*
Acrylonitrile	107-13-1	**X**	**X**	3, 9
Aldrin	309-00-2	**X**	**X**	3, 9
Aluminum	*7429-90-5*		**X**	*3, 9, 10*
Ammonia	*7664-41-7*			*3, 9, 10*
Antimony	7440-36-0		**X**	3, 9, 10
Aroclor 1248	12672-29-6	**X**		3, 9
Arsenic	*7440-38-2*		**X**	*3, 9, 10*
Barium	7440-39-3		**X**	3, 9, 10
Benzene	*71-43-2*	**X**	**X**	*3, 9, 10*
Benzo(a)pyrene	50-32-8	**X**	**X**	3, 9
Benzo(b)fluoranthene	205-99-2	**X**	**X**	3, 9
Benzo(g,h,i)perylene	191-24-2	**X**		3, 9, 10
Benzo(k)fluoranthene	207-08-9	**X**	**X**	3, 9
Benzyl alcohol	100-51-6	**X**	**X**	3, 9, 10
Beryllium	7440-41-7		**X**	3, 9, 10
beta-Hexachlorocyclohexane	319-85-7	**X**	**X**	3, 9
Bis(2-chloroethyl) ether	*111-44-4*	**X**	**X**	*3, 9*
Boron	7440-42-8		**X**	3, 9, 10
Bromide	24959-67-9			3, 9, 10
Bromodichloromethane	75-27-4	**X**	**X**	3
Bromoform	75-25-2	**X**	**X**	3, 9, 10
Butanoic acid	107-92-6	**X**		9, 10
Butylbenzene	104-51-8	**X**	**X**	9, 10
Cadmium	7440-43-9		**X**	3, 9, 10
Caesium-137	10045-97-3			3
Calcium	7440-70-2			3, 9, 10
Carbon dioxide	*124-38-9*	**X**		*3, 9, 10*

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Carbon disulfide	75-15-0	X	X	3, 9
Chloride	*16887-00-6*			*3, 9, 10*
Chlorine	*7782-50-5*		X	*3, 10*
Chlorodibromomethane	124-48-1	X	X	3
Chloroform	67-66-3	X	X	3, 9, 10
Chloromethane	74-87-3	X		3, 10
Chromium	7440-47-3			3, 9, 10
Chromium (III)	*16065-83-1*		X	*3*
Chromium (VI)	*18540-29-9*		X	*3, 10*
Cobalt	7440-48-4		X	3, 9, 10
Copper	*7440-50-8*		X	*3, 9, 10*
Cumene	*98-82-8*	X	X	*3, 9*
Cyanide	57-12-5	X	X	3, 9, 10
delta-Hexachlorocyclohexane	319-86-8	X		9
Di(2-ethylhexyl) phthalate	*117-81-7*	X	X	*3, 9, 10*
Dibenz(a,h)anthracene	53-70-3	X	X	3, 9
Dibutyl phthalate	84-74-2	X	X	3, 9, 10
Dichloromethane	*75-09-2*	X	X	*9, 10*
Dieldrin	60-57-1	X	X	9
Diethyl phthalate	84-66-2	X	X	9
Dioctyl phthalate	117-84-0	X	X	9, 10
Diphenylamine	122-39-4	X	X	3, 9
Endosulfan I	959-98-8	X		3, 9
Endosulfan II	33213-65-9	X		3, 9
Endrin aldehyde	7421-93-4	X		3, 9
Ethylbenzene	*100-41-4*	*X*	*X*	*3, 9, 10*
Ethylene glycol	*107-21-1*	*X*	*X*	*3, 9*
Fluoranthene	206-44-0	X	X	3, 9
Fluorene	86-73-7	X	X	3, 9, 10
Fluoride	16984-48-8			3, 9, 10

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Formic acid	*64-18-6*	***X***	***X***	*10*
Heptachlor	76-44-8	**X**	**X**	3, 9
Heptachlor epoxide	1024-57-3	**X**	**X**	3, 9
Heptanoic acid	111-14-8	**X**		10
Hexanoic acid	142-62-1	**X**		10
Indeno(1,2,3-cd)pyrene	193-39-5	**X**	**X**	3, 9
Iron	*7439-89-6*		***X***	*3, 9, 10*
Isopropanol	*67-63-0*	***X***		*3, 9*
Isovaleric acid	503-74-2	**X**		10
Lead	*7439-92-1*		***X***	*3, 9, 10*
Lindane	58-89-9	**X**	**X**	3, 9
Lithium	7439-93-2		**X**	3, 9, 10
Magnesium	7439-95-4			3, 9, 10
Manganese	7439-96-5		**X**	3, 9, 10
m-Cresol	108-39-4	**X**	**X**	3, 9, 10
Mercury	7439-97-6		**X**	3, 9, 10
Methanol	*67-56-1*	***X***	***X***	*3, 9*
Methyl bromide	74-83-9	**X**	**X**	3, 9
Methyl ethyl ketone	78-93-3	**X**	**X**	3, 9, 10
Molybdenum	7439-98-7		**X**	3, 9, 10
Naphthalene	*91-20-3*	***X***	***X***	*3, 9, 10*
Nickel	7440-02-0			3, 9, 10
Nitrate	14797-55-8		**X**	3, 9, 10
Nitrite	14797-65-0		**X**	3, 9, 10
N-Nitrosodiphenylamine	86-30-6	**X**	**X**	3, 9
o-Cresol	95-48-7	**X**	**X**	3, 9, 10
p,p'-DDE	72-55-9	**X**	**X**	3, 9
p-Cresol	106-44-5	**X**	**X**	3, 9, 10
p-Cymene	99-87-6	**X**		9, 10
Pentanoic acid	109-52-4	**X**		10

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Phenanthrene	*85-01-8*	***X***		*3, 9, 10*
Phenol	*108-95-2*	***X***	***X***	*3, 9, 10*
Phorate	298-02-2	**X**	**X**	9
Phosphorus	7723-14-0		**X**	3, 9
Potassium	7440-09-7			3, 9, 10
Propionic acid	79-09-4	**X**		10
Propylbenzene	103-65-1	**X**		9
Pyrene	129-00-0	**X**	**X**	9, 10
Pyridine	110-86-1	**X**	**X**	3, 9, 10
Radium	7440-14-4			3
Radium-226	13982-63-3			3, 10
Radium-228	15262-20-1			3, 10
Safrole	94-59-7	**X**	**X**	3, 9
sec-Butylbenzene	135-98-8	**X**		9
Selenium	7782-49-2		**X**	3, 9, 10
Silica	*7631-86-9*			*10*
Silicon	7440-21-3			10
Silver	7440-22-4		**X**	3, 9, 10
Sodium	7440-23-5			3, 9, 10
Strontium	7440-24-6		**X**	3, 9, 10
Sulfate	*14808-79-8*			*3, 9, 10*
Sulfite	14265-45-3			3
Tetrachloroethylene	127-18-4	**X**	**X**	3, 9
Thallium	7440-28-0			3, 9, 10
Tin	7440-31-5		**X**	9, 10
Titanium	7440-32-6			3, 9, 10
Toluene	*108-88-3*	***X***	***X***	*3, 9, 10*
Vanadium	7440-62-2		**X**	3, 10

Chemical name	CASRN	Physico-chemical properties	Selected toxicity reference value	Reference
Xylenes	*1330-20-7*	***X***	***X***	*3, 9, 10*
Zinc	*7440-66-6*		**X**	*3, 9, 10*
Zirconium	7440-67-7			3

A.2. References for Appendix A

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Appendix B

Water Acquisition Tables

Appendix B. Water Acquisition Tables

B.1. Supplemental Tables

Table B-1. Annual average hydraulic fracturing water use and consumption in 2011 and 2012 compared to total annual water use and consumption in 2010 by state.

Hydraulic fracturing water use data from the EPA's project database of disclosures to FracFocus 1.0 (U.S. EPA, 2015c). Annual total water use data from the U.S. Geological Survey (USGS) Water Census (Maupin et al., 2014). Estimates of consumptions derived from hydraulic fracturing water use and total water use data. States listed in descending order by the volume of hydraulic fracturing water use.

State	Total annual water use in 2010 (millions of gal)[a,b]	Annual average hydraulic fracturing water use in 2011 and 2012 (millions of gal)[c]	Hydraulic fracturing water use compared to total water use (%)[d]	Hydraulic fracturing water consumption compared to total water consumption (%)[d,e]
Texas	9,052,000	19,942	0.2	0.7
Pennsylvania	2,967,450	5,105	0.2	1.4
Arkansas	4,124,500	3,676	0.1	0.1
Colorado	4,015,000	3,277	0.1	0.1
Oklahoma	1,157,050	2,949	0.3	0.8
Louisiana	3,117,100	2,462	0.1	0.4
North Dakota	419,750	2,181	0.5	2.9
West Virginia	1,288,450	657	0.1	0.5
Wyoming	1,715,500	538	<0.1	<0.1
New Mexico	1,153,400	371	<0.1	<0.1
Ohio	3,445,600	273	<0.1	0.1
Utah	1,627,900	251	<0.1	<0.1
Montana	2,792,250	155	<0.1	<0.1
Kansas	1,460,000	66	<0.1	<0.1
California	13,870,000	44	<0.1	<0.1
Michigan	3,942,000	28	<0.1	<0.1

State	Total annual water use in 2010 (millions of gal)[a,b]	Annual average hydraulic fracturing water use in 2011 and 2012 (millions of gal)[c]	Hydraulic fracturing water use compared to total water use (%)[d]	Hydraulic fracturing water consumption compared to total water consumption (%)[d,e]
Mississippi	1,434,450	18	<0.1	<0.1
Alaska[f]	397,850	7	<0.1	<0.1
Virginia	2,792,250	1	<0.1	<0.1
Alabama	3,635,400	1	<0.1	<0.1
TOTAL for all 20 states	64,407,900	42,001	0.1	0.2

[a] Texas, Colorado, Pennsylvania, North Dakota, Oklahoma, and Utah all made some degree of reporting to FracFocus mandatory rather than voluntary during this time period analyzed, January 1, 2011, to February 28, 2013. 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 time studied (U.S. EPA, 2015a).

[b] State-level data accessed from the USGS website (http://water.usgs.gov/watuse/data/2010/) on January 27, 2015. Total water withdrawals per day (located in downloaded Table 1) were multiplied by 365 days to estimate total water use for the year (Maupin et al., 2014).

[c] Average of water used for hydraulic fracturing in 2011 and 2012 as reported to FracFocus (U.S. EPA, 2015c).

[d] Percentages were calculated by averaging annual water use for hydraulic fracturing reported in FracFocus in 2011 and 2012 for a given state (U.S. EPA, 2015c), and then dividing by 2010 USGS hydraulic fracturing water use (Maupin et al., 2014) and multiplying by 100. Note that the annual hydraulic fracturing water use reported in FracFocus (the numerator) was not added to the 2010 total USGS water use value in the denominator, and the percentage is simply calculated as by dividing annual hydraulic fracturing use by 2010 total water use or consumption. This was done because of the difference in years between the two datasets, and because the USGS 2010 Census (Maupin et al., 2014) already included an estimate of hydraulic fracturing water use in its mining category. This approach is also consistent with that of other literature on this topic; see Nicot and Scanlon (2012).

[e] 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 (USGS, 2014). We used a rate of 71.6% for aquaculture (from Verdegem and Bosma, 2009) (evaporation per kg fish + infiltration per kg)/(total water use per kg) *100. These rates were multiplied by each USGS water use value (Maupin et al., 2014) to yield a total water consumption estimate. To calculate a consumption amount for hydraulic fracturing, we used a consumption rate of 82.5%. This was 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 that this is likely a low estimate of consumption since much of this return water is not subsequently treated and reused, but rather disposed of in underground injection wells—see Chapter 8.

[f] All reported hydraulic fracturing disclosures for Alaska passed state locational quality assurance methods, but not county methods (U.S. EPA, 2015c). Thus, only state-level cumulative values were reported here, and no county-level data are provided in subsequent tables.

Table B-2. Annual average hydraulic fracturing water use and consumption in 2011 and 2012 compared to total annual water use and consumption in 2010 by county.

Counties listed contained wells used for hydraulic fracturing according to the EPA's project database of disclosures to FracFocus 1.0 (U.S. EPA, 2015c). Annual total water use data from the USGS Water Census (Maupin et al., 2014). Estimates of consumption derived from hydraulic fracturing water use and total water use data.

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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]
Alabama	Jefferson	29,685.5	0.6	<0.1	<0.1
	Tuscaloosa	14,319.0	0.5	<0.1	<0.1
Arkansas	Cleburne	9,471.8	740.9	7.8	32.9
	Conway	10,643.4	798.1	7.5	21.2
	Faulkner	3,204.7	284.0	8.9	13.7
	Independence	57,195.5	80.3	0.1	0.3
	Logan	1,525.7	2.4	0.2	0.3
	Sebastian	1,365.1	0.6	<0.1	<0.1
	Van Buren	1,587.8	899.6	56.7	168.8
	White	32,131.0	869.8	2.7	4.7
	Yell	1,507.5	<0.1	<0.1	<0.1
California	Colusa	304,782.3	<0.1	<0.1	<0.1
	Glenn	221,420.0	<0.1	<0.1	<0.1
	Kern	788,359.9	41.7	<0.1	<0.1
	Los Angeles	1,118,363.7	0.2	<0.1	<0.1
	Sutter	263,511.8	0.2	<0.1	<0.1
	Ventura	262,610.2	1.8	<0.1	<0.1
Colorado	Adams	84,285.8	3.2	<0.1	<0.1
	Arapahoe	68,255.0	4.0	<0.1	<0.1
	Boulder	84,537.7	4.1	<0.1	<0.1

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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]
Colorado, cont.	Broomfield	2,336.0	4.5	0.2	0.4
	Delta	131,221.2	0.5	<0.1	<0.1
	Dolores	2,040.4	0.1	<0.1	<0.1
	El Paso	42,380.2	<0.1	<0.1	<0.1
	Elbert	5,040.7	<0.1	<0.1	<0.1
	Fremont	53,366.7	0.6	<0.1	<0.1
	Garfield	95,436.6	1,804.2	1.9	2.7
	Jackson	126,968.9	1.0	<0.1	<0.1
	La Plata	122,873.6	3.5	<0.1	<0.1
	Larimer	150,690.3	5.4	<0.1	<0.1
	Las Animas	26,911.5	7.9	<0.1	<0.1
	Mesa	275,476.5	122.1	<0.1	0.1
	Moffat	62,093.8	14.5	<0.1	<0.1
	Morgan	67,901.0	3.9	<0.1	<0.1
	Phillips	21,509.5	0.2	<0.1	<0.1
	Rio Blanco	97,513.4	147.3	0.2	0.2
	Routt	74,460.0	0.1	<0.1	<0.1
	San Miguel	13,848.1	0.3	<0.1	<0.1
	Weld	168,677.5	1,149.4	0.7	1.0
	Yuma	80,595.7	0.4	<0.1	<0.1
Kansas	Barber	2,164.5	9.9	0.5	0.7
	Clark	1,898.0	0.8	<0.1	0.1
	Comanche	3,011.3	25.6	0.9	1.2
	Finney	102,685.5	2.4	<0.1	<0.1
	Grant	47,128.8	0.2	<0.1	<0.1

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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]
Kansas, cont.	Gray	69,379.2	3.3	<0.1	<0.1
	Harper	1,357.8	17.3	1.3	2.0
	Haskell	72,496.3	0.1	<0.1	<0.1
	Hodgeman	8,460.7	2.7	<0.1	<0.1
	Kearny	64,134.2	<0.1	<0.1	<0.1
	Lane	5,628.3	0.8	<0.1	<0.1
	Meade	55,958.2	<0.1	<0.1	<0.1
	Morton	17,403.2	<0.1	<0.1	<0.1
	Ness	1,478.3	1.6	0.1	0.2
	Seward	57,443.7	<0.1	<0.1	<0.1
	Sheridan	26,393.2	0.7	<0.1	<0.1
	Stanton	41,420.2	<0.1	<0.1	<0.1
	Stevens	72,124.0	0.1	<0.1	<0.1
	Sumner	3,442.0	0.2	<0.1	<0.1
Louisiana	Allen	8,942.5	0.1	<0.1	<0.1
	Beauregard	10,161.6	2.3	<0.1	0.1
	Bienville	4,810.7	108.9	2.3	10.0
	Bossier	5,599.1	110.1	2.0	4.9
	Caddo	53,644.1	153.6	0.3	1.7
	Calcasieu	81,621.3	0.1	<0.1	<0.1
	Caldwell	1,398.0	<0.1	<0.1	<0.1
	Claiborne	952.7	3.8	0.4	1.1
	De Soto	13,373.6	1,085.9	8.1	47.4
	East Feliciana	1,350.5	3.7	0.3	0.7
	Jackson	1,456.4	<0.1	<0.1	<0.1

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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]
Louisiana, cont.	Lincoln	3,000.3	3.3	0.1	0.3
	Natchitoches	12,530.5	12.7	0.1	0.2
	Rapides	199,976.2	1.7	<0.1	<0.1
	Red River	1,606.0	569.6	35.5	83.2
	Sabine	1,522.1	395.2	26.0	76.6
	Tangipahoa	7,329.2	1.9	<0.1	0.1
	Union	1,481.9	4.9	0.3	1.0
	Webster	2,664.5	1.2	<0.1	0.1
	West Feliciana	15,191.3	2.3	<0.1	0.1
	Winn	846.8	1.1	0.1	0.4
Michigan	Cheboygan	2,777.7	<0.1	<0.1	<0.1
	Gladwin	850.5	1.1	0.1	0.4
	Kalkaska	1,233.7	24.0	1.9	3.7
	Missaukee	1,423.5	<0.1	<0.1	<0.1
	Ogemaw	1,179.0	<0.1	<0.1	<0.1
	Roscommon	1,000.1	2.4	0.2	0.9
Mississippi	Amite	792.1	14.4	1.8	3.8
	Wilkinson	1,270.2	3.2	0.3	0.4
Montana	Daniels	1,408.9	0.6	<0.1	0.1
	Garfield	1,631.6	0.5	<0.1	<0.1
	Glacier	46,760.2	5.1	<0.1	<0.1
	Musselshell	26,827.5	0.4	<0.1	<0.1
	Richland	94,797.8	83.5	0.1	0.1

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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]
Montana, cont.	Roosevelt	31,539.7	52.1	0.2	0.2
	Rosebud	71,412.3	3.5	<0.1	<0.1
	Sheridan	7,354.8	9.7	0.1	0.2
New Mexico	Chaves	88,078.2	2.8	<0.1	<0.1
	Colfax	17,450.7	0.7	<0.1	<0.1
	Eddy	70,612.9	225.6	0.3	0.5
	Harding	1,168.0	0.1	<0.1	<0.1
	Lea	64,057.5	113.7	0.2	0.3
	Rio Arriba	39,080.6	16.5	<0.1	0.1
	Roosevelt	63,367.7	<0.1	<0.1	<0.1
	San Juan	125,432.3	11.6	<0.1	<0.1
	Sandoval	23,922.1	0.4	<0.1	<0.1
North Dakota	Billings	762.9	44.4	5.8	16.2
	Bottineau	1,164.4	0.1	<0.1	<0.1
	Burke	394.2	63.6	16.1	40.8
	Divide	806.7	102.2	12.7	18.6
	Dunn	1,076.8	309.5	28.7	43.1
	Golden Valley	208.1	4.6	2.2	3.8
	Mckenzie	13,753.2	588.4	4.3	6.2
	Mclean	7,873.1	12.2	0.2	0.4
	Mountrail	1,248.3	449.4	36.0	98.3
	Stark	1,168.0	48.0	4.1	8.5
	Williams	7,705.2	558.5	7.2	11.3

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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]
Ohio	Ashland	2,033.1	1.5	0.1	0.2
	Belmont	65,528.5	1.9	<0.1	0.1
	Carroll	1,127.9	152.7	13.5	37.3
	Columbiana	3,763.2	30.7	0.8	2.2
	Coshocton	53,775.5	5.4	<0.1	0.1
	Guernsey	2,379.8	8.4	0.4	0.7
	Harrison	481.8	16.5	3.4	7.3
	Jefferson	632,917.3	26.2	<0.1	0.1
	Knox	3,270.4	1.1	<0.1	0.1
	Medina	3,540.5	1.3	<0.1	0.1
	Muskingum	6,018.9	5.1	0.1	0.3
	Noble	478.2	8.3	1.7	3.4
	Portage	18,414.3	3.2	<0.1	0.1
	Stark	16,479.8	2.4	<0.1	<0.1
	Tuscarawas	14,165.7	6.7	<0.1	0.2
	Wayne	6,051.7	1.7	<0.1	0.1
Oklahoma	Alfalfa	2,996.7	182.7	6.1	12.0
	Beaver	15,341.0	23.1	0.2	0.3
	Beckham	4,099.0	108.0	2.6	4.7
	Blaine	3,763.2	203.3	5.4	9.3
	Bryan	5,062.6	10.3	0.2	0.4
	Caddo	24,064.5	25.4	0.1	0.3
	Canadian	5,584.5	441.9	7.9	15.6
	Carter	159,906.5	161.9	0.1	0.5
	Coal	1,193.6	85.9	7.2	21.5

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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]
Oklahoma, cont.	Custer	3,281.4	19.0	0.6	1.2
	Dewey	10,953.7	162.6	1.5	6.2
	Ellis	8,486.3	184.3	2.2	3.2
	Garvin	16,279.0	15.0	0.1	0.4
	Grady	13,537.9	111.5	0.8	2.3
	Grant	5,569.9	77.8	1.4	5.2
	Harper	3,266.8	8.8	0.3	0.4
	Hughes	3,394.5	30.5	0.9	2.2
	Jefferson	4,496.8	<0.1	<0.1	<0.1
	Johnston	1,671.7	32.9	2.0	4.7
	Kay	16,957.9	17.3	0.1	0.4
	Kingfisher	3,744.9	10.2	0.3	0.5
	Kiowa	5,022.4	0.1	<0.1	<0.1
	Latimer	1,062.2	0.6	0.1	0.1
	Le Flore	8,635.9	0.3	<0.1	<0.1
	Logan	4,077.1	4.2	0.1	0.3
	Love	2,011.2	4.4	0.2	0.5
	Major	6,321.8	1.2	<0.1	<0.1
	Marshall	2,613.4	98.4	3.8	7.2
	McClain	2,952.9	2.1	0.1	0.2
	Noble	12,990.4	25.3	0.2	1.8
	Oklahoma	47,836.9	1.2	<0.1	<0.1
	Osage	6,971.5	3.8	0.1	0.2
	Pawnee	4,839.9	15.7	0.3	1.4
	Payne	4,332.6	9.9	0.2	0.6

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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]
Oklahoma, cont.	Pittsburg	6,314.5	349.0	5.5	16.0
	Roger Mills	2,847.0	235.5	8.3	12.6
	Seminole	124,837.3	0.1	<0.1	<0.1
	Stephens	49,990.4	27.7	0.1	0.3
	Texas	110,208.1	0.1	<0.1	<0.1
	Washita	3,310.6	102.1	3.1	5.4
	Woods	4,139.1	155.1	3.7	10.9
Pennsylvania	Allegheny	234,140.2	13.6	<0.1	<0.1
	Armstrong	65,853.3	55.7	0.1	1.8
	Beaver	157,793.2	30.5	<0.1	0.2
	Blair	8,303.8	5.9	0.1	0.2
	Bradford	4,354.5	1,059.4	24.3	78.2
	Butler	5,730.5	121.8	2.1	6.0
	Cameron	292.0	6.6	2.3	4.1
	Centre	16,560.1	38.5	0.2	0.5
	Clarion	1,843.3	8.1	0.4	1.4
	Clearfield	111,051.3	111.5	0.1	2.3
	Clinton	6,161.2	94.4	1.5	3.0
	Columbia	3,810.6	5.6	0.1	0.4
	Crawford	5,091.8	2.4	<0.1	0.1
	Elk	7,876.7	37.5	0.5	1.9
	Fayette	16,465.2	120.2	0.7	2.7
	Forest	744.6	7.7	1.0	1.6
	Greene	13,023.2	359.0	2.8	24.7
	Huntingdon	5,121.0	2.7	0.1	0.2

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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]
Pennsylvania, cont.	Indiana	21,819.7	16.2	0.1	0.7
	Jefferson	1,730.1	13.8	0.8	1.7
	Lawrence	36,598.6	27.0	0.1	1.0
	Lycoming	5,854.6	704.6	12.0	33.8
	McKean	4,723.1	60.5	1.3	4.9
	Potter	2,281.3	16.5	0.7	1.0
	Somerset	10,833.2	5.8	0.1	0.2
	Sullivan	222.7	66.5	29.9	79.8
	Susquehanna	1,617.0	751.3	46.5	123.4
	Tioga	2,909.1	566.3	19.5	47.3
	Venango	2,989.4	2.4	0.1	0.3
	Warren	5,099.1	2.3	<0.1	0.2
	Washington	130,535.0	433.7	0.3	4.6
	Westmoreland	14,607.3	207.0	1.4	3.8
	Wyoming	4,788.8	150.0	3.1	15.2
Texas	Andrews	23,363.7	236.2	1.0	2.7
	Angelina	5,540.7	0.8	<0.1	<0.1
	Archer	2,536.8	0.1	<0.1	<0.1
	Atascosa	15,038.0	327.3	2.2	4.0
	Austin	2,555.0	2.1	0.1	0.1
	Bee	3,087.9	20.0	0.6	1.1
	Borden	2,427.3	8.0	0.3	1.0
	Bosque	3,544.2	0.7	<0.1	<0.1
	Brazos	24,790.8	7.7	<0.1	0.1
	Brooks	1,204.5	1.5	0.1	0.3

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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, cont.	Burleson	10,694.5	3.0	<0.1	<0.1
	Cherokee	24,845.6	0.5	<0.1	<0.1
	Clay	1,963.7	<0.1	<0.1	<0.1
	Cochran	24,035.3	3.0	<0.1	<0.1
	Coke	12,713.0	0.3	<0.1	<0.1
	Colorado	52,465.1	0.1	<0.1	<0.1
	Concho	2,832.4	<0.1	<0.1	<0.1
	Cooke	4,533.3	454.3	10.0	29.9
	Cottle	733.7	0.3	<0.1	0.1
	Crane	8,566.6	92.3	1.1	5.7
	Crockett	4,281.5	279.0	6.5	29.5
	Crosby	27,261.9	1.3	<0.1	<0.1
	Culberson	14,311.7	37.7	0.3	0.4
	Dallas	112,204.7	5.6	<0.1	<0.1
	Dawson	28,842.3	17.5	0.1	0.1
	DeWitt	2,394.4	546.6	22.8	48.6
	Denton	60,684.9	455.0	0.7	2.3
	Dimmit	4,073.4	1,794.2	44.0	81.3
	Ector	21,958.4	226.5	1.0	4.6
	Edwards	332.2	<0.1	<0.1	<0.1
	Ellis	8,530.1	4.2	<0.1	0.1
	Erath	5,876.5	0.8	<0.1	<0.1
	Fayette	9,008.2	13.7	0.2	1.2
	Fisher	2,854.3	1.8	0.1	0.1
	Franklin	1,956.4	<0.1	<0.1	<0.1

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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, cont.	Freestone	297,861.9	53.9	<0.1	0.5
	Frio	20,589.7	127.5	0.6	0.9
	Gaines	121,778.6	21.6	<0.1	<0.1
	Garza	5,234.1	0.6	<0.1	<0.1
	Glasscock	20,680.9	598.1	2.9	4.2
	Goliad	142,963.2	<0.1	<0.1	<0.1
	Gonzales	7,121.2	577.9	8.1	17.6
	Grayson	8,143.2	9.3	0.1	0.3
	Gregg	33,010.6	9.4	<0.1	0.2
	Grimes	112,500.3	15.5	<0.1	0.3
	Hansford	43,643.1	2.9	<0.1	<0.1
	Hardeman	2,230.2	0.4	<0.1	<0.1
	Hardin	2,376.2	0.1	<0.1	<0.1
	Harrison	11,869.8	141.6	1.2	6.0
	Hartley	113,555.2	1.9	<0.1	<0.1
	Haskell	12,143.6	0.1	<0.1	<0.1
	Hemphill	3,150.0	263.9	8.4	16.3
	Hidalgo	171,630.3	8.0	<0.1	<0.1
	Hockley	46,314.9	3.0	<0.1	<0.1
	Hood	9,351.3	76.0	0.8	2.2
	Houston	3,686.5	8.6	0.2	0.6
	Howard	10,811.3	97.6	0.9	2.7
	Hutchinson	34,437.8	0.3	<0.1	<0.1
	Irion	1,335.9	411.4	30.8	74.5
	Jack	2,241.1	14.0	0.6	2.2

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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, cont.	Jefferson	88,585.5	<0.1	<0.1	<0.1
	Jim Hogg	306.6	0.1	<0.1	0.1
	Johnson	9,241.8	582.0	6.3	18.5
	Jones	5,679.4	<0.1	<0.1	<0.1
	Karnes	1,861.5	1,055.2	56.7	120.1
	Kenedy	456.3	0.2	0.1	0.1
	Kent	6,132.0	0.4	<0.1	<0.1
	King	1,485.6	<0.1	<0.1	<0.1
	Kleberg	1,171.7	3.4	0.3	0.5
	Knox	9,800.3	<0.1	<0.1	<0.1
	La Salle	2,474.7	1,288.7	52.1	93.7
	Lavaca	3,763.2	45.0	1.2	2.0
	Lee	3,120.8	1.2	<0.1	0.1
	Leon	2,171.8	56.2	2.6	6.6
	Liberty	20,662.7	<0.1	<0.1	<0.1
	Limestone	11,158.1	10.7	0.1	0.9
	Lipscomb	11,015.7	89.0	0.8	1.1
	Live Oak	1,916.3	294.0	15.3	40.1
	Loving	781.1	138.4	17.7	94.1
	Lynn	19,892.5	1.1	<0.1	<0.1
	Madison	1,554.9	45.3	2.9	8.2
	Marion	3,606.2	5.9	0.2	0.9
	Martin	14,063.5	432.0	3.1	4.7
	Maverick	20,498.4	52.4	0.3	0.4
	McMullen	657.0	745.9	113.5	350.4

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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, cont.	Medina	19,228.2	0.2	<0.1	<0.1
	Menard	1,014.7	<0.1	<0.1	<0.1
	Midland	12,891.8	307.4	2.4	3.7
	Milam	16,665.9	4.9	<0.1	0.1
	Mitchell	6,559.1	11.0	0.2	0.3
	Montague	3,989.5	925.3	23.2	77.8
	Montgomery	32,565.3	0.2	<0.1	<0.1
	Moore	57,075.1	<0.1	<0.1	<0.1
	Nacogdoches	5,891.1	271.7	4.6	12.5
	Navarro	18,699.0	4.8	<0.1	0.1
	Newton	2,263.0	0.2	<0.1	<0.1
	Nolan	4,124.5	4.5	0.1	0.2
	Nueces	85,767.7	1.0	<0.1	<0.1
	Ochiltree	21,348.9	33.3	0.2	0.2
	Oldham	2,124.3	1.3	0.1	0.1
	Orange	150,128.2	0.3	<0.1	<0.1
	Palo Pinto	18,403.3	9.6	0.1	0.3
	Panola	6,365.6	346.5	5.4	20.7
	Parker	8,241.7	261.7	3.2	9.8
	Pecos	52,954.2	8.2	<0.1	<0.1
	Polk	204,009.5	0.2	<0.1	<0.1
	Potter	2,029.4	0.4	<0.1	<0.1
	Reagan	9,333.1	410.5	4.4	7.8
	Reeves	20,772.2	164.2	0.8	1.1
	Roberts	7,690.6	38.2	0.5	1.2

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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, cont.	Robertson	158,344.3	45.4	<0.1	0.2
	Runnels	2,847.0	<0.1	<0.1	<0.1
	Rusk	582,134.9	65.8	<0.1	0.3
	Sabine	799.4	31.1	3.9	13.9
	San Augustine	1,131.5	182.1	16.1	50.8
	San Patricio	4,172.0	1.1	<0.1	<0.1
	Schleicher	967.3	27.0	2.8	5.0
	Scurry	14,187.6	1.1	<0.1	<0.1
	Shelby	4,920.2	133.6	2.7	8.2
	Sherman	78,073.5	<0.1	<0.1	<0.1
	Smith	11,231.1	0.2	<0.1	<0.1
	Somervell	746,005.3	4.8	<0.1	<0.1
	Starr	9,552.1	5.0	0.1	0.1
	Stephens	13,446.6	2.6	<0.1	0.1
	Sterling	719.1	36.6	5.1	11.9
	Stonewall	923.5	0.9	0.1	0.3
	Sutton	1,153.4	1.6	0.1	0.3
	Tarrant	104,430.2	1,443.0	1.4	3.9
	Terrell	543.9	0.1	<0.1	<0.1
	Terry	48,362.5	7.5	<0.1	<0.1
	Tyler	1,872.5	0.1	<0.1	<0.1
	Upshur	8,610.4	0.2	<0.1	<0.1
	Upton	7,975.3	462.6	5.8	14.2
	Van Zandt	4,139.1	0.1	<0.1	<0.1
	Walker	4,478.6	3.4	0.1	0.2

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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, cont.	Waller	9,829.5	0.1	<0.1	<0.1
	Ward	6,909.5	107.3	1.6	4.6
	Washington	2,430.9	2.2	0.1	0.2
	Webb	15,862.9	1,117.8	7.0	18.2
	Wharton	81,606.7	<0.1	<0.1	<0.1
	Wheeler	6,522.6	858.0	13.2	21.5
	Wichita	25,936.9	0.1	<0.1	<0.1
	Wilbarger	12,683.8	0.2	<0.1	<0.1
	Willacy	15,209.6	0.1	<0.1	<0.1
	Wilson	7,843.9	84.5	1.1	1.7
	Winkler	5,274.3	7.7	0.1	0.5
	Wise	24,966.0	529.7	2.1	8.9
	Wood	19,334.1	0.2	<0.1	<0.1
	Yoakum	77,325.3	7.5	<0.1	<0.1
	Young	21,162.7	0.1	<0.1	<0.1
	Zapata	2,697.4	1.1	<0.1	0.1
	Zavala	14,410.2	130.0	0.9	1.3
Utah	Carbon	15,067.2	7.3	<0.1	0.1
	Duchesne	119,811.3	85.5	0.1	0.1
	San Juan	10,632.5	0.3	<0.1	<0.1
	Sevier	52,512.6	<0.1	<0.1	<0.1
	Uintah	100,229.0	157.5	0.2	0.2
Virginia	Buchanan	313.9	0.6	0.2	0.3
	Dickenson	1,741.1	0.8	<0.1	0.2
	Wise	1,927.2	0.1	<0.1	<0.1

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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]
West Virginia	Barbour	773.8	19.9	2.6	6.9
	Brooke	4,551.6	54.8	1.2	5.1
	Doddridge	405.2	78.5	19.4	69.4
	Hancock	28,718.2	1.2	<0.1	<0.1
	Harrison	20,232.0	40.2	0.2	1.9
	Lewis	901.6	2.4	0.3	0.8
	Marion	5,982.4	70.1	1.2	4.9
	Marshall	158,358.9	84.5	0.1	0.7
	Monongalia	42,102.8	6.8	<0.1	0.1
	Ohio	3,825.2	116.5	3.0	10.4
	Pleasants	24,703.2	<0.1	<0.1	<0.1
	Preston	2,890.8	8.4	0.3	1.4
	Ritchie	587.7	2.8	0.5	1.7
	Taylor	824.9	52.9	6.4	17.6
	Tyler	4,934.8	2.1	<0.1	0.2
	Upshur	1,814.1	34.9	1.9	6.8
	Webster	1,292.1	2.3	0.2	0.3
	Wetzel	1,467.3	78.2	5.3	11.9
Wyoming	Big Horn	143,368.4	2.9	<0.1	<0.1
	Campbell	44,318.3	11.7	<0.1	0.1
	Carbon	137,130.5	4.5	<0.1	<0.1
	Converse	56,972.9	106.8	0.2	0.3
	Fremont	186,150.0	28.2	<0.1	<0.1
	Goshen	144,248.0	5.8	<0.1	<0.1
	Hot Springs	28,572.2	0.3	<0.1	<0.1

State	County	Total annual water use in 2010 (millions of gal)[a]	Annual average 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]
Wyoming, cont.	Johnson	43,205.1	<0.1	<0.1	<0.1
	Laramie	86,297.0	18.3	<0.1	<0.1
	Lincoln	74,562.2	0.8	<0.1	<0.1
	Natrona	62,885.9	1.8	<0.1	<0.1
	Niobrara	25,148.5	0.1	<0.1	<0.1
	Park	111,317.7	0.9	<0.1	<0.1
	Sublette	61,006.1	314.8	0.5	0.7
	Sweetwater	61,699.6	39.4	0.1	0.1
	Uinta	79,518.9	0.6	<0.1	<0.1
	Washakie	60,400.2	1.1	<0.1	<0.1

[a] County-level data accessed from the USGS website (http://water.usgs.gov/watuse/data/2010/) on November 11, 2014. Total daily water withdrawals 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, as reported to FracFocus (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 county (U.S. EPA, 2015c), and then dividing by 2010 USGS total water use for that county (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 (USGS, 2014). We used a rate of 71.6% for aquaculture (from Verdegem and Bosma, 2009) (evaporation per kg fish + infiltration per kg)/(total water use per kg)*100. These rates were multiplied by each USGS water use value (Maupin et al., 2014) to yield a total water consumption estimate. To calculate a consumption amount for hydraulic fracturing, we used a consumption rate of 82.5%. This was 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 that this is likely a low estimate of consumption since much of this return water is not subsequently treated and reused, but rather disposed of in underground injection wells—see Chapter 8.

Table B-3. Comparison of water use per well estimates from the EPA's project database of disclosures to FracFocus 1.0 (U.S. EPA, 2015c) and literature sources.

Source: (U.S. EPA, 2015c)

State	Basin[a]	Water use per well (gal) - FracFocus estimate[b]	Water use per well (gal) - Literature estimate[b,c]	FracFocus estimate as a percentage of literature estimate (%)
Colorado	Denver	403,686	2,900,000	14
North Dakota		2,140,842	2,200,000	97
Oklahoma		2,591,778	3,000,000	86
Pennsylvania[d]		4,301,701	4,450,000	97
Texas	Fort Worth	3,881,220	4,500,000	86
Texas	Salt	3,139,980	4,000,000	78
Texas	Western Gulf	3,777,648	4,600,000	82
Average[e]				77
Median[e]				86

[a] In cases where a basin is not specified, estimates were for the entire state and not specific to a particular basin. Basin boundaries for the FracFocus estimates were determined from data from the U.S. EIA (see U.S. EPA, 2015b).

[b] The type of literature estimate determined the specific comparison with FracFocus. If averages were given in the literature (as for North Dakota and Pennsylvania), those values were compared with FracFocus averages; where medians were given in the literature (as for Colorado, Oklahoma, and Texas), they were compared with FracFocus medians.

[c] Literature estimates were from the following sources: Colorado (Goodwin et al., 2014), North Dakota (North Dakota State Water Commission, 2014), Pennsylvania (Mitchell et al., 2013), and Texas (Nicot et al., 2012)—see far right-column and footnotes in Table B-5 for details on literature estimates. Where the literature provided a range, the mid-point was used. Only literature estimates that were not directly derived from FracFocus were included.

[d] The results from Mitchell et al. (2013) were used for Pennsylvania since they were derived from Pennsylvania Department of Environment Protection records. Estimates from Hansen et al. (2013) were not included here because they were based on FracFocus.

[e] Average and median percentage calculations were not weighted by the number of wells for a given estimate.

Table B-4. Comparison of well counts from the EPA's project database of disclosures to FracFocus 1.0 (U.S. EPA, 2015c) and state databases for North Dakota, Pennsylvania, and West Virginia.

State	FracFocus well counts[a]			State database well counts			FracFocus counts as a percentage of state database counts		
	2011	2012	Total	2011	2012	Total	2011	2012	Total
North Dakota[b]	613	1,458	2,071	1,225	1,740	2,965	50%	84%	70%
Pennsylvania[c]	1,137	1,257	2,394	1,963	1,347	3,310	58%	93%	72%
West Virginia[d]	93	176	269	214	251	465	43%	70%	58%
Average							50%	82%	67%

[a] FracFocus disclosures from U.S. EPA (2015c).

[b] For North Dakota state well counts, we used a North Dakota Department of Mineral Resources online database containing a list of horizontal wells completed in the Bakken Formation. Data for North Dakota were accessed on July 9, 2014 at https://www.dmr.nd.gov/oilgas/bakkenwells.asp.

[c] For Pennsylvania state well counts, we used completed horizontal wells as a proxy for hydraulically fractured wells in the state. The Pennsylvania Department of Environmental Protection has online databases of permitted and spudded wells, which differentiate between conventional and unconventional wells and can generate summary statistics at both the county and state scale. The number of spudded wells (i.e., wells drilled) provided a better comparison with the number of hydraulically fractured wells in FracFocus than that of permitted wells. The number of permitted wells was nearly double that of spudded in 2011 and 2012, indicating that almost half of the wells permitted were not drilled in that same year. Therefore, we used spudded wells here. Data for Pennsylvania were accessed on February 11, 2014 from http://www.depreportingservices.state.pa.us/ReportServer/Pages/ReportViewer.aspx?/Oil_Gas/Spud_External_Data.

[d] For West Virginia state well counts, data on the number of hydraulically fractured wells per year were received from the West Virginia Department of Environmental Protection on February 25, 2014.

Table B-5. Water use per hydraulically fractured well as reported in the EPA's project database of disclosures to FracFocus 1.0 (U.S. EPA, 2015c) by state and basin.

Souce: (U.S. EPA, 2015c)
Other literature estimates are also included where available. NA indicates other literature estimates were not available. All FracFocus estimates were limited to disclosures with valid state, county, and volume information. States listed in order addressed in Chapter 4.

State	Basin/total[a]	Number of disclosures	Mean (gal)	Median (gal)	10th percentile (gal)	90th percentile (gal)	Literature estimates
Texas	Permian	8,419	1,068,511	841,134	40,090	1,814,633	Many formations reported[b]
	Western Gulf	4,549	3,915,540	3,777,648	173,832	6,786,052	4.5–4.7 million gal (median, Eagle Ford play)[b]
	Fort Worth	2,564	3,880,724	3,881,220	923,381	6,649,406	4.5 million gal (median, Barnett play)[b]
	TX-LA-MS Salt	626	4,261,363	3,139,980	193,768	10,010,707	6–7.5 million gal (median, Texas-Haynesville play) and 0.5-1 million gallons (median, Cotton Valley play)[b]
	Anadarko	604	4,128,702	3,341,310	492,421	8,292,996	Many formations reported[b]
	Other	120	1,601,897	184,239	21,470	5,678,588	NA
	Total	16,882	2,494,452	1,420,613	58,709	6,115,195	Not reported by state[b]
Colorado	Denver	3,166	753,887	403,686	143,715	2,588,946	2.9 million gal (median, Wattenberg field of Niobrara play)[c]
	Uinta-Piceance	1,520	2,739,523	1,798,414	840,778	5,066,380	NA
	Raton	146	108,003	95,974	24,917	211,526	NA
	Other	66	605,740	183,408	34,412	601,816	NA
	Total	4,898	1,348,842	463,462	147,353	3,092,024	NA

State	Basin/total[a]	Number of disclosures	Mean (gal)	Median (gal)	10th percentile (gal)	90th percentile (gal)	Literature estimates
Wyoming	Greater Green River	861	841,702	752,979	147,020	1,493,266	NA
	Powder River	351	739,129	5,927	5,353	2,863,182	NA
	Other	193	613,618	41,664	22,105	1,818,606	NA
	Total	1,405	784,746	322,793	5,727	1,837,602	NA
Pennsylvania	Appalachian	2,445	4,301,701	4,184,936	2,313,649	6,615,981	4.2-4.6 million gal (average, Marcellus play, Susquehanna River Basin)[d]
	Total	2,445	4,301,701	4,184,936	2,313,649	6,615,981	4.1-4.5[d] and 4.3-4.6[e] million gal (average)
West Virginia	Appalachian	273	5,034,217	5,012,238	3,170,210	7,297,080	NA
	Total	273	5,034,217	5,012,238	3,170,210	7,297,080	4.7-6 million gal (average)[d]
Ohio	Appalachian	146	4,206,955	3,887,499	2,885,568	5,571,027	NA
	Total	146	4,206,955	3,887,499	2,885,568	5,571,027	NA
North Dakota	Williston	2,109	2,140,842	2,022,380	969,380	3,313,482	NA
	Total	2,109	2,140,842	2,022,380	969,380	3,313,482	2.2 million gal (average)[f]
Montana	Williston	187	1,640,085	1,552,596	375,864	3,037,398	NA
	Other	20	945,541	1,017,701	157,639	1,575,197	NA
	Total	207	1,572,979	1,455,757	367,326	2,997,552	NA
Oklahoma	Anadarko	935	3,742,703	3,259,774	1,211,700	6,972,652	Many formations reported[g]
	Arkoma	158	6,323,750	6,655,929	172,375	9,589,554	Many formations reported[g]
	Ardmore	98	6,637,332	8,021,559	81,894	8,835,842	Many formations reported[g]
	Other	592	1,963,480	1,866,144	1,319,247	2,785,352	NA
	Total	1,783	3,539,775	2,591,778	1,260,906	7,402,230	3 million gal (median)[g]

State	Basin/total[a]	Number of disclosures	Mean (gal)	Median (gal)	10th percentile (gal)	90th percentile (gal)	Literature estimates
Kansas	Total	121	1,135,973	1,453,788	10,836	2,227,926	NA
Arkansas	Arkoma	1,423	5,190,254	5,259,965	3,234,963	7,121,249	NA
	Total	1,423	5,190,254	5,259,965	3,234,963	7,121,249	NA
Louisiana	TX-LA-MS Salt	939	5,289,100	5,116,650	2,851,654	7,984,838	NA
	Other	27	896,899	232,464	87,003	3,562,400	NA
	Total	966	5,166,337	5,077,863	1,812,099	7,945,630	NA
Utah	Uinta-Piceance	1,396	375,852	304,105	77,166	770,699	NA
	Other	10	58,874	56,245	28,745	97,871	NA
	Total	1,406	373,597	302,075	76,286	769,360	NA
New Mexico	Permian	732	991,369	426,258	89,895	2,502,923	NA
	San Juan	363	159,680	97,734	27,217	313,919	NA
	Other	50	33,787	8,358	1,100	98,841	NA
	Total	1,145	685,882	175,241	35,638	1,871,666	NA

State	Basin/total[a]	Number of disclosures	Mean (gal)	Median (gal)	10th percentile (gal)	90th percentile (gal)	Literature estimates
California	San Joaquin	677	131,653	77,238	22,100	285,029	NA
	Other	34	132,391	36,099	13,768	361,192	NA
	Total	711	131,689	76,818	21,462	285,306	130,000 gallon (average) [h]

[a] Basin boundaries for the FracFocus estimates were determined from data from the U.S. EIA (see U.S. EPA, 2015b).

[b] Literature estimates for Texas were from Nicot et al. (2012), using proprietary data from IHS. In most cases, Nicot et al. reported at the play scale or smaller, rather than the EIA basin scale used for FracFocus. We reference 2011 and 2012 (partial year) for Nicot et al. where possible to overlap with the period of study for FracFocus, though more years were available for most formations. A range is reported for some medians because median water use was different for the two years. There were five formations reported for the Permian Basin (Wolfberry, Wolfcamp, Canyon, Clearfork, and San Andres-Greyburg). The most active area in the Permian Basin in 2011–2012 was the Wolfberry, which reported a median of 1 to 1.1 million gallons per well—these were mostly vertical wells. For the TX-LA-MS Salt Basin, Nicot et al. reported two formations (TX-Haynesville and Cotton Valley), with similar levels of activity in 2011-2012. Wells in TX-Haynesville were predominantly horizontal, while those in Cotton Valley were predominantly vertical (though horizontal wells in Cotton Valley were also reported). There were three fields reported in the Anadarko Basin (Granite Wash, Cleveland, and Marmaton). The most active area in the Anadarko Basin in 2011-2012 was the Granite Wash, which reported a median of 3.3 to 5.2 million gallons per well and where wells were mostly horizontal.

[c] Literature estimates for the Denver Basin were from Goodwin et al. (2014). Goodwin et al. assessed 200 randomly sampled wells in the Wattenberg Field of the Denver Basin (Niobrara Play), using industry data for wells operated by Noble Energy, drilled between January 1, 2010, and July 1, 2013. Water consumption is reported rather than water use, but Goodwin et al. assume, based on Noble Energy practices, that water use and water consumption were identical because none of the flowback or produced water is reused for hydraulic fracturing. Goodwin et al. reported drilling water consumed, hydraulic fracturing water consumed, and total water consumed. We present hydraulic fracturing water consumption here (hydraulic fracturing water consumption was approximately 95% of the total).

[d] Hansen et al. (2013), using data from FracFocus via Skytruth. For the Susquehanna River Basin portion of the Marcellus play, and for Pennsylvania as a whole, the range of annual averages is reported for 2011 and 2012. Similarly, for West Virginia, the range of annual averages is reported for 2011 and 2012 (partial year).

[e] Mitchell et al. (2013), using data reported to the Pennsylvania Department of Environmental Protection. Mitchell et al. reported water use in the Ohio River Basin for 2011 and 2012 (partial year) for horizontal and vertical wells. Here we report results for horizontal wells, which made up the majority of wells over the two-year period (i.e., 93%, 1,191 horizontal wells versus 96 vertical wells). A range is reported as before because the average water use differed between the two years.

[f] Literature estimates for North Dakota were from an informational bulletin from the North Dakota State Water Commission (2014). No further information was available.

[g] Murray (2013), who assessed water use for oil and gas operations from 2000–2010 for eight formations in Oklahoma using data from the Oklahoma Corporation Commission. It is not possible to extract an estimate corresponding to 2011–2012 from Murray without the raw data, because medians were presented for the 10-year period rather than separated by year.

[h] Literature estimates for California were from a California Council on Science and Technology report using data from FracFocus (CCST, 2014).

Table B-6. Estimated percent domestic use water from ground water and self-supplied by county.

Counties listed contained hydraulically fractured wells with valid state, county, and volume information (U.S. EPA, 2015c).
Data estimated from the USGS Water Census (Maupin et al., 2014).

State	County	Percent domestic use water from ground water[a,b]	Percent domestic use water self supplied[a,c]
Alabama	Jefferson	11.9	0.8
	Tuscaloosa	10.7	6.1
Arkansas	Cleburne	0.0	0.0
	Conway	8.6	8.6
	Faulkner	48.0	3.5
	Independence	20.5	9.4
	Logan	0.0	0.0
	Sebastian	0.0	0.0
	Van Buren	6.4	6.4
	White	0.4	0.0
	Yell	1.8	1.8
California	Colusa	97.9	10.3
	Glenn	96.5	21.6
	Kern	74.5	1.7
	Los Angeles	45.0	4.2
	Sutter	19.4	4.6
	Ventura	30.9	3.9
Colorado	Adams	18.1	2.8
	Arapahoe	19.3	1.3
	Boulder	1.7	1.5
	Broomfield	0.0	0.0
	Delta	59.6	28.4
	Dolores	55.2	51.4
	El Paso	19.6	5.1
	Elbert	100.0	75.2
	Fremont	15.6	15.6

State	County	Percent domestic use water from ground water[a,b]	Percent domestic use water self supplied[a,c]
Colorado, cont.	Garfield	36.7	28.5
	Jackson	84.4	40.7
	La Plata	24.4	11.3
	Larimer	2.3	0.8
	Las Animas	26.3	16.0
	Mesa	7.3	6.2
	Moffat	36.4	25.8
	Morgan	57.9	4.9
	Phillips	100.0	25.3
	Rio Blanco	60.2	32.5
	Routt	22.6	5.9
	San Miguel	71.4	32.5
	Weld	4.7	0.7
	Yuma	100.0	38.1
Kansas	Barber	100.0	19.0
	Clark	100.0	24.2
	Comanche	100.0	19.2
	Finney	100.0	2.1
	Grant	100.0	23.8
	Gray	100.0	36.4
	Harper	100.0	10.3
	Haskell	100.0	35.2
	Hodgeman	100.0	42.3
	Kearny	100.0	14.6
	Lane	100.0	24.1
	Meade	100.0	25.4
	Morton	100.0	21.7
	Ness	100.0	24.2
	Seward	100.0	15.7

State	County	Percent domestic use water from ground water[a,b]	Percent domestic use water self supplied[a,c]
Kansas, cont.	Sheridan	100.0	44.9
	Stanton	100.0	29.8
	Stevens	100.0	25.9
	Sumner	51.3	0.0
Louisiana	Allen	100.0	7.5
	Beauregard	100.0	20.6
	Bienville	100.0	16.8
	Bossier	29.4	14.6
	Caddo	12.2	8.8
	Calcasieu	98.3	12.7
	Caldwell	100.0	6.5
	Claiborne	100.0	10.4
	De Soto	55.8	21.8
	East Feliciana	100.0	11.8
	Jackson	100.0	13.8
	Lincoln	100.0	4.2
	Natchitoches	23.2	11.4
	Rapides	100.0	3.3
	Red River	83.2	27.6
	Sabine	67.5	36.2
	Tangipahoa	100.0	26.9
	Union	100.0	11.2
	Webster	100.0	11.3
	West Feliciana	100.0	2.4
	Winn	100.0	16.4
Michigan	Cheboygan	100.0	76.4
	Gladwin	100.0	84.5
	Kalkaska	100.0	89.0
	Missaukee	100.0	90.6
	Ogemaw	100.0	90.8
	Roscommon	100.0	91.9

State	County	Percent domestic use water from ground water[a,b]	Percent domestic use water self supplied[a,c]
Mississippi	Amite	100.0	26.0
	Wilkinson	100.0	11.1
Montana	Daniels	100.0	29.4
	Garfield	100.0	70.0
	Glacier	62.1	17.7
	Musselshell	89.9	54.5
	Richland	100.0	30.8
	Roosevelt	84.2	20.9
	Rosebud	51.3	10.3
	Sheridan	100.0	31.0
New Mexico	Chaves	100.0	11.8
	Colfax	30.7	2.6
	Eddy	100.0	2.2
	Harding	100.0	25.0
	Lea	100.0	17.4
	Rio Arriba	84.0	42.3
	Roosevelt	100.0	8.9
	San Juan	14.6	12.9
	Sandoval	98.9	23.2
North Dakota	Billings	NA	33.3
	Bottineau	100.0	13.7
	Burke	100.0	12.5
	Divide	100.0	12.5
	Dunn	100.0	21.4
	Golden Valley	100.0	7.7
	Mckenzie	75.8	15.7
	Mclean	12.5	9.9
	Mountrail	65.7	11.5
	Stark	NA	5.7
	Williams	27.4	7.3

State	County	Percent domestic use water from ground water[a,b]	Percent domestic use water self supplied[a,c]
Ohio	Ashland	98.8	57.4
	Belmont	76.4	8.9
	Carroll	96.4	76.4
	Columbiana	63.2	43.2
	Coshocton	99.3	34.9
	Guernsey	37.6	9.5
	Harrison	65.6	45.9
	Jefferson	33.1	10.2
	Knox	99.2	41.1
	Medina	98.4	83.1
	Muskingum	93.4	17.0
	Noble	8.0	8.0
	Portage	32.6	18.3
	Stark	91.2	30.9
	Tuscarawas	94.0	23.5
	Wayne	99.1	49.0
Oklahoma	Alfalfa	100.0	14.6
	Beaver	100.0	47.9
	Beckham	100.0	10.6
	Blaine	100.0	8.8
	Bryan	26.0	7.8
	Caddo	45.4	35.1
	Canadian	100.0	0.0
	Carter	17.5	0.5
	Coal	31.5	27.5
	Custer	70.8	13.2
	Dewey	100.0	22.5
	Ellis	100.0	31.4
	Garvin	41.3	15.8
	Grady	100.0	34.2
	Grant	100.0	13.2
	Harper	100.0	22.6

State	County	Percent domestic use water from ground water[a,b]	Percent domestic use water self supplied[a,c]
Oklahoma, cont.	Hughes	23.6	6.7
	Jefferson	13.5	1.8
	Johnston	53.4	1.1
	Kay	39.2	4.6
	Kingfisher	100.0	28.3
	Kiowa	10.3	0.0
	Latimer	12.6	12.6
	Le Flore	14.3	13.1
	Logan	61.1	34.6
	Love	100.0	3.8
	Major	100.0	28.1
	Marshall	20.1	4.4
	Mcclain	95.9	23.9
	Noble	23.3	14.3
	Oklahoma	22.0	2.5
	Osage	18.0	14.9
	Pawnee	38.2	27.7
	Payne	47.9	12.6
	Pittsburg	0.6	0.0
	Roger Mills	80.1	19.4
	Seminole	78.8	16.1
	Stephens	99.2	14.9
	Texas	100.0	10.9
	Washita	53.9	18.2
	Woods	100.0	14.7
Pennsylvania	Allegheny	15.7	15.3
	Armstrong	45.3	36.8
	Beaver	54.7	26.8
	Blair	34.9	24.0
	Bradford	100.0	65.2
	Butler	51.8	42.8
	Cameron	29.0	29.0

State	County	Percent domestic use water from ground water[a,b]	Percent domestic use water self supplied[a,c]
Pennsylvania, cont.	Centre	93.1	21.3
	Clarion	61.5	55.8
	Clearfield	38.4	22.7
	Clinton	48.4	38.1
	Columbia	77.5	56.7
	Crawford	97.7	66.0
	Elk	25.3	15.6
	Fayette	19.2	16.1
	Forest	100.0	78.3
	Greene	31.9	31.9
	Huntingdon	73.2	57.8
	Indiana	52.2	49.1
	Jefferson	60.7	46.1
	Lawrence	40.5	38.8
	Lycoming	60.0	29.3
	McKean	56.6	33.3
	Potter	93.7	58.1
	Somerset	42.6	33.5
	Sullivan	100.0	76.9
	Susquehanna	79.9	74.7
	Tioga	81.3	58.3
	Venango	95.9	32.7
	Warren	96.9	49.4
	Washington	21.6	21.5
	Westmoreland	21.3	19.8
	Wyoming	100.0	70.6
Texas	Andrews	100.0	23.4
	Angelina	100.0	9.8
	Archer	16.9	16.9
	Atascosa	100.0	16.3
	Austin	100.0	55.6
	Bee	100.0	52.5

State	County	Percent domestic use water from ground water[a,b]	Percent domestic use water self supplied[a,c]
Texas, cont.	Borden	100.0	71.4
	Bosque	88.7	30.3
	Brazos	100.0	2.1
	Brooks	100.0	35.3
	Burleson	100.0	42.9
	Cherokee	87.5	26.1
	Clay	44.6	36.7
	Cochran	100.0	23.3
	Coke	29.0	28.9
	Colorado	100.0	45.4
	Concho	96.8	5.0
	Cooke	75.5	8.9
	Cottle	100.0	21.4
	Crane	100.0	14.3
	Crockett	100.0	42.5
	Crosby	35.6	19.0
	Culberson	100.0	13.8
	Dallas	1.0	0.7
	Dawson	100.0	33.8
	DeWitt	100.0	42.3
	Denton	9.0	3.6
	Dimmit	100.0	30.5
	Ector	100.0	28.3
	Edwards	100.0	42.1
	Ellis	32.2	7.9
	Erath	100.0	43.3
	Fayette	100.0	27.6
	Fisher	NA	36.8
	Franklin	0.9	0.0
	Freestone	100.0	31.2
	Frio	100.0	20.4
	Gaines	100.0	45.5

State	County	Percent domestic use water from ground water[a,b]	Percent domestic use water self supplied[a,c]
Texas, cont.	Garza	20.1	17.2
	Glasscock	NA	100.0
	Goliad	NA	66.7
	Gonzales	96.8	15.9
	Grayson	56.0	4.2
	Gregg	20.8	14.1
	Grimes	100.0	26.0
	Hansford	100.0	16.4
	Hardeman	87.6	13.3
	Hardin	100.0	29.5
	Harrison	43.8	24.8
	Hartley	100.0	39.7
	Haskell	100.0	15.7
	Hemphill	100.0	27.5
	Hidalgo	9.2	1.6
	Hockley	100.0	27.4
	Hood	70.8	39.8
	Houston	79.7	36.6
	Howard	100.0	19.8
	Hutchinson	27.3	14.9
	Irion	100.0	50.0
	Jack	46.7	43.8
	Jefferson	25.0	5.8
	Jim Hogg	NA	25.0
	Johnson	34.9	6.8
	Jones	60.5	60.5
	Karnes	100.0	17.6
	Kenedy	100.0	25.0
	Kent	100.0	37.5
	King	100.0	33.3
	Kleberg	100.0	1.9
	Knox	86.2	24.2

State	County	Percent domestic use water from ground water[a,b]	Percent domestic use water self supplied[a,c]
Texas, cont.	La Salle	100.0	43.3
	Lavaca	100.0	56.0
	Lee	100.0	15.9
	Leon	100.0	41.4
	Liberty	98.5	42.5
	Limestone	46.5	32.5
	Lipscomb	100.0	23.5
	Live Oak	32.8	32.1
	Loving	NA	0.0
	Lynn	64.1	32.2
	Madison	100.0	66.9
	Marion	13.7	8.4
	Martin	100.0	48.9
	Maverick	27.6	27.6
	McMullen	100.0	40.0
	Medina	98.0	23.6
	Menard	36.4	36.4
	Midland	100.0	22.1
	Milam	82.5	41.1
	Mitchell	100.0	14.7
	Montague	57.1	49.7
	Montgomery	100.0	26.6
	Moore	100.0	8.1
	Nacogdoches	55.6	21.6
	Navarro	22.0	22.0
	Newton	100.0	63.7
	Nolan	100.0	17.6
	Nueces	5.6	5.6
	Ochiltree	100.0	16.8
	Oldham	100.0	58.8
	Orange	99.1	41.2
	Palo Pinto	11.7	11.7

State	County	Percent domestic use water from ground water[a,b]	Percent domestic use water self supplied[a,c]
Texas, cont.	Panola	96.6	58.7
	Parker	63.5	41.1
	Pecos	100.0	31.3
	Polk	41.9	41.7
	Potter	100.0	12.6
	Reagan	100.0	16.2
	Reeves	100.0	31.1
	Roberts	100.0	33.3
	Robertson	97.1	22.5
	Runnels	13.5	13.5
	Rusk	90.7	41.8
	Sabine	76.2	69.0
	San Augustine	78.0	74.4
	San Patricio	88.8	21.8
	Schleicher	100.0	40.0
	Scurry	32.5	27.7
	Shelby	66.2	58.2
	Sherman	100.0	33.3
	Smith	48.0	13.7
	Somervell	87.7	69.3
	Starr	23.2	23.2
	Stephens	13.5	13.5
	Sterling	NA	18.8
	Stonewall	NA	40.0
	Sutton	100.0	26.7
	Tarrant	3.7	1.3
	Terrell	100.0	25.0
	Terry	100.0	16.7
	Tyler	100.0	73.6
	Upshur	54.1	23.2
	Upton	100.0	15.2
	Van Zandt	65.7	39.0

State	County	Percent domestic use water from ground water[a,b]	Percent domestic use water self supplied[a,c]
Texas, cont.	Walker	57.7	30.6
	Waller	100.0	37.2
	Ward	100.0	4.5
	Washington	48.2	36.0
	Webb	99.4	0.5
	Wharton	100.0	45.9
	Wheeler	100.0	31.3
	Wichita	8.8	2.9
	Wilbarger	100.0	11.5
	Willacy	28.4	28.4
	Wilson	100.0	6.9
	Winkler	100.0	3.8
	Wise	51.3	50.4
	Wood	21.3	12.9
	Yoakum	100.0	36.0
	Young	19.3	18.9
	Zapata	13.9	13.9
	Zavala	100.0	15.2
Utah	Carbon	50.0	1.2
	Duchesne	57.1	10.4
	San Juan	68.3	47.5
	Sevier	100.0	10.0
	Uintah	87.7	3.1
Virginia	Buchanan	NA	27.6
	Dickenson	2.5	2.5
	Wise	5.9	2.3
West Virginia	Barbour	24.1	24.8
	Brooke	33.4	6.8
	Doddridge	60.6	62.1
	Hancock	67.7	6.9
	Harrison	8.8	8.9
	Lewis	29.5	30.3

State	County	Percent domestic use water from ground water[a,b]	Percent domestic use water self supplied[a,c]
West Virginia, cont.	Marion	5.8	4.9
	Marshall	96.5	12.0
	Monongalia	5.3	5.5
	Ohio	5.4	3.4
	Pleasants	100.0	27.9
	Preston	66.1	41.0
	Ritchie	45.2	46.4
	Taylor	14.9	14.9
	Tyler	44.4	39.2
	Upshur	27.3	27.8
	Webster	41.9	43.2
	Wetzel	96.3	28.6
Wyoming	Big Horn	79.4	11.3
	Campbell	100.0	0.6
	Carbon	63.8	6.7
	Converse	96.5	17.0
	Fremont	49.3	23.7
	Goshen	100.0	21.1
	Hot Springs	31.9	8.2
	Johnson	40.8	35.4
	Laramie	38.1	13.0
	Lincoln	82.4	9.0
	Natrona	69.0	6.6
	Niobrara	100.0	16.3
	Park	18.9	13.7

State	County	Percent domestic use water from ground water[a,b]	Percent domestic use water self supplied[a,c]
Wyoming, cont.	Sublette	54.6	22.1
	Sweetwater	3.5	0.4
	Uinta	19.5	11.5
	Washakie	100.0	16.0

[a] Data accessed from the USGS website (http://water.usgs.gov/watuse/data/2010/) on November 11, 2014. Domestic water use is water used 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 (Maupin et al., 2014).

[b] Percent domestic water use from ground water estimated with the following equation: (Domestic public supply volume from ground water + Domestic self-supplied volume from ground water)/ Domestic total water use volume * 100. Domestic public supply volume from ground water was estimated by multiplying the volume of domestic water from public supply by the ratio of public supply volume from ground water to total public supply volume.

[c] Percent domestic water use self-supplied estimated by dividing the volume of domestic water self-supplied by total domestic water use volume.

Table B-7. Projected hydraulic fracturing water use by Texas counties between 2015 and 2060, expressed as a percentage of 2010 total county water use.

Hydraulic fracturing water use data from Nicot et al. (2012). Total water use data from 2010 from the USGS Water Census (Maupin et al., 2014). All 254 Texas counties are listed by descending order of percentages in 2030.

Texas county	Projected hydraulic fracturing water use as a percentage of 2010 total water use[a,b]									
	2015	2020	2025	2030	2035	2040	2045	2050	2055	2060
McMullen	126.2	137.0	152.1	165.1	176.7	164.0	145.3	126.6	108.0	89.3
Irion	36.1	59.2	70.5	63.7	53.4	43.1	32.8	22.4	12.1	5.4
La Salle	58.4	58.3	59.7	60.8	61.9	54.6	45.3	36.0	26.7	17.4
San Augustine	60.2	56.2	52.2	48.2	44.2	40.2	36.2	32.1	28.1	24.1
Sterling	12.0	32.0	39.9	40.5	41.0	34.7	28.3	21.9	15.6	10.7
Dimmit	38.2	38.1	38.9	39.0	38.7	33.9	27.9	22.0	16.0	10.1
Sabine	9.6	19.2	28.7	38.3	35.1	31.9	28.7	25.6	22.3	19.2
Leon	9.9	19.3	27.0	34.6	32.9	29.0	25.1	21.2	17.3	13.5
Karnes	48.1	43.0	37.9	32.6	27.2	21.8	16.4	11.0	5.6	0.2
Loving	13.1	17.4	23.4	29.4	28.8	26.2	23.6	20.9	18.3	15.7
Shackelford	0.0	7.9	15.7	23.6	21.2	18.9	16.5	14.1	11.8	9.4
Madison	5.5	11.8	15.7	19.7	17.4	15.2	13.0	10.9	8.7	6.5
Schleicher	10.5	15.8	19.1	19.7	17.1	14.5	11.9	9.3	6.7	4.7
Sutton	0.0	11.0	15.1	19.1	23.2	20.6	18.1	15.5	12.9	10.3
Shelby	11.0	20.4	19.4	18.4	17.4	15.7	14.1	12.5	10.9	9.3
DeWitt	26.9	24.1	21.4	18.4	15.4	12.3	9.3	6.3	3.2	0.2
Hemphill	25.7	23.1	20.5	17.8	15.2	12.6	10.0	7.3	4.7	2.1

Texas county	Projected hydraulic fracturing water use as a percentage of 2010 total water use[a,b]									
	2015	2020	2025	2030	2035	2040	2045	2050	2055	2060
Terrell	0.0	9.7	13.2	16.8	20.4	18.2	15.9	13.6	11.3	9.0
Coryell	7.0	24.4	22.8	16.5	10.1	3.8	0.0	0.0	0.0	0.0
Montague	28.6	24.5	20.4	16.3	12.2	8.2	4.1	0.0	0.0	0.0
Crockett	7.6	12.5	14.8	13.4	11.2	9.1	6.9	4.7	2.5	1.1
Upton	12.1	15.2	14.1	12.9	11.7	9.8	7.9	5.9	4.0	2.7
Borden	3.1	8.6	12.0	12.1	12.2	10.3	8.4	6.4	4.5	3.1
Live Oak	13.3	12.4	11.5	11.8	12.2	12.7	13.2	11.7	9.8	7.8
Reagan	11.2	14.0	12.7	11.3	9.9	8.1	6.4	4.6	2.8	1.6
Clay	3.2	5.9	8.6	11.3	10.3	9.4	8.4	7.5	6.6	5.6
Wheeler	17.6	15.3	13.1	10.8	8.6	6.3	4.1	1.8	0.0	0.0
Lavaca	7.9	13.2	12.0	10.7	9.4	8.1	6.7	5.4	4.0	2.7
Washington	0.0	6.7	11.8	10.7	9.6	8.6	7.5	6.4	5.3	4.3
Nacogdoches	7.9	11.4	10.7	10.0	9.2	8.3	7.5	6.6	5.7	4.9
Hill	17.1	14.7	12.2	9.8	7.3	4.9	2.4	0.0	0.0	0.0
Jack	3.5	5.3	7.1	8.8	7.9	7.1	6.2	5.3	4.4	3.5
Panola	7.2	10.2	9.2	8.5	7.7	7.0	6.3	5.5	4.8	4.0
Jim Hogg	4.8	6.4	8.0	8.0	6.9	6.0	4.9	3.9	2.9	1.8
Howard	4.4	7.1	8.5	8.0	6.8	5.6	4.4	3.2	2.1	1.3
Parker	3.7	5.0	6.3	7.6	6.8	6.1	5.3	4.5	3.8	3.0
Hamilton	8.8	10.7	8.9	7.1	5.3	3.5	1.8	0.0	0.0	0.0
Johnson	14.2	11.9	9.5	7.1	4.7	2.4	0.0	0.0	0.0	0.0
Midland	6.7	8.3	7.7	7.1	6.2	5.2	4.1	3.0	2.0	1.2

Texas county	Projected hydraulic fracturing water use as a percentage of 2010 total water use[a,b]									
	2015	2020	2025	2030	2035	2040	2045	2050	2055	2060
Kenedy	4.1	5.4	6.8	6.8	5.9	5.1	4.1	3.3	2.4	1.6
Fayette	3.9	8.4	7.6	6.6	5.5	4.4	3.4	2.3	1.2	0.2
Lee	2.1	4.1	5.3	6.5	5.8	5.1	4.3	3.6	2.9	2.1
Winkler	2.9	3.8	5.1	6.3	6.0	5.4	4.7	4.1	3.4	2.8
Wilson	6.7	7.7	7.0	6.2	5.4	4.6	3.9	3.1	2.3	1.5
Martin	5.7	7.1	6.5	6.0	5.3	4.4	3.5	2.6	1.8	1.2
Burleson	1.0	2.9	4.3	5.7	5.1	4.5	3.9	3.3	2.6	2.0
Atascosa	6.3	5.7	5.6	5.6	5.6	5.6	5.0	4.2	3.4	2.7
Bosque	1.8	3.0	4.3	5.5	5.1	4.6	4.2	3.7	3.2	2.8
Webb	7.5	7.1	6.3	5.4	4.6	3.8	3.1	2.3	1.4	0.5
Gonzales	8.0	7.1	6.2	5.3	4.4	3.6	2.7	1.8	0.9	0.0
Marion	1.1	2.4	3.8	5.1	5.2	4.7	4.2	3.7	3.2	2.7
Harrison	4.3	6.1	5.5	5.1	4.6	4.2	3.7	3.3	2.9	2.4
Eastland	0.0	3.9	5.9	5.0	4.2	3.3	2.5	1.7	0.8	0.0
Archer	1.0	2.4	3.6	4.9	4.5	4.1	3.7	3.3	2.9	2.5
Zavala	4.7	5.5	5.2	4.9	4.6	4.3	4.0	3.4	2.7	2.0
Roberts	6.9	6.0	5.1	4.2	3.4	2.5	1.6	0.7	0.0	0.0
Maverick	2.5	3.0	3.6	4.2	4.8	4.5	4.0	3.6	3.1	2.6
Cooke	11.9	9.3	6.7	4.1	1.5	0.0	0.0	0.0	0.0	0.0
Ward	2.7	3.2	4.2	4.1	4.0	3.6	3.2	2.7	2.3	1.9
Austin	0.0	1.2	2.5	3.7	3.4	3.0	2.6	2.2	1.9	1.5
Reeves	1.4	1.8	2.7	3.7	3.9	3.6	3.3	3.0	2.6	2.3

Texas county	Projected hydraulic fracturing water use as a percentage of 2010 total water use[a,b]									
	2015	2020	2025	2030	2035	2040	2045	2050	2055	2060
Glasscock	3.1	4.1	3.9	3.6	3.1	2.6	2.1	1.5	1.0	0.7
Tyler	1.9	2.6	3.2	3.2	2.8	2.4	2.0	1.6	1.1	0.7
Hood	1.4	2.0	2.6	3.2	2.9	2.6	2.2	1.9	1.6	1.3
Garza	1.5	2.0	2.5	2.9	2.7	2.4	2.1	1.8	1.5	1.2
Andrews	2.3	3.0	2.9	2.7	2.6	2.3	2.0	1.7	1.4	1.1
Crane	1.3	1.7	2.1	2.6	3.1	2.8	2.5	2.2	1.9	1.7
Erath	0.9	1.4	1.9	2.4	2.2	2.0	1.8	1.6	1.4	1.2
Wise	3.6	3.2	2.8	2.4	2.0	1.6	1.2	0.8	0.4	0.0
Upshur	0.2	0.9	1.7	2.4	2.9	2.6	2.3	2.1	1.8	1.5
Mitchell	1.2	1.6	2.0	2.4	2.1	1.9	1.7	1.4	1.2	0.9
Ector	1.5	2.0	2.1	2.3	2.2	1.9	1.7	1.4	1.2	1.0
Culberson	0.3	0.4	1.3	2.2	2.9	2.6	2.4	2.1	1.9	1.6
Lipscomb	1.7	3.0	2.6	2.1	1.7	1.3	0.8	0.4	0.0	0.0
Angelina	0.4	0.9	1.5	2.1	2.2	2.0	1.8	1.6	1.4	1.2
Houston	2.1	2.7	2.4	2.1	1.8	1.5	1.2	0.9	0.6	0.3
Frio	1.8	1.8	1.9	1.9	1.8	1.8	1.7	1.5	1.2	0.9
Newton	1.8	2.3	2.1	1.8	1.6	1.3	1.0	0.8	0.5	0.3
Kleberg	1.0	1.4	1.7	1.7	1.5	1.3	1.1	0.8	0.6	0.4
Brooks	1.0	1.3	1.7	1.7	1.5	1.2	1.0	0.8	0.6	0.4
Brazos	0.4	0.9	1.2	1.5	1.4	1.2	1.0	0.8	0.7	0.5
Comanche	0.4	0.7	1.0	1.4	1.2	1.1	1.0	0.8	0.7	0.5
Ochiltree	0.6	1.1	1.5	1.2	1.0	0.7	0.5	0.2	0.0	0.0

Texas county	Projected hydraulic fracturing water use as a percentage of 2010 total water use[a,b]									
	2015	2020	2025	2030	2035	2040	2045	2050	2055	2060
Palo Pinto	0.3	0.6	0.9	1.2	1.1	1.0	0.8	0.7	0.6	0.5
Limestone	0.9	1.0	1.1	1.2	1.1	1.0	0.8	0.7	0.6	0.4
Duval	0.7	0.9	1.1	1.1	1.0	0.8	0.7	0.5	0.4	0.3
Stephens	0.1	0.4	0.8	1.1	1.0	0.9	0.8	0.6	0.5	0.4
Dawson	0.5	0.8	1.0	1.1	1.1	1.0	0.8	0.6	0.5	0.3
Scurry	0.0	0.6	0.8	1.0	1.2	1.1	0.9	0.8	0.7	0.5
Bee	0.8	1.1	1.1	1.0	0.9	0.7	0.6	0.4	0.3	0.1
Val Verde	0.0	0.5	0.8	0.9	1.1	1.0	0.9	0.8	0.6	0.5
Colorado	<0.1	0.3	0.6	0.9	0.8	0.7	0.6	0.5	0.4	0.4
Tarrant	2.1	1.7	1.3	0.9	0.4	0.0	0.0	0.0	0.0	0.0
Zapata	0.5	0.7	0.8	0.8	0.7	0.6	0.5	0.4	0.3	0.2
Ellis	0.3	0.5	0.6	0.8	0.7	0.6	0.6	0.5	0.4	0.3
Jim Wells	0.4	0.6	0.7	0.7	0.6	0.5	0.4	0.4	0.3	0.2
Lynn	0.0	0.4	0.6	0.7	0.8	0.8	0.7	0.6	0.5	0.4
Henderson	0.1	0.3	0.5	0.7	0.8	0.7	0.6	0.5	0.4	0.4
Hansford	0.0	0.4	0.8	0.7	0.5	0.4	0.3	0.2	0.1	0
Gaines	0.2	0.3	0.5	0.5	0.5	0.4	0.4	0.3	0.2	0.2
Gregg	0.1	0.2	0.3	0.4	0.4	0.4	0.4	0.3	0.3	0.2
Refugio	0.2	0.3	0.4	0.4	0.3	0.3	0.2	0.2	0.1	0.1
Caldwell	0.4	0.5	0.4	0.4	0.3	0.3	0.2	0.2	0.1	0.1
Pecos	0.1	0.1	0.2	0.4	0.5	0.4	0.4	0.3	0.3	0.2
Anderson	0.1	0.2	0.3	0.4	0.4	0.4	0.4	0.3	0.3	0.2

Texas county	Projected hydraulic fracturing water use as a percentage of 2010 total water use[a,b]									
	2015	2020	2025	2030	2035	2040	2045	2050	2055	2060
Young	0.0	0.1	0.2	0.4	0.3	0.3	0.3	0.2	0.2	0.1
San Patricio	0.2	0.3	0.4	0.4	0.3	0.3	0.2	0.2	0.1	0.1
Smith	0.1	0.1	0.2	0.3	0.4	0.3	0.3	0.3	0.2	0.2
Cherokee	0.1	0.2	0.2	0.3	0.4	0.3	0.3	0.2	0.2	0.2
McLennan	0.1	0.1	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.1
Terry	0.0	0.2	0.2	0.3	0.3	0.3	0.3	0.2	0.2	0.2
Starr	0.2	0.2	0.3	0.3	0.2	0.2	0.2	0.1	0.1	0.1
Cochran	0.1	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.1
Jasper	0.2	0.3	0.2	0.2	0.2	0.1	0.1	0.1	0.1	<0.1
Dallas	0.2	0.3	0.2	0.2	0.1	0.1	<0.1	0.0	0.0	0.0
Robertson	0.1	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1
Grimes	<0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
Yoakum	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1
Freestone	0.1	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.1	0.1
Cass	<0.1	0.1	0.1	0.2	0.2	0.2	0.1	0.1	0.1	0.1
Hutchinson	0.0	0.1	0.2	0.1	0.1	0.1	0.1	<0.1	<0.1	0.0
Rusk	<0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	<0.1
Willacy	<0.1	0.1	0.1	0.1	0.1	0.1	0.1	<0.1	<0.1	<0.1
Victoria	<0.1	0.1	0.1	0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1
Sherman	0.0	0.0	<0.1	0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1
Calhoun	<0.1	0.1	0.1	0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1
Lubbock	0.0	0.0	<0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

Texas county	Projected hydraulic fracturing water use as a percentage of 2010 total water use[a,b]									
	2015	2020	2025	2030	2035	2040	2045	2050	2055	2060
Jackson	<0.1	<0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Matagorda	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Polk	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Wharton	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Nueces	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Hidalgo	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cameron	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Somervell	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Goliad	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Brazoria	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fort Bend	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Aransas	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Armstrong	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bailey	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bandera	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bastrop	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Baylor	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bell	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bexar	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Blanco	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bowie	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Brewster	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Texas county	Projected hydraulic fracturing water use as a percentage of 2010 total water use[a,b]									
	2015	2020	2025	2030	2035	2040	2045	2050	2055	2060
Briscoe	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Brown	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Burnet	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Callahan	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Camp	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Carson	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Castro	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chambers	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Childress	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Coke	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Coleman	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Collin	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Collingsworth	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Comal	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Concho	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cottle	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Crosby	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Dallam	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Deaf Smith	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Delta	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Denton	1.7	1.1	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Dickens	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Texas county	Projected hydraulic fracturing water use as a percentage of 2010 total water use[a,b]									
	2015	2020	2025	2030	2035	2040	2045	2050	2055	2060
Donley	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Edwards	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
El Paso	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Falls	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fannin	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fisher	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Floyd	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Foard	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Franklin	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Galveston	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gillespie	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gray	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Grayson	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Guadalupe	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hale	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hall	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hardeman	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hardin	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Harris	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hartley	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Haskell	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hays	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Texas county	Projected hydraulic fracturing water use as a percentage of 2010 total water use[a,b]									
	2015	2020	2025	2030	2035	2040	2045	2050	2055	2060
Hockley	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hopkins	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hudspeth	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hunt	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Jeff Davis	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Jefferson	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Jones	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Kaufman	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Kendall	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Kent	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Kerr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Kimble	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
King	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Kinney	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Knox	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Lamar	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Lamb	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Lampasas	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Liberty	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Llano	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
McCulloch	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mason	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Texas county	Projected hydraulic fracturing water use as a percentage of 2010 total water use[a,b]									
	2015	2020	2025	2030	2035	2040	2045	2050	2055	2060
Medina	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Menard	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Milam	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mills	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Montgomery	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Moore	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Morris	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Motley	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Navarro	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Nolan	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Oldham	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Orange	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Parmer	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Potter	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Presidio	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Rains	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Randall	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Real	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Red River	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Rockwall	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Runnels	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
San Jacinto	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Texas county	Projected hydraulic fracturing water use as a percentage of 2010 total water use[a,b]									
	2015	2020	2025	2030	2035	2040	2045	2050	2055	2060
San Saba	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Stonewall	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Swisher	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Taylor	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Throckmorton	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Titus	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Tom Green	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Travis	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Trinity	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Uvalde	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Van Zandt	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Walker	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Waller	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Wichita	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Wilbarger	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Williamson	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Wood	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

[a] Total water use data accessed from the USGS website (http://water.usgs.gov/watuse/data/2010/) on April 21, 2015. Data from Nicot et al. (2012) transcribed.

[b] Percentages calculated by dividing projected hydraulic fracturing water use volumes from Nicot et al. (2012) by 2010 total water use from the USGS and multiplying by 100. Percentages less than 0.1 were not rounded and simply noted as "<0.1", but where the percentage was actually zero because there was no projected hydraulic fracturing water use we noted that as "0.0".

B.2. References for Appendix B

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Appendix C

Chemical Mixing Supplemental Tables and Information

Appendix C. Chemical Mixing Supplemental Tables and Information

C.1. Supplemental Tables and Information

Table C-1. Chemicals reported to FracFocus in 10% or more of disclosures for gas-producing wells, with the number of disclosures where chemical is reported, percentage of disclosures, and the median maximum concentration (% by mass) of that chemical in hydraulic fracturing fluid.

Chemicals ranked by frequency of occurrence (U.S. EPA, 2015c).

Chemical name	CASRN	Number of disclosures	Percentage of disclosures	Median maximum concentration in hydraulic fracturing fluid (% by mass)
Hydrochloric acid	7647-01-0	12,351	72.8%	15%
Methanol	67-56-1	12,269	72.3%	30%
Distillates, petroleum, hydrotreated light	64742-47-8	11,897	70.1%	30%
Isopropanol	67-63-0	8,008	47.2%	30%
Water	7732-18-5	7,998	47.1%	63%
Ethanol	64-17-5	6,325	37.3%	5%
Propargyl alcohol	107-19-7	5,811	34.2%	10%
Glutaraldehyde	111-30-8	5,635	33.2%	30%
Ethylene glycol	107-21-1	5,493	32.4%	35%
Citric acid	77-92-9	4,832	28.5%	60%
Sodium hydroxide	1310-73-2	4,656	27.4%	5%
Peroxydisulfuric acid, diammonium salt	7727-54-0	4,618	27.2%	100%
Quartz	14808-60-7	3,758	22.1%	10%
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	3,668	21.6%	100%
Sodium chloride	7647-14-5	3,608	21.3%	30%
Guar gum	9000-30-0	3,586	21.1%	60%
Acetic acid	64-19-7	3,563	21.0%	50%
2-Butoxyethanol	111-76-2	3,325	19.6%	10%
Naphthalene	91-20-3	3,294	19.4%	5%
Solvent naphtha, petroleum, heavy arom.	64742-94-5	3,287	19.4%	30%
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides	68424-85-1	3,259	19.2%	7%
Potassium hydroxide	1310-58-3	2,843	16.8%	15%
Ammonium chloride	12125-02-9	2,483	14.6%	10%
Choline chloride	67-48-1	2,477	14.6%	75%

Chemical name	CASRN	Number of disclosures	Percentage of disclosures	Median maximum concentration in hydraulic fracturing fluid (% by mass)
Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture)	127087-87-0	2,455	14.5%	5%
Sodium chlorite	7758-19-2	2,372	14.0%	10%
1,2,4-Trimethylbenzene	95-63-6	2,229	13.1%	1%
Carbonic acid, dipotassium salt	584-08-7	2,154	12.7%	60%
Methenamine	100-97-0	2,134	12.6%	1%
Formic acid	64-18-6	2,118	12.5%	60%
Didecyl dimethyl ammonium chloride	7173-51-5	2,063	12.2%	10%
N,N-Dimethylformamide	68-12-2	1,892	11.2%	13%
Phenolic resin	9003-35-4	1,852	10.9%	5%
Thiourea polymer	68527-49-1	1,702	10.0%	30%
Polyethylene glycol	25322-68-3	1,696	10.0%	60%

Note: Analysis considered 17,035 disclosures and 291,363 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 (1,587) or other, query-specific criteria were excluded from analysis.

Table C-2. Chemicals reported to FracFocus in 10% or more of disclosures for oil-producing wells, with the number of disclosures where chemical is reported, percentage of disclosures, and the median maximum concentration (% by mass) of that chemical in hydraulic fracturing fluid.

Chemicals ranked by frequency of occurrence (U.S. EPA, 2015c).

Chemical name	CASRN	Number of disclosures	Percentage of disclosures	Median maximum concentration in hydraulic fracturing fluid (% by mass)
Methanol	67-56-1	12,484	71.8%	30%
Distillates, petroleum, hydrotreated light	64742-47-8	10,566	60.8%	40%
Peroxydisulfuric acid, diammonium salt	7727-54-0	10,350	59.6%	100%
Ethylene glycol	107-21-1	10,307	59.3%	30%
Hydrochloric acid	7647-01-0	10,029	57.7%	15%
Guar gum	9000-30-0	9,110	52.4%	50%
Sodium hydroxide	1310-73-2	8,609	49.5%	10%
Quartz	14808-60-7	8,577	49.4%	2%
Water	7732-18-5	8,538	49.1%	67%
Isopropanol	67-63-0	8,031	46.2%	15%
Potassium hydroxide	1310-58-3	7,206	41.5%	15%
Glutaraldehyde	111-30-8	5,927	34.1%	15%
Propargyl alcohol	107-19-7	5,599	32.2%	5%
Acetic acid	64-19-7	4,623	26.6%	30%
2-Butoxyethanol	111-76-2	4,022	23.1%	10%
Solvent naphtha, petroleum, heavy arom.	64742-94-5	3,821	22.0%	5%
Sodium chloride	7647-14-5	3,692	21.2%	25%
Ethanol	64-17-5	3,536	20.3%	45%
Citric acid	77-92-9	3,310	19.0%	60%
Phenolic resin	9003-35-4	3,109	17.9%	5%
Naphthalene	91-20-3	3,060	17.6%	5%
Nonyl phenol ethoxylate	9016-45-9	2,829	16.3%	20%
Diatomaceous earth, calcined	91053-39-3	2,655	15.3%	100%
Methenamine	100-97-0	2,559	14.7%	1%
Tetramethylammonium chloride	75-57-0	2,428	14.0%	1%
Carbonic acid, dipotassium salt	584-08-7	2,402	13.8%	60%
Ethoxylated propoxylated C12-14 alcohols	68439-51-0	2,342	13.5%	2%
Choline chloride	67-48-1	2,264	13.0%	75%
Boron sodium oxide	1330-43-4	2,228	12.8%	30%
Tetrakis(hydroxymethyl)phosphonium sulfate	55566-30-8	2,130	12.3%	50%
1,2,4-Trimethylbenzene	95-63-6	2,118	12.2%	1%

Chemical name	CASRN	Number of disclosures	Percentage of disclosures	Median maximum concentration in hydraulic fracturing fluid (% by mass)
Boric acid	10043-35-3	2,070	11.9%	25%
Polyethylene glycol	25322-68-3	2,025	11.7%	5%
2-Mercaptoethanol	60-24-2	2,012	11.6%	100%
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	1,988	11.4%	98%
Formic acid	64-18-6	1,948	11.2%	60%
Sodium persulfate	7775-27-1	1,914	11.0%	100%
Phosphonic acid	13598-36-2	1,865	10.7%	1%
Sodium tetraborate decahydrate	1303-96-4	1,862	10.7%	30%
Potassium metaborate	13709-94-9	1,682	9.7%	60%
Ethylenediaminetetraacetic acid tetrasodium salt hydrate	64-02-8	1,676	9.6%	0%
Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture)	127087-87-0	1,668	9.6%	5%

Note: Analysis considered 17,640 disclosures and 385,013 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 (2,268) or other, query-specific criteria were excluded from analysis.

Table C-3a. Top chemicals reported to FracFocus for each state and number (and percentage) of disclosures where a chemical is reported for that state, Alabama to Montana (U.S. EPA, 2015c).

Source: (U.S. EPA, 2015c). The top 20 most frequent chemicals were identified for the 20 states that reported to FracFocus, resulting in a total of 93 chemicals. The chemicals were ranked by counting the number of states where that chemical was in the top 20; chemicals used most widely among the most states come first. For example, methanol is reported in 19 of 20 states, so methanol is ranked first.

Chemical name	CASRN	Alabama	Alaska	Arkansas	California	Colorado	Kansas	Louisiana	Michigan	Mississippi	Montana
Methanol	67-56-1	55 (100%)		1333 (99.7%)	228 (39.0%)	2883 (63.3%)	77 (79.4%)	596 (59.2%)	13 (92.9%)	3 (75%)	121 (62.7%)
Distillates, petroleum, hydrotreated light	64742-47-8		9 (45%)	743 (55.6%)	322 (55.0%)	3358 (73.7%)	87 (89.7%)	844 (83.9%)	14 (100%)	4 (100%)	115 (59.6%)
Ethylene glycol	107-21-1	55 (100%)	20 (100%)	291 (21.8%)	350 (59.8%)		61 (62.9%)	341 (33.9%)	10 (71.4%)	3 (75%)	95 (49.2%)
Isopropanol	67-63-0	55 (100%)	13 (65%)	586 (43.9%)		2586 (56.8%)	24 (24.7%)	515 (51.2%)	11 (78.6%)		123 (63.7%)
Quartz	14808-60-7		20 (100%)		519 (88.7%)	1048 (23.0%)	22 (22.7%)	377 (37.5%)		2 (50%)	124 (64.2%)
Sodium hydroxide	1310-73-2		20 (100%)	285 (21.3%)	403 (68.9%)	996 (21.9%)	27 (27.8%)	535 (53.2%)		2 (50%)	105 (54.4%)
Ethanol	64-17-5			603 (45.1%)		2258 (49.6%)	78 (80.4%)	420 (41.7%)		4 (100%)	
Guar gum	9000-30-0		10 (50%)		545 (93.2%)			494 (49.1%)		2 (50%)	83 (43.0%)
Hydrochloric acid	7647-01-0	55 (100%)		1330 (99.5%)		2408 (52.9%)	82 (84.5%)	569 (56.6%)			45 (23.3%)
Peroxydisulfuric acid, diammonium salt	7727-54-0		10 (50%)		484 (82.7%)		21 (21.6%)	273 (27.2%)	8 (57.1%)		119 (61.7%)

Chemical name	CASRN	Alabama	Alaska	Arkansas	California	Colorado	Kansas	Louisiana	Michigan	Mississippi	Montana
Propargyl alcohol	107-19-7			813 (60.8%)			69 (71.1%)	299 (29.7%)	5 (35.7%)		
Glutaraldehyde	111-30-8			737 (55.1%)			73 (75.3%)	364 (36.3%)		2 (50%)	
Naphthalene	91-20-3	55 (100%)				1363 (29.9%)	41 (42.3%)	293 (29.2%)	12 (85.7%)		95 (49.2%)
2-Butoxyethanol	111-76-2	55 (100%)	20 (100%)						11 (78.6%)		
Citric acid	77-92-9						45 (46.4%)				
Saline	7647-14-5					1574 (34.5%)		408 (40.6%)		2 (50%)	
Solvent naphtha, petroleum, heavy arom.	64742-94-5					1507 (33.1%)	42 (43.3%)				135 (70.0%)
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides	68424-85-1			375 (28.0%)			52 (53.6%)			2 (50%)	
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	55 (100%)				2215 (48.6%)			10 (71.4%)		70 (36.3%)
Potassium hydroxide	1310-58-3							340 (33.8%)		4 (100%)	115 (59.6%)
Choline chloride	67-48-1					1235 (27.1%)					
Polyethylene glycol	25322-68-3	55 (100%)							7 (50%)		69 (35.8%)
1,2,4-Trimethylbenzene	95-63-6					1211 (26.63%)	39 (40.2%)				

Chemical name	CASRN	Alabama	Alaska	Arkansas	California	Colorado	Kansas	Louisiana	Michigan	Mississippi	Montana
Ammonium chloride	12125-02-9			277 (20.7%)		1280 (28.0%)					
Diatomaceous earth, calcined	91053-39-3		20 (100%)		417 (71.3%)						
Didecyl dimethyl ammonium chloride	7173-51-5			317 (23.7%)						2 (50%)	
Sodium chlorite	7758-19-2							352 (35.0%)		4 (100%)	
Sodium erythorbate	6381-77-7			435 (32.5%)			29 (29.9%)				
N,N-Dimethylformamide	68-12-2										
Nonyl phenol ethoxylate	9016-45-9										
Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture)	127087-87-0				1150 (25.2%)	39 (40.2%)					
Sodium persulfate	7775-27-1									4 (100%)	
Tetramethylammonium chloride	75-57-0										85 (44.0%)
1,2-Propylene glycol	57-55-6								10 (71.4%)		
5-Chloro-2-methyl-3(2H)-isothiazolone	26172-55-4		20 (100%)		389 (66.5%)						
Acetic acid	64-19-7					959 (21.0%)		284 (28.2%)			
Ammonium acetate	631-61-8									2 (50%)	

Chemical name	CASRN	Alabama	Alaska	Arkansas	California	Colorado	Kansas	Louisiana	Michigan	Mississippi	Montana
Boric acid	10043-35-3		3 (15%)								
Carbonic acid, dipotassium salt	584-08-7					1159 (25.4%)					
Cristobalite	14464-46-1		20 (100%)		389 (66.5%)						
Formic acid	64-18-6	55 (100%)						293 (29.1%)			
Hemicellulase enzyme	9012-54-8										
Hemicellulase enzyme concentrate	9025-56-3				395 (67.5%)						
Iron(II) sulfate heptahydrate	7782-63-0								7 (50%)		
Magnesium chloride	7786-30-3		20 (100%)		389 (66.5%)						
Magnesium nitrate	10377-60-3		20 (100%)		389 (66.5%)						
Phenolic resin	9003-35-4										
Sodium hypochlorite	7681-52-9					1046 (23.0%)					
Sodium tetraborate decahydrate	1303-96-4		14 (70%)								
Solvent naphtha, petroleum, heavy aliph.	64742-96-7								7 (50%)	2 (50%)	
1-Butoxy-2-propanol	5131-66-8				315 (53.8%)						

Chemical name	CASRN	Alabama	Alaska	Arkansas	California	Colorado	Kansas	Louisiana	Michigan	Mississippi	Montana
1-Propanol	71-23-8					1232 (27.0%)					
1,2-Ethanediaminium, N, N'-bis[2-[bis(2-hydroxyethyl)methylammonio]ethyl]-N,N'bis(2-hydroxyethyl)-N,N'-dimethyl-,tetrachloride	138879-94-4			343 (58.6%)							
2-bromo-3-nitrilopropionamide	1113-55-9										
2-Ethylhexanol	104-76-7										83 (43.0052%)
2-Methyl-3(2H)-isothiazolone	2682-20-4		20 (100%)		389 (66.5%)						
2-Propenoic acid, polymer with 2-propenamide	9003-06-9										
Alkenes, C>10 .alpha.-	64743-02-8			241 (18.0%)							
Benzene, 1,1'-oxybis-, tetrapropylene derivs., sulfonated	119345-03-8										50 (25.9%)
Benzenesulfonic acid, dodecyl-, compd. with N1-(2-aminoethyl)-1,2-ethanediamine (1:?)	40139-72-8										48 (24.9%)
Benzyldimethyldodecylammonium chloride	139-07-1			268 (20.0%)							

Chemical name	CASRN	Alabama	Alaska	Arkansas	California	Colorado	Kansas	Louisiana	Michigan	Mississippi	Montana
Benzylhexadecyldimethylammonium chloride	122-18-9			268 (20.0%)							
Boron sodium oxide	1330-43-4				361 (61.7%)						
C10-C16 ethoxylated alcohol	68002-97-1		3 (15%)								
Calcium chloride	10043-52-4		20 (100%)								
Carbon dioxide	124-38-9								7 (50%)		
Cinnamaldehyde (3-phenyl-2-propenal)	104-55-2	55 (100%)									
Diethylene glycol	111-46-6										
Diethylene glycol monobutyl ether	112-34-5								7 (50%)		
Diethylenetriamine	111-40-0										55 (28.5%)
Distillates, petroleum, hydrotreated light paraffinic	64742-55-8				314 (53.7%)						
Distillates, petroleum, hydrotreated middle	64742-46-7		3 (15%)								
Ethoxylated C12-16 alcohols	68551-12-2										
Ethoxylated C14-15 alcohols	68951-67-7			241 (18.0%)							
Formic acid, potassium salt	590-29-4										

Chemical name	CASRN	Alabama	Alaska	Arkansas	California	Colorado	Kansas	Louisiana	Michigan	Mississippi	Montana
Glycerin, natural	56-81-5								7 (50%)		
Isotridecanol, ethoxylated	9043-30-5				312 (53.3%)						
Methenamine	100-97-0							298 (29.6%)			
Naphtha, petroleum, hydrotreated heavy	64742-48-9										
Poly(oxy-1,2-ethanediyl), .alpha.,.alpha.'-[[(9Z)-9-octadecenylimino]di-2,1-ethanediyl]bis[.omega.-hydroxy-	26635-93-8								9 (64.3%)		
Potassium chloride	7447-40-7								7 (50%)		
Sodium bromate	7789-38-0								7 (50%)		
Sodium perborate tetrahydrate	10486-00-7										
Sulfamic acid	5329-14-6									2 (50%)	
Terpenes and Terpenoids, sweet orange-oil	68647-72-3									2 (50%)	
Tetradecyl dimethyl benzyl ammonium chloride	139-08-2			268 (20.0%)							
Tetrakis(hydroxymethyl)phosphonium sulfate	55566-30-8										

Chemical name	CASRN	Alabama	Alaska	Arkansas	California	Colorado	Kansas	Louisiana	Michigan	Mississippi	Montana
Thiourea polymer	68527-49-1			384 (28.7%)							
Tri-n-butyl tetradecyl phosphonium chloride	81741-28-8										
Trisodium phosphate	7601-54-9						19 (19.6%)				

Note for Table C-3a and C-3b: 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.

Table C-3b. Top chemicals reported to FracFocus for each state and number (and percentage) of disclosures where a chemical is reported for that state, New Mexico to Wyoming (U.S. EPA, 2015c).

Source: (U.S. EPA, 2015c). The top 20 most frequent chemicals were identified for the 20 states that reported to FracFocus, resulting in a total of 93 chemicals. The chemicals were ranked by counting the number of states where that chemical was in the top 20; chemicals used most widely among the most states come first. For example, methanol is reported in 19 of 20 states, so methanol is ranked first.

Chemical name	CASRN	New Mexico	North Dakota	Ohio	Oklahoma	Pennsylvania	Texas	Utah	Virginia	West Virginia	Wyoming
Methanol	67-56-1	1012 (90.8%)	1059 (53.3%)	76 (52.1%)	1270 (70.3%)	1633 (68.6%)	12664 (78.5%)	984 (78.5%)	48 (60.8%)	153 (64.0%)	460 (38.4%)
Distillates, petroleum, hydrotreated light	64742-47-8	699 (62.7%)	943 (47.5%)	122 (83.6%)	1270 (70.3%)	1434 (60.2%)	10677 (66.1%)	934 (74.5%)		196 (82.0%)	612 (51.1%)
Ethylene glycol	107-21-1	503 (45.1%)	724 (36.4%)	83 (56.8%)	843 (46.7%)	807 (33.9%)	9591 (59.4%)	1065 (85.0%)	22 (27.8%)	141 (59.0%)	
Isopropanol	67-63-0	695 (62.3%)	739 (37.2%)	71 (48.6%)	764 (42.28%)	735 (30.9%)	7731 (47.9%)	661 (52.8%)	43 (54.4%)	74 (31.0%)	516 (43.1%)

Chemical name	CASRN	New Mexico	North Dakota	Ohio	Oklahoma	Pennsylvania	Texas	Utah	Virginia	West Virginia	Wyoming
Quartz	14808-60-7	762 (68.3%)	920 (46.3%)	66 (45.2%)	491 (27.2%)		6869 (42.6%)	503 (40.1%)		53 (22.2%)	356 (29.7%)
Sodium hydroxide	1310-73-2	329 (29.5%)	1028 (51.7%)		490 (27.1%)	406 (17.0%)	7371 (45.7%)	466 (37.2%)			688 (57.4%)
Ethanol	64-17-5	529 (47.4%)	545 (27.4%)	87 (59.6%)	838 (46.4%)	388 (16.3%)	3439 (21.3%)		50 (63.3%)	130 (54.3%)	298 (24.9%)
Guar gum	9000-30-0	702 (63.0%)	1094 (55.1%)	74 (50.7%)	457 (25.3%)	538 (22.6%)	6863 (42.5%)	538 (42.9%)		55 (23.0%)	823 (68.7%)
Hydrochloric acid	7647-01-0	880 (78.9%)		145 (99.3%)	1372 (75.9%)	2279 (95.7%)	11424 (70.8%)	1064 (84.9%)	68 (86.1%)	229 (95.8%)	
Peroxydisulfuric acid, diammonium salt	7727-54-0	836 (75.0%)	1089 (54.8%)	93 (63.7%)	713 (39.5%)		8666 (53.7%)	483 (38.5%)		128 (53.6%)	771 (64.4%)
Propargyl alcohol	107-19-7	760 (68.2%)		72 (49.3%)	732 (40.5%)	1371 (57.6%)	6269 (38.8%)	456 (36.4%)	22 (27.8%)	138 (57.7%)	
Glutaraldehyde	111-30-8	632 (56.7%)		105 (71.9%)	989 (54.7%)	819 (34.4%)	6470 (40.1%)			169 (70.7%)	260 (21.7%)
Naphthalene	91-20-3		864 (43.5%)		448 (24.8%)			478 (38.1%)	7 (8.9%)		
2-Butoxyethanol	111-76-2	412 (37.0%)				498 (20.9%)	3898 (24.1%)	663 (52.9%)	70 (88.6%)	62 (25.9%)	
Citric acid	77-92-9	447 (40.1%)		96 (65.8%)	644 (35.6%)	701 (29.4%)	3820 (23.7%)	992 (79.2%)	63 (79.8%)	98 (41.0%)	
Saline	7647-14-5		491 (24.7%)				3462 (21.4%)		7 (8.9%)	53 (22.2%)	274 (22.9%)
Solvent naphtha, petroleum, heavy arom.	64742-94-5		981 (49.4%)		557 (30.8%)		2751 (17.0%)		7 (8.9%)		415 (34.6%)

Chemical name	CASRN	New Mexico	North Dakota	Ohio	Oklahoma	Pennsylvania	Texas	Utah	Virginia	West Virginia	Wyoming
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides	68424-85-1			54 (37.0%)	597 (33.0%)	373 (15.7%)				53 (22.2%)	
2,2-Dibromo-3-nitrilopropionamide	10222-01-2					804 (33.8%)			22 (27.8%)		
Potassium hydroxide	1310-58-3		1176 (59.2%)	106 (72.6%)			6369 (39.5%)				
Choline chloride	67-48-1	384 (34.4%)		55 (37.7%)				649 (51.8%)	45 (57.0%)		
Polyethylene glycol	25322-68-3		567 (28.5%)			688 (28.9%)					
1,2,4-Trimethylbenzene	95-63-6		496 (25.0%)						7 (8.9%)		
Ammonium chloride	12125-02-9					732 (30.7%)				50 (20.9%)	
Diatomaceous earth, calcined	91053-39-3	419 (37.6%)						435 (34.7%)			
Didecyl dimethyl ammonium chloride	7173-51-5			46 (31.6%)						49 (20.5%)	
Sodium chlorite	7758-19-2		482 (24.3%)								271 (22.6%)
Sodium erythorbate	6381-77-7								10 (12.7%)	76 (31.8%)	
N,N-Dimethylformamide	68-12-2			68 (46.6%)	355 (19.6%)			410 (32.7%)			
Nonyl phenol ethoxylate	9016-45-9	333 (29.9%)						447 (35.7%)	25 (31.6%)		

Chemical name	CASRN	New Mexico	North Dakota	Ohio	Oklahoma	Pennsylvania	Texas	Utah	Virginia	West Virginia	Wyoming
Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy (mixture)	127087-87-0								7 (8.9%)		
Sodium persulfate	7775-27-1					373 (15.7%)					308 (25.7%)
Tetramethylammonium chloride	75-57-0		579 (29.1%)								315 (26.3%)
1,2-Propylene glycol	57-55-6								22 (27.8%)		
5-Chloro-2-methyl-3(2H)-isothiazolone	26172-55-4										
Acetic acid	64-19-7										
Ammonium acetate	631-61-8										323 (27.0%)
Boric acid	10043-35-3			82 (56.2%)							
Carbonic acid, dipotassium salt	584-08-7		482 (24.2%)								
Cristobalite	14464-46-1										
Formic acid	64-18-6										
Hemicellulase enzyme	9012-54-8					367 (15.4%)			11 (13.9%)		
Hemicellulase enzyme concentrate	9025-56-3	331 (29.7%)									
Iron(II) sulfate heptahydrate	7782-63-0								22 (27.8%)		
Magnesium chloride	7786-30-3										

Chemical name	CASRN	New Mexico	North Dakota	Ohio	Oklahoma	Pennsylvania	Texas	Utah	Virginia	West Virginia	Wyoming
Magnesium nitrate	10377-60-3										
Phenolic resin	9003-35-4	419 (37.6%)					2903 (18.0%)				
Sodium hypochlorite	7681-52-9										282 (23.5%)
Sodium tetraborate decahydrate	1303-96-4										265 (22.1%)
Solvent naphtha, petroleum, heavy aliph.	64742-96-7										
1-Butoxy-2-propanol	5131-66-8										
1-Propanol	71-23-8										
1,2-Ethanediaminium, N, N'-bis[2-[bis(2-hydroxy ethyl) methylammonio] ethyl]-N,N'bis(2-hydroxyethyl)-N,N'-dimethyl-, tetrachloride	138879-94-4										
2-Bromo-3-nitrilopropionamide	1113-55-9								11 (13.9%)		
2-Ethylhexanol	104-76-7										
2-Methyl-3(2H)-isothiazolone	2682-20-4										
2-Propenoic acid, polymer with 2-propenamide	9003-06-9							486 (38.8%)			
Alkenes, C>10 .alpha.-	64743-02-8										

Chemical name	CASRN	New Mexico	North Dakota	Ohio	Oklahoma	Pennsylvania	Texas	Utah	Virginia	West Virginia	Wyoming
Benzene, 1,1'-oxybis-, tetrapropylene derivs., sulfonated	119345-03-8										
Benzenesulfonic acid, dodecyl-, compd. with N1-(2-aminoethyl)-1,2-ethanediamine (1:?)	40139-72-8										
Benzyldimethyldodecylammonium chloride	139-07-1										
Benzylhexadecyldimethylammonium chloride	122-18-9										
Boron sodium oxide	1330-43-4										
C10-C16 ethoxylated alcohol	68002-97-1										
Calcium chloride	10043-52-4										
Carbon dioxide	124-38-9										
Cinnamaldehyde (3-phenyl-2-propenal)	104-55-2										
Diethylene glycol	111-46-6			45 (30.8%)							
Diethylene glycol monobutyl ether	112-34-5										
Diethylenetriamine	111-40-0										
Distillates, petroleum, hydrotreated light paraffinic	64742-55-8										

Chemical name	CASRN	New Mexico	North Dakota	Ohio	Oklahoma	Pennsylvania	Texas	Utah	Virginia	West Virginia	Wyoming
Distillates, petroleum, hydrotreated middle	64742-46-7										
Ethoxylated C12-16 alcohols	68551-12-2									57 (23.8%)	
Ethoxylated C14-15 alcohols	68951-67-7										
Formic acid, potassium salt	590-29-4										361 (30.1%)
Glycerin, natural	56-81-5										
Isotridecanol, ethoxylated	9043-30-5										
Methenamine	100-97-0										
Naphtha, petroleum, hydrotreated heavy	64742-48-9										384 (32.1%)
Poly(oxy-1,2-ethanediyl), .alpha.,.alpha.'-[[(9Z)-9-octadecenylimino]di-2,1-ethanediyl]bis[.omega.-hydroxy-	26635-93-8										
Potassium chloride	7447-40-7										
Sodium bromate	7789-38-0										
Sodium perborate tetrahydrate	10486-00-7				351 (19.4%)						
Sulfamic acid	5329-14-6										
Terpenes and terpenoids, sweet orange-oil	68647-72-3										

Chemical name	CASRN	New Mexico	North Dakota	Ohio	Oklahoma	Pennsylvania	Texas	Utah	Virginia	West Virginia	Wyoming
Tetradecyl dimethyl benzyl ammonium chloride	139-08-2										
Tetrakis(hydroxymethyl)phosphonium sulfate	55566-30-8							945 (75.4%)			
Thiourea polymer	68527-49-1										
Tri-n-butyl tetradecyl phosphonium chloride	81741-28-8					350 (14.7%)					
Trisodium phosphate	7601-54-9										

Note for Table C-3a and C-3b: 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.

Table C-4. Estimated mean, median, 5th percentile, and 95th percentile volumes in gallons for chemicals reported to FracFocus in 100 or more disclosures, where density information was available.

Chemicals are listed in alphabetical order. Density information came from Reaxys® and other sources. All density sources are referenced in Table C-7.

Name	CASRN	Volume (gallons)			
		Mean	Median	5th Percentile	95th Percentile
(4R)-1-methyl-4-(prop-1-en-2-yl)cyclohexene	5989-27-5	2,702	406	0	19,741
1-Butoxy-2-propanol	5131-66-8	167	21	5	654
1-Decanol	112-30-1	28	4	0	33
1-Octanol	111-87-5	5	4	0	10
1-Propanol	71-23-8	128	55	6	367
1,2-Propylene glycol	57-55-6	13,105	72	4	61,071
1,2,4-Trimethylbenzene	95-63-6	38	6	0	43
2-Butoxyethanol	111-76-2	385	26	0	1,811
2-Ethylhexanol	104-76-7	100	11	0	292
2-Mercaptoethanol	60-24-2	1,175	445	0	4,194
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	183	5	0	341
Acetic acid	64-19-7	646	47	0	1,042
Acetic anhydride	108-24-7	239	50	3	722
Acrylamide	79-06-1	95	3	0	57
Adipic acid	124-04-9	153	0	0	109
Aluminum chloride	7446-70-0	2	0	0	0
Ammonia	7664-41-7	44	35	2	138
Ammonium acetate	631-61-8	839	117	0	1,384
Ammonium chloride	12125-02-9	440	48	3	458
Ammonium hydroxide	1336-21-6	7	2	0	14
Benzyl chloride	100-44-7	52	0	0	40
Carbonic acid, dipotassium salt	584-08-7	467	113	0	1,729
Chlorine dioxide	10049-04-4	31	11	0	28
Choline chloride	67-48-1	2,131	290	28	4,364
Cinnamaldehyde (3-phenyl-2-propenal)	104-55-2	68	3	0	697

Name	CASRN	Volume (gallons)			
		Mean	Median	5th Percentile	95th Percentile
Citric acid	77-92-9	163	20	1	269
Dibromoacetonitrile	3252-43-5	22	13	1	45
Diethylene glycol	111-46-6	168	16	0	102
Diethylenetriamine	111-40-0	92	21	0	207
Dodecane	112-40-3	190	31	0	151
Ethanol	64-17-5	831	121	1	2,645
Ethanolamine	141-43-5	70	30	0	283
Ethyl acetate	141-78-6	0	0	0	0
Ethylene glycol	107-21-1	614	184	4	2,470
Ferric chloride	7705-08-0	0	0	0	0
Formalin	50-00-0	200	0	0	8
Formic acid	64-18-6	501	38	1	1,229
Fumaric acid	110-17-8	2	0	0	12
Glutaraldehyde	111-30-8	1,313	122	2	1,165
Glycerin, natural	56-81-5	413	109	10	911
Glycolic acid	79-14-1	38	10	4	94
Hydrochloric acid	7647-01-0	28,320	3,110	96	26,877
Isopropanol	67-63-0	2,095	55	0	1,264
Isopropylamine	75-31-0	83	121	0	172
Magnesium chloride	7786-30-3	14	0	0	2
Methanol	67-56-1	1,218	110	2	3,731
Methenamine	100-97-0	3,386	100	0	3,648
Methoxyacetic acid	625-45-6	36	4	2	115
N,N-Dimethylformamide	68-12-2	119	10	0	216
Naphthalene	91-20-3	72	12	0	204
Nitrogen, liquid	7727-37-9	41,841	26,610	3,091	108,200
Ozone	10028-15-6	15,844	15,473	8,785	26,063
Peracetic acid	79-21-0	300	268	50	663
Phosphonic acid	13598-36-2	1,201	0	0	3
Phosphoric acid Divosan X-Tend formulation	7664-38-2	13	4	0	15
Potassium acetate	127-08-2	204	1	0	974

Name	CASRN	Volume (gallons)			
		Mean	Median	5th Percentile	95th Percentile
Propargyl alcohol	107-19-7	183	2	0	51
Saline	7647-14-5	876	85	0	1,544
Saturated sucrose	57-50-1	1	1	0	2
Silica, amorphous	7631-86-9	6,877	8	0	38,371
Sodium carbonate	497-19-8	228	16	0	1,319
Sodium formate	141-53-7	0	0	0	0
Sodium hydroxide	1310-73-2	551	38	0	1,327
Sulfur dioxide	7446-09-5	0	0	0	0
Sulfuric acid	7664-93-9	3	0	0	3
tert-Butyl hydroperoxide (70% solution in Water)	75-91-2	156	64	0	557
Tetramethylammonium chloride	75-57-0	970	483	2	3,508
Thioglycolic acid	68-11-1	55	7	2	229
Toluene	108-88-3	18	0	0	11
Tridecane	629-50-5	190	31	0	190
Triethanolamine	102-71-6	846	60	0	2,264
Triethyl phosphate	78-40-0	55	1	0	533
Triethylene glycol	112-27-6	5,198	116	28	945
Triisopropanolamine	122-20-3	46	4	1	330
Trimethyl borate	121-43-7	83	40	4	283
Undecane	1120-21-4	273	29	0	1,641

Note: Analysis considered 34,495 disclosures and 672,358 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; criteria for water volumes; valid CASRN; and valid concentrations. Disclosures that did not meet quality assurance criteria (4,035) or other, query-specific criteria were excluded from analysis.

Table C-5. Estimated mean, median, 5th percentile, and 95th percentile volumes in liters for chemicals reported to FracFocus in 100 or more disclosures, where density information was available.

Chemicals are listed in alphabetical order. Density information came from Reaxys® and other sources. All density sources are referenced in Table C-7.

Name	CASRN	Volume (L)			
		Mean	Median	5th Percentile	95th Percentile
(4R)-1-methyl-4-(prop-1-en-2-yl)cyclohexene	5989-27-5	10,229	1,536	0	74,729
1-Butoxy-2-propanol	5131-66-8	631	80	18	2,475
1-Decanol	112-30-1	107	14	1	123
1-Octanol	111-87-5	21	14	1	39
1-Propanol	71-23-8	483	208	22	1,391
1,2-Propylene glycol	57-55-6	49,607	274	15	231,179
1,2,4-Trimethylbenzene	95-63-6	145	24	0	165
2-Butoxyethanol	111-76-2	1,459	98	0	6,856
2-Ethylhexanol	104-76-7	377	40	1	1,106
2-Mercaptoethanol	60-24-2	4,449	1,685	0	15,878
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	692	18	0	1,292
Acetic acid	64-19-7	2,446	176	0	3,945
Acetic anhydride	108-24-7	906	189	12	2,734
Acrylamide	79-06-1	361	10	0	216
Adipic acid	124-04-9	578	0	0	414
Aluminum chloride	7446-70-0	6	0	0	0
Ammonia	7664-41-7	166	134	7	523
Ammonium acetate	631-61-8	3,177	444	0	5,238
Ammonium chloride	12125-02-9	1,666	182	11	1,733
Ammonium hydroxide	1336-21-6	27	6	1	52
Benzyl chloride	100-44-7	196	1	0	151
Carbonic acid, dipotassium salt	584-08-7	1,769	429	0	6,544
Chlorine dioxide	10049-04-4	117	43	1	106
Choline chloride	67-48-1	8,068	1,096	107	16,521
Cinnamaldehyde (3-phenyl-2-propenal)	104-55-2	258	12	0	2,638
Citric acid	77-92-9	618	77	5	1,019

Name	CASRN	Volume (L)			
		Mean	Median	5th Percentile	95th Percentile
Dibromoacetonitrile	3252-43-5	82	50	4	170
Diethylene glycol	111-46-6	636	61	1	384
Diethylenetriamine	111-40-0	347	80	0	785
Dodecane	112-40-3	719	117	0	572
Ethanol	64-17-5	3,144	458	6	10,011
Ethanolamine	141-43-5	264	112	0	1,070
Ethyl acetate	141-78-6	0	0	0	0
Ethylene glycol	107-21-1	2,324	697	14	9,349
Ferric chloride	7705-08-0	0	0	0	0
Formalin	50-00-0	756	2	0	31
Formic acid	64-18-6	1,896	144	2	4,653
Fumaric acid	110-17-8	9	0	0	46
Glutaraldehyde	111-30-8	4,972	462	6	4,409
Glycerin, natural	56-81-5	1,565	412	38	3,447
Glycolic acid	79-14-1	146	39	14	356
Hydrochloric acid	7647-01-0	107,204	11,772	362	101,741
Isopropanol	67-63-0	7,932	210	1	4,786
Isopropylamine	75-31-0	314	458	0	652
Magnesium chloride	7786-30-3	52	0	0	8
Methanol	67-56-1	4,609	416	6	14,125
Methenamine	100-97-0	12,817	378	0	13,810
Methoxyacetic acid	625-45-6	136	17	8	436
N,N-Dimethylformamide	68-12-2	449	38	2	819
Naphthalene	91-20-3	271	44	0	774
Nitrogen, liquid	7727-37-9	158,384	100,731	11,700	409,583
Ozone	10028-15-6	59,976	58,570	33,254	98,658
Peracetic acid	79-21-0	1,137	1,016	190	2,511
Phosphonic acid	13598-36-2	4,547	2	0	11
Phosphoric acid Divosan X-Tend formulation	7664-38-2	51	15	0	57
Potassium acetate	127-08-2	775	3	0	3,690
Propargyl alcohol	107-19-7	693	9	0	193

Name	CASRN	Volume (L)			
		Mean	Median	5th Percentile	95th Percentile
Saline	7647-14-5	3,317	321	0	5,844
Saturated sucrose	57-50-1	5	2	0	6
Silica, amorphous	7631-86-9	26,031	32	0	145,251
Sodium carbonate	497-19-8	862	62	0	4,991
Sodium formate	141-53-7	1	1	0	1
Sodium hydroxide	1310-73-2	2,087	144	1	5,024
Sulfur dioxide	7446-09-5	2	0	0	0
Sulfuric acid	7664-93-9	10	0	0	12
tert-Butyl hydroperoxide (70% solution in Water)	75-91-2	591	242	0	2,109
Tetramethylammonium chloride	75-57-0	3,672	1,830	8	13,279
Thioglycolic acid	68-11-1	208	28	6	868
Toluene	108-88-3	69	0	0	41
Tridecane	629-50-5	721	118	0	721
Triethanolamine	102-71-6	3,203	228	0	8,570
Triethyl phosphate	78-40-0	209	6	0	2,019
Triethylene glycol	112-27-6	19,676	439	106	3,579
Triisopropanolamine	122-20-3	174	16	4	1,249
Trimethyl borate	121-43-7	314	152	16	1,072
Undecane	1120-21-4	1,035	111	0	6,212

Note: Analysis considered 34,495 disclosures and 672,358 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; criteria for water volumes; valid CASRN; and valid concentrations. Disclosures that did not meet quality assurance criteria (4,035) or other, query-specific criteria were excluded from analysis.

Table C-6. Calculated mean, median, 5th percentile, and 95th percentile chemical masses reported to FracFocus in 100 or more disclosures, where density information was available.

Density information came from Reaxys® and other sources. All density sources are referenced in Table C-7. Number of disclosures reported for each chemical is also included.

Name	CASRN	Mass (kg)				Disclosures
		Mean	Median	5th Percentile	95th Percentile	
(4R)-1-methyl-4-(prop-1-en-2-yl)cyclohexene	5989-27-5	8,593	1,290	0	62,772	578
1-Butoxy-2-propanol	5131-66-8	555	71	16	2,178	773
1-Decanol	112-30-1	89	12	1	102	434
1-Octanol	111-87-5	17	12	1	32	434
1-Propanol	71-23-8	386	167	18	1,113	1,481
1,2-Propylene glycol	57-55-6	51,095	282	15	238,114	1,023
1,2,4-Trimethylbenzene	95-63-6	126	21	0	143	3,976
2-Butoxyethanol	111-76-2	1,313	88	0	6,170	6,778
2-Ethylhexanol	104-76-7	313	34	0	918	1,291
2-Mercaptoethanol	60-24-2	489	185	0	1,747	2,051
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	1,660	44	0	3,102	4,927
Acetic acid	64-19-7	2,544	183	0	4,103	7,643
Acetic anhydride	108-24-7	969	203	12	2,925	1,377
Acrylamide	79-06-1	408	11	0	244	251
Adipic acid	124-04-9	785	0	0	564	233
Aluminum chloride	7446-70-0	15	0	0	0	122
Ammonia	7664-41-7	111	90	4	351	398
Ammonium acetate	631-61-8	3,718	520	0	6,129	1,504
Ammonium chloride	12125-02-9	2,530	277	16	2,633	3,288
Ammonium hydroxide	1336-21-6	48	11	2	94	1,173
Benzyl chloride	100-44-7	214	1	0	165	1,833
Carbonic acid, dipotassium salt	584-08-7	4,298	1,042	0	15,902	4,093
Chlorine dioxide	10049-04-4	321	117	3	291	331
Choline chloride	67-48-1	9,440	1,282	125	19,329	4,241
Cinnamaldehyde (3-phenyl-2-propenal)	104-55-2	284	13	0	2,902	1,377

Name	CASRN	Mass (kg)				Disclosures
		Mean	Median	5th Percentile	95th Percentile	
Citric acid	77-92-9	989	123	8	1,630	7,503
Dibromoacetonitrile	3252-43-5	193	118	11	403	272
Diethylene glycol	111-46-6	712	68	1	430	1,732
Diethylenetriamine	111-40-0	330	76	0	746	784
Dodecane	112-40-3	539	88	0	429	131
Ethanol	64-17-5	2,484	361	4	7,908	9,233
Ethanolamine	141-43-5	267	113	0	1,081	585
Ethyl acetate	141-78-6	0	0	0	0	110
Ethylene glycol	107-21-1	2,557	767	15	10,283	14,767
Ferric chloride	7705-08-0	0	0	0	0	118
Formalin	50-00-0	816	2	0	34	456
Formic acid	64-18-6	2,313	176	2	5,677	3,781
Fumaric acid	110-17-8	15	0	0	75	224
Glutaraldehyde	111-30-8	4,972	462	6	4,409	10,963
Glycerin, natural	56-81-5	1,972	519	47	4,343	1,829
Glycolic acid	79-14-1	217	58	21	530	595
Hydrochloric acid	7647-01-0	107,204	11,772	362	101,741	20,996
Isopropanol	67-63-0	6,187	163	1	3,733	15,058
Isopropylamine	75-31-0	213	311	0	444	255
Magnesium chloride	7786-30-3	120	1	0	18	1,113
Methanol	67-56-1	3,641	329	5	11,159	23,225
Methenamine	100-97-0	15,380	454	0	16,572	4,412
Methoxyacetic acid	625-45-6	161	20	9	514	584
N,N-Dimethylformamide	68-12-2	422	36	2	770	2,972
Naphthalene	91-20-3	220	35	0	627	5,945
Nitrogen, liquid	7727-37-9	129,875	82,599	9,594	335,858	713
Ozone	10028-15-6	129	126	71	212	209
Peracetic acid	79-21-0	1,251	1,117	209	2,762	221
Phosphonic acid	13598-36-2	7,730	3	0	18	2,216
Phosphoric acid Divosan X-Tend formulation	7664-38-2	48	14	0	54	315
Potassium acetate	127-08-2	1,216	5	0	5,793	325

Name	CASRN	Mass (kg)				Disclosures
		Mean	Median	5th Percentile	95th Percentile	
Propargyl alcohol	107-19-7	658	9	0	183	10,771
Saline	7647-14-5	7,197	696	0	12,682	6,673
Saturated sucrose	57-50-1	6	2	0	7	125
Silica, amorphous	7631-86-9	57,267	71	0	319,553	2,423
Sodium carbonate	497-19-8	2,191	158	0	12,678	396
Sodium formate	141-53-7	2	1	1	2	204
Sodium hydroxide	1310-73-2	4,445	306	2	10,701	12,585
Sulfur dioxide	7446-09-5	2	0	0	0	224
Sulfuric acid	7664-93-9	18	0	0	22	402
tert-Butyl hydroperoxide (70% solution in water)	75-91-2	532	218	0	1,898	814
Tetramethylammonium chloride	75-57-0	4,296	2,141	10	15,537	3,162
Thioglycolic acid	68-11-1	277	37	8	1,155	156
Toluene	108-88-3	59	0	0	35	214
Tridecane	629-50-5	541	88	0	541	132
Triethanolamine	102-71-6	3,588	255	0	9,599	1,498
Triethyl phosphate	78-40-0	222	6	0	2,140	991
Triethylene glycol	112-27-6	22,038	491	119	4,008	528
Triisopropanolamine	122-20-3	177	17	4	1,274	251
Trimethyl borate	121-43-7	292	141	14	997	294
Undecane	1120-21-4	766	82	0	4,597	241

Note: Analysis considered 34,495 disclosures and 672,358 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; criteria for water volumes; valid CASRN; and valid concentrations. Disclosures that did not meet quality assurance criteria (4,035) or other, query-specific criteria were excluded from analysis.

Table C-7. Associated chemical densities and references used to calculate chemical mass and estimate chemical volume.

Name	CASRN	Density (g/mL)	Reference
(4R)-1-methyl-4-(prop-1-en-2-yl)cyclohexene	5989-27-5	0.84	Dejoye Tanzi et al. (2012)
1-Butoxy-2-propanol	5131-66-8	0.88	Pal et al. (2013)
1-Decanol	112-30-1	0.83	Faria et al. (2013)
1-Octanol	111-87-5	0.82	Dubey and Kumar (2013)
1-Propanol	71-23-8	0.8	Rani and Maken (2013)
1,2-Propylene glycol	57-55-6	1.03	Moosavi et al. (2013)
1,2,4-Trimethylbenzene	95-63-6	0.87	He et al. (2008)
2-Butoxyethanol	111-76-2	0.9	Dhondge et al. (2010)
2-Ethylhexanol	104-76-7	0.83	Laavi et al. (2012)
2-Mercaptoethanol	60-24-2	0.11	Rawat et al. (1976)
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	2.4	Fels (1900)
Acetic acid	64-19-7	1.04	Chafer et al. (2010)
Acetic anhydride	108-24-7	1.07	Radwan and Hanna (1976)
Acrylamide	79-06-1	1.13	Carpenter and Davis (1957)
Adipic acid	124-04-9	1.36	Thalladi et al. (2000)
Aluminum chloride	7446-70-0	2.44	Sigma-Aldrich (2015a)
Ammonia	7664-41-7	0.67	Harlow et al. (1997)
Ammonium acetate	631-61-8	1.17	Biltz and Balz (1928)
Ammonium chloride	12125-02-9	1.519	Haynes (2014)
Ammonium hydroxide	1336-21-6	1.8	Xiao et al. (2013)
Benzyl chloride	100-44-7	1.09	Sarkar et al. (2012)
Carbonic acid, dipotassium salt	584-08-7	2.43	Sigma-Aldrich (2014b)
Chlorine dioxide	10049-04-4	2.757	Haynes (2014)
Choline chloride	67-48-1	1.17	Shanley and Collin (1961)
Cinnamaldehyde (3-phenyl-2-propenal)	104-55-2	1.1	Masood et al. (1976)
Citric acid	77-92-9	1.6	Bennett and Yuill (1935)
Dibromoacetonitrile	3252-43-5	2.37	Wilt (1956)
Diethylene glycol	111-46-6	1.12	Chasib (2013)
Diethylenetriamine	111-40-0	0.95	Dubey and Kumar (2011)
Dodecane	112-40-3	0.75	Baragi et al. (2013)

Name	CASRN	Density (g/mL)	Reference
Ethanol	64-17-5	0.79	Kiselev et al. (2012)
Ethanolamine	141-43-5	1.01	Blanco et al. (2013)
Ethyl acetate	141-78-6	0.89	Laavi et al. (2013)
Ethylene glycol	107-21-1	1.1	Rodnikova et al. (2012)
Ferric chloride	7705-08-0	2.9	Haynes (2014)
Formalin	50-00-0	1.08	Alfa Aesar (2015)
Formic acid	64-18-6	1.22	Casanova et al. (1981)
Fumaric acid	110-17-8	1.64	Huffman and Fox (1938)
Glutaraldehyde	111-30-8	1	Oka (1962)
Glycerin, natural	56-81-5	1.26	Egorov et al. (2013)
Glycolic acid	79-14-1	1.49	Pijper (1971)
Hydrochloric acid	7647-01-0	1	Steinhauser et al. (1990)
Isopropanol	67-63-0	0.78	Zhang et al. (2013)
Isopropylamine	75-31-0	0.68	Sarkar and Roy (2009)
Magnesium chloride	7786-30-3	2.32	Haynes (2014)
Methanol	67-56-1	0.79	Kiselev et al. (2012)
Methenamine	100-97-0	1.2	Mak (1965)
Methoxyacetic acid	625-45-6	1.18	Haynes (2014)
N,N-Dimethylformamide	68-12-2	0.94	Smirnov and Badelin (2013)
Naphthalene	91-20-3	0.81	Dyshin et al. (2008)
Nitrogen, liquid	7727-37-9	0.8	finemech (2012)
Ozone	10028-15-6	0.002144	Haynes (2014)
Peracetic acid	79-21-0	1.1	Sigma-Aldrich (2015b)
Phosphonic acid	13598-36-2	1.7	Sigma-Aldrich (2014a)
Phosphoric acid Divosan X-Tend formulation	7664-38-2	0.94	Fadeeva et al. (2004)
Potassium acetate	127-08-2	1.57	Haynes (2014)
Propargyl alcohol	107-19-7	0.95	Vijaya Kumar et al. (1996)
Saline	7647-14-5	2.17	Sigma-Aldrich (2010)
Saturated sucrose	57-50-1	1.13	Hagen and Kaatze (2004)
Silica, amorphous	7631-86-9	2.2	Fujino et al. (2004)
Sodium carbonate	497-19-8	2.54	Haynes (2014)
Sodium formate	141-53-7	1.97	Fuess et al. (1982)

Name	CASRN	Density (g/mL)	Reference
Sodium hydroxide	1310-73-2	2.13	Haynes (2014)
Sulfur dioxide	7446-09-5	1.3	Sigma-Aldrich (2015c)
Sulfuric acid	7664-93-9	1.83	Sigma-Aldrich (2015d)
tert-Butyl hydroperoxide (70% solution in water)	75-91-2	0.9	Sigma-Aldrich (2007)
Tetramethylammonium chloride	75-57-0	1.17	Haynes (2014)
Thioglycolic acid	68-11-1	1.33	Biilmann (1906)
Toluene	108-88-3	0.86	Martinez-Reina et al. (2012)
Tridecane	629-50-5	0.75	Zhang et al. (2011)
Triethanolamine	102-71-6	1.12	Blanco et al. (2013)
Triethyl phosphate	78-40-0	1.06	Krakowiak et al. (2001)
Triethylene glycol	112-27-6	1.12	Afzal et al. (2009)
Triisopropanolamine	122-20-3	1.02	IUPAC (2014)
Trimethyl borate	121-43-7	0.93	Sigma-Aldrich (2015e)
Undecane	1120-21-4	0.74	de Oliveira et al. (2011)

Table C-8. Selected physicochemical properties of chemicals reported as used in hydraulic fracturing fluids.

Properties are provided for chemicals, where available from EPI Suite™ version 4.1 (U.S. EPA, 2012a).

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
(13Z)-N,N-bis(2-hydroxyethyl)-N-methyldocos-13-en-1-aminium chloride	120086-58-0	4.38	--	0.3827	3.32×10^{-15}	--	--
(2,3-Dihydroxypropyl)trimethyl ammonium chloride	34004-36-9	-5.8	--	1.00×10^{6}	9.84×10^{-18}	--	--
(E)-Crotonaldehyde	123-73-9	0.6	--	4.15×10^{4}	5.61×10^{-5}	1.90×10^{-5}	1.94×10^{-5}
[Nitrilotris(methylene)]tris-phosphonic acid pentasodium salt	2235-43-0	−5.45	−3.53	1.00×10^{6}	1.65×10^{-34}	--	--
1-(1-Naphthylmethyl)quinolinium chloride	65322-65-8	5.57	--	0.02454	1.16×10^{-7}	--	--
1-(Alkyl* amino)-3-aminopropane *(42%C12, 26%C18, 15%C14, 8%C16, 5%C10, 4%C8)	68155-37-3	4.74	--	23.71	6.81×10^{-8}	2.39×10^{-8}	--
1-(Phenylmethyl)pyridinium Et Me derivatives, chlorides	68909-18-2	4.1	--	14.13	1.78×10^{-5}	--	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
1,2,3-Trimethylbenzene	526-73-8	3.63	3.66	75.03	7.24×10^{-3}	6.58×10^{-3}	4.36×10^{-3}
1,2,4-Trimethylbenzene	95-63-6	3.63	3.63	79.59	7.24×10^{-3}	6.58×10^{-3}	6.16×10^{-3}
1,2-Benzisothiazolin-3-one	2634-33-5	0.64	--	2.14×10^{4}	6.92×10^{-9}	--	--
1,2-Dibromo-2,4-dicyanobutane	35691-65-7	1.63	--	424	3.94×10^{-10}	--	--
1,2-Dimethylbenzene	95-47-6	3.09	3.12	224.1	6.56×10^{-3}	6.14×10^{-3}	5.18×10^{-3}
1,2-Ethanediaminium, N,N'-bis[2-[bis(2-hydroxyethyl)methylammonio]ethyl]-N,N'-bis(2-hydroxyethyl)-N,N'-dimethyl-, tetrachloride	138879-94-4	−23.19	--	1.00×10^{6}	2.33×10^{-35}	--	--
1,2-Propylene glycol	57-55-6	-0.78	−0.92	8.11×10^{5}	1.74×10^{-7}	1.31×10^{-10}	1.29×10^{-8}
1,2-Propylene oxide	75-56-9	0.37	0.03	1.29×10^{5}	1.60×10^{-4}	1.23×10^{-4}	6.96×10^{-5}
1,3,5-Triazine	290-87-9	−0.2	0.12	1.03×10^{5}	1.21×10^{-6}	--	--
1,3,5-Triazine-1,3,5(2H,4H,6H)-triethanol	4719-04-4	−4.67	--	1.00×10^{6}	1.08×10^{-11}	--	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
1,3,5-Trimethylbenzene	108-67-8	3.63	3.42	120.3	7.24×10^{-3}	6.58×10^{-3}	8.77×10^{-3}
1,3-Butadiene	106-99-0	2.03	1.99	792.3	7.79×10^{-2}	7.05×10^{-2}	7.36×10^{-2}
1,3-Dichloropropene	542-75-6	2.29	2.04	1,994	2.45×10^{-2}	3.22×10^{-3}	3.55×10^{-3}
1,4-Dioxane	123-91-1	−0.32	−0.27	2.14×10^{5}	5.91×10^{-6}	1.12×10^{-7}	4.80×10^{-6}
1,6-Hexanediamine	124-09-4	0.35	--	5.34×10^{5}	3.21×10^{-9}	7.05×10^{-10}	--
1,6-Hexanediamine dihydrochloride	6055-52-3	0.35	--	5.34×10^{5}	3.21×10^{-9}	7.05×10^{-10}	--
1-[2-(2-Methoxy-1-methylethoxy)-1-methylethoxy]-2-propanol	20324-33-8	−0.2	--	1.96×10^{5}	2.36×10^{-11}	4.55×10^{-13}	--
1-Amino-2-propanol	78-96-6	−1.19	−0.96	1.00×10^{6}	4.88×10^{-10}	2.34×10^{-10}	--
1-Benzylquinolinium chloride	15619-48-4	4.4	--	6.02	1.19×10^{-6}	--	--
1-Butanol	71-36-3	0.84	0.88	7.67×10^{4}	9.99×10^{-6}	9.74×10^{-6}	8.81×10^{-6}
1-Butoxy-2-propanol	5131-66-8	0.98	--	4.21×10^{4}	1.30×10^{-7}	4.88×10^{-8}	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
1-Decanol	112-30-1	3.79	4.57	28.21	5.47×10^{-5}	7.73×10^{-5}	3.20×10^{-5}
1-Dodecyl-2-pyrrolidinone	2687-96-9	5.3	4.2	5.862	7.12×10^{-7}	--	--
1-Eicosene	3452-07-1	10.03	--	1.26×10^{-5}	1.89×10^{1}	6.74×10^{1}	--
1-Ethyl-2-methylbenzene	611-14-3	3.58	3.53	96.88	8.71×10^{-3}	9.52×10^{-3}	5.53×10^{-3}
1-Hexadecene	629-73-2	8.06	--	0.001232	6.10	1.69×10^{1}	--
1-Hexanol	111-27-3	1.82	2.03	6,885	1.76×10^{-5}	1.94×10^{-5}	1.71×10^{-5}
1-Methoxy-2-propanol	107-98-2	−0.49	--	1.00×10^{6}	5.56×10^{-8}	1.81×10^{-8}	9.20×10^{-7}
1-Octadecanamine, acetate (1:1)	2190-04-7	7.71	--	0.04875	9.36×10^{-4}	2.18×10^{-3}	--
1-Octadecanamine, N,N-dimethyl-	124-28-7	8.39	--	0.008882	4.51×10^{-3}	3.88×10^{-2}	--
1-Octadecene	112-88-9	9.04	--	1.256×10^{-4}	10.7	3.38×10^{1}	--
1-Octanol	111-87-5	2.81	3	814	3.10×10^{-5}	3.88×10^{-5}	2.45×10^{-5}
1-Pentanol	71-41-0	1.33	1.51	2.09×10^{4}	1.33×10^{-5}	1.38×10^{-5}	1.30×10^{-5}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
1-Propanaminium, 3-chloro-2-hydroxy-N,N,N-trimethyl-, chloride	3327-22-8	−4.48	--	1.00×10^{6}	9.48×10^{-17}	--	--
1-Propanesulfonic acid	5284-66-2	−1.4	--	1.00×10^{6}	2.22×10^{-8}	--	--
1-Propanol	71-23-8	0.35	0.25	2.72×10^{5}	7.52×10^{-6}	6.89×10^{-6}	7.41×10^{-6}
1-Propene	115-07-1	1.68	1.77	1,162	1.53×10^{-1}	1.58×10^{-1}	1.96×10^{-1}
1-tert-Butoxy-2-propanol	57018-52-7	0.87	--	5.24×10^{4}	1.30×10^{-7}	5.23×10^{-8}	--
1-Tetradecene	1120-36-1	7.08	--	0.01191	3.46	8.48	--
1-Tridecanol	112-70-9	5.26	--	4.533	1.28×10^{-4}	2.18×10^{-4}	--
1-Undecanol	112-42-5	4.28	--	43.04	7.26×10^{-5}	1.09×10^{-4}	--
2-(2-Butoxyethoxy)ethanol	112-34-5	0.29	0.56	7.19×10^{4}	1.52×10^{-9}	4.45×10^{-11}	7.20×10^{-9}
2-(2-Ethoxyethoxy)ethanol	111-90-0	−0.69	−0.54	8.28×10^{5}	8.63×10^{-10}	2.23×10^{-11}	2.23×10^{-8}
2-(2-Ethoxyethoxy)ethyl acetate	112-15-2	0.32	--	3.09×10^{4}	5.62×10^{-8}	7.22×10^{-10}	2.29×10^{-8}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
2-(Dibutylamino)ethanol	102-81-8	2.01	2.65	3,297	9.70×10^{-9}	1.02×10^{-8}	--
2-(Hydroxymethylamino)ethanol	34375-28-5	−1.53	--	1.00×10^{6}	1.62×10^{-12}	--	--
2-(Thiocyanomethylthio)benzothiazole	21564-17-0	3.12	3.3	41.67	6.49×10^{-12}	--	--
2,2'-(Diazene-1,2-diyldiethane-1,1-diyl)bis-4,5-dihydro-1H-imidazole dihydrochloride	27776-21-2	2.12	--	193.3	3.11×10^{-14}	--	--
2,2'-(Octadecylimino)diethanol	10213-78-2	6.85	--	0.08076	1.06×10^{-8}	7.39×10^{-12}	--
2,2'-[Ethane-1,2-diylbis(oxy)]diethanamine	929-59-9	−2.17	--	1.00×10^{6}	2.50×10^{-13}	8.10×10^{-16}	--
2,2'-Azobis(2-amidinopropane) dihydrochloride	2997-92-4	−3.28	--	1.00×10^{6}	1.21×10^{-14}	--	--
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	1.01	0.82	2,841	6.16×10^{-14}	--	1.91×10^{-8}
2,2-Dibromopropanediamide	73003-80-2	0.37	--	1.00×10^{4}	3.58×10^{-14}	--	--
2,4-Hexadienoic acid, potassium salt, (2E,4E)-	24634-61-5	1.62	1.33	1.94×10^{4}	5.72×10^{-7}	4.99×10^{-8}	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
2,6,8-Trimethyl-4-nonanol	123-17-1	4.48	--	24.97	9.63×10^{-5}	4.45×10^{-4}	--
2-Acrylamido-2-methyl-1-propanesulfonic acid	15214-89-8	−2.19	--	1.00×10^{6}	5.18×10^{-15}	--	--
2-Amino-2-methylpropan-1-ol	124-68-5	−0.74	--	1.00×10^{6}	6.48×10^{-10}	--	--
2-Aminoethanol hydrochloride	2002-24-6	−1.61	−1.31	1.00×10^{6}	3.68×10^{-10}	9.96×10^{-11}	--
2-Bromo-3-nitrilopropionamide	1113-55-9	−0.31	--	3,274	5.35×10^{-13}	--	--
2-Butanone oxime	96-29-7	1.69	0.63	3.66×10^{4}	1.04×10^{-5}	--	--
2-Butoxy-1-propanol	15821-83-7	0.98	--	4.21×10^{4}	1.30×10^{-7}	4.88×10^{-8}	--
2-Butoxyethanol	111-76-2	0.57	0.83	6.45×10^{4}	9.79×10^{-8}	2.08×10^{-8}	1.60×10^{-6}
2-Dodecylbenzenesulfonic acid- N-(2-aminoethyl)ethane-1,2-diamine(1:1)	40139-72-8	4.78	--	0.7032	6.27×10^{-8}	--	--
2-Ethoxyethanol	110-80-5	−0.42	−0.32	7.55×10^{5}	5.56×10^{-8}	1.04×10^{-8}	4.70×10^{-7}
2-Ethoxynaphthalene	93-18-5	3.74	--	38.32	4.13×10^{-5}	4.06×10^{-4}	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
2-Ethyl-1-hexanol	104-76-7	2.73	--	1,379	3.10×10^{-5}	4.66×10^{-5}	2.65×10^{-5}
2-Ethyl-2-hexenal	645-62-5	2.62	--	548.6	2.06×10^{-4}	4.88×10^{-4}	--
2-Ethylhexyl benzoate	5444-75-7	5.19	--	1.061	2.52×10^{-4}	2.34×10^{-4}	--
2-Hydroxyethyl acrylate	818-61-1	−0.25	−0.21	5.07×10^{5}	4.49×10^{-9}	7.22×10^{-10}	--
2-Hydroxyethylammonium hydrogen sulphite	13427-63-9	−1.61	−1.31	1.00×10^{6}	3.68×10^{-10}	9.96×10^{-11}	--
2-Hydroxy-N,N-bis(2-hydroxyethyl)-N-methylethanaminium chloride	7006-59-9	−6.7	--	1.00×10^{6}	4.78×10^{-19}	--	--
2-Mercaptoethanol	60-24-2	−0.2	--	1.94×10^{5}	1.27×10^{-7}	3.38×10^{-8}	1.80×10^{-7}
2-Methoxyethanol	109-86-4	−0.91	−0.77	1.00×10^{6}	4.19×10^{-8}	7.73×10^{-9}	3.30×10^{-7}
2-Methyl-1-propanol	78-83-1	0.77	0.76	9.71×10^{4}	9.99×10^{-6}	1.17×10^{-5}	9.78×10^{-6}
2-Methyl-2,4-pentanediol	107-41-5	0.58	--	3.26×10^{4}	4.06×10^{-7}	3.97×10^{-10}	--
2-Methyl-3(2H)-isothiazolone	2682-20-4	−0.83	--	5.37×10^{5}	4.96×10^{-8}	--	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
2-Methyl-3-butyn-2-ol	115-19-5	0.45	0.28	2.40×10^{5}	1.04×10^{-6}	--	3.91×10^{-6}
2-Methylbutane	78-78-4	2.72	--	184.6	1.29	1.44	1.40
2-Methylquinoline hydrochloride	62763-89-7	2.69	2.59	498.5	7.60×10^{-7}	2.13×10^{-6}	--
2-Phosphono-1,2,4-butanetricarboxylic acid	37971-36-1	−1.66	--	1.00×10^{6}	1.17×10^{-26}	--	--
2-Phosphonobutane-1,2,4-tricarboxylic acid, potassium salt (1:x)	93858-78-7	−1.66	--	1.00×10^{6}	1.17×10^{-26}	--	--
2-Propenoic acid, 2-(2-hydroxyethoxy)ethyl ester	13533-05-6	−0.52	−0.3	3.99×10^{5}	6.98×10^{-11}	1.54×10^{-12}	--
3-(Dimethylamino)propylamine	109-55-7	−0.45	--	1.00×10^{6}	6.62×10^{-9}	4.45×10^{-9}	--
3,4,4-Trimethyloxazolidine	75673-43-7	0.13	--	8.22×10^{5}	6.63×10^{-6}	--	--
3,5,7-Triazatricyclo(3.3.1.13,7))decane, 1-(3-chloro-2-propenyl)-, chloride, (Z)-	51229-78-8	−5.92	--	1.00×10^{6}	1.76×10^{-8}	--	--
3,7-Dimethyl-2,6-octadienal	5392-40-5	3.45	--	84.71	3.76×10^{-4}	4.35×10^{-5}	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
3-Hydroxybutanal	107-89-1	−0.72	--	1.00×10^{6}	4.37×10^{-9}	2.28×10^{-9}	--
3-Methoxypropylamine	5332-73-0	−0.42	--	1.00×10^{6}	1.56×10^{-7}	1.94×10^{-8}	--
3-Phenylprop-2-enal	104-55-2	1.82	1.9	2,150	1.60×10^{-6}	3.38×10^{-7}	--
4,4-Dimethyloxazolidine	51200-87-4	−0.08	--	1.00×10^{6}	3.02×10^{-6}	--	--
4,6-Dimethyl-2-heptanone	19549-80-5	2.56	--	528.8	2.71×10^{-4}	4.55×10^{-4}	--
4-[Abieta-8,11,13-trien-18-yl(3-oxo-3-phenylpropyl)amino]butan-2-one hydrochloride	143106-84-7	7.72	--	0.002229	2.49×10^{-12}	1.20×10^{-14}	--
4-Ethyloct-1-yn-3-ol	5877-42-9	2.87	--	833.9	4.27×10^{-6}	--	--
4-Hydroxy-3-methoxybenzaldehyde	121-33-5	1.05	1.21	6,875	8.27×10^{-11}	2.81×10^{-9}	2.15×10^{-9}
4-Methoxybenzyl formate	122-91-8	1.61	--	2,679	1.15×10^{-6}	2.13×10^{-6}	--
4-Methoxyphenol	150-76-5	1.59	1.58	1.65×10^{4}	3.32×10^{-8}	5.35×10^{-7}	--
4-Methyl-2-pentanol	108-11-2	1.68	--	1.38×10^{4}	1.76×10^{-5}	3.88×10^{-5}	4.45×10^{-5}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
4-Methyl-2-pentanone	108-10-1	1.16	1.31	8,888	1.16×10^{-4}	1.34×10^{-4}	1.38×10^{-4}
4-Nonylphenol	104-40-5	5.99	5.76	1.57	5.97×10^{-6}	1.23×10^{-5}	3.40×10^{-5}
5-Chloro-2-methyl-3(2H)-isothiazolone	26172-55-4	−0.34	--	1.49×10^{5}	3.57×10^{-8}	--	--
Acetaldehyde	75-07-0	−0.17	−0.34	2.57×10^{5}	6.78×10^{-5}	6.00×10^{-5}	6.67×10^{-5}
Acetic acid	64-19-7	0.09	−0.17	4.76×10^{5}	5.48×10^{-7}	2.94×10^{-7}	1.00×10^{-7}
Acetic acid, C6-8-branched alkyl esters	90438-79-2	3.25	--	117.8	9.60×10^{-4}	1.07×10^{-3}	--
Acetic acid, hydroxy-, reaction products with triethanolamine	68442-62-6	−2.48	−1	1.00×10^{6}	4.18×10^{-12}	3.38×10^{-19}	7.05×10^{-13}
Acetic acid, mercapto-, monoammonium salt	5421-46-5	0.03	0.09	2.56×10^{5}	1.94×10^{-8}	--	--
Acetic anhydride	108-24-7	−0.58	--	3.59×10^{5}	3.57×10^{-5}	--	5.71×10^{-6}
Acetone	67-64-1	−0.24	−0.24	2.20×10^{5}	4.96×10^{-5}	3.97×10^{-5}	3.50×10^{-5}
Acetonitrile, 2,2',2''-nitrilotris-	7327-60-8	−1.39	--	1.00×10^{6}	2.61×10^{-15}	--	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Acetophenone	98-86-2	1.67	1.58	4,484	9.81×10^{-6}	1.09×10^{-5}	1.04×10^{-5}
Acetyltriethyl citrate	77-89-4	1.34	--	688.2	6.91×10^{-11}	--	--
Acrolein	107-02-8	0.19	−0.01	1.40×10^{5}	3.58×10^{-5}	1.94×10^{-5}	1.22×10^{-4}
Acrylamide	79-06-1	−0.81	−0.67	5.04×10^{5}	5.90×10^{-9}	--	1.70×10^{-9}
Acrylic acid	79-10-7	0.44	0.35	1.68×10^{5}	2.89×10^{-7}	1.17×10^{-7}	3.70×10^{-7}
Acrylic acid, with sodium-2-acrylamido-2-methyl-1-propanesulfonate and sodium phosphinate	110224-99-2	−2.19	--	1.00×10^{6}	5.18×10^{-15}	--	--
Alcohols, C10-12, ethoxylated	67254-71-1	5.47	--	0.9301	1.95×10^{-2}	2.03×10^{-2}	--
Alcohols, C11-14-iso-, C13-rich	68526-86-3	5.19	--	5.237	1.28×10^{-4}	2.62×10^{-4}	--
Alcohols, C11-14-iso-, C13-rich, ethoxylated	78330-21-9	4.91	--	5.237	1.25×10^{-6}	7.73×10^{-7}	--
Alcohols, C12-13, ethoxylated	66455-14-9	5.96	--	0.2995	2.58×10^{-2}	2.87×10^{-2}	--

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		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Alcohols, C12-14, ethoxylated propoxylated	68439-51-0	6.67	--	0.02971	7.08×10^{-4}	1.23×10^{-4}	--
Alcohols, C12-14-secondary	126950-60-5	5.19	--	5.237	1.28×10^{-4}	3.62×10^{-4}	--
Alcohols, C12-16, ethoxylated	68551-12-2	6.45	--	0.09603	3.43×10^{-2}	4.06×10^{-2}	--
Alcohols, C14-15, ethoxylated	68951-67-7	7.43	--	0.009765	6.04×10^{-2}	8.10×10^{-2}	--
Alcohols, C6-12, ethoxylated	68439-45-2	4.49	--	8.832	1.10×10^{-2}	1.02×10^{-2}	--
Alcohols, C7-9-iso-, C8-rich, ethoxylated	78330-19-5	2.46	--	1,513	3.04×10^{-7}	1.38×10^{-7}	--
Alcohols, C9-11, ethoxylated	68439-46-3	4.98	--	2.874	1.47×10^{-2}	1.44×10^{-2}	--
Alcohols, C9-11-iso-, C10-rich, ethoxylated	78330-20-8	4.9	--	3.321	1.47×10^{-2}	2.39×10^{-2}	--
Alkanes, C12-14-iso-	68551-19-9	6.65	--	0.03173	1.24×10^{1}	2.28×10^{1}	--
Alkanes, C13-16-iso-	68551-20-2	7.63	--	0.003311	2.19×10^{1}	4.55×10^{1}	--
Alkenes, C>10 alpha-	64743-02-8	8.55	--	0.0003941	8.09	2.39×10^{1}	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Alkyl* dimethyl ethylbenzyl ammonium chloride *(50%C12, 30%C14, 17%C16, 3%C18)	85409-23-0_1	3.97	--	3.23	1.11×10^{-11}	--	--
Alkyl* dimethyl ethylbenzyl ammonium chloride *(60%C14, 30%C16, 5%C12, 5%C18)	68956-79-6	4.95	--	0.3172	1.96×10^{-11}	--	--
Alkylbenzenesulfonate, linear	42615-29-2	4.71	--	0.8126	6.27×10^{-8}	--	--
alpha-Lactose monohydrate	5989-81-1	−5.12	--	1.00×10^{6}	4.47×10^{-22}	9.81×10^{-45}	--
alpha-Terpineol	98-55-5	3.33	2.98	371.7	1.58×10^{-5}	3.15×10^{-6}	1.22×10^{-5}
Amaranth	915-67-3	1.63	--	1.789	1.49×10^{-30}	--	--
Aminotrimethylene phosphonic acid	6419-19-8	−5.45	−3.53	1.00×10^{6}	1.65×10^{-34}	--	--
Ammonium acetate	631-61-8	0.09	−0.17	4.76×10^{5}	5.48×10^{-7}	2.94×10^{-7}	1.00×10^{-7}
Ammonium acrylate	10604-69-0	0.44	0.35	1.68×10^{5}	2.89×10^{-7}	1.17×10^{-7}	3.70×10^{-7}
Ammonium citrate (1:1)	7632-50-0	−1.67	−1.64	1.00×10^{6}	8.33×10^{-18}	--	4.33×10^{-14}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Ammonium citrate (2:1)	3012-65-5	−1.67	−1.64	1.00×10^{6}	8.33×10^{-18}	--	4.33×10^{-14}
Ammonium dodecyl sulfate	2235-54-3	2.42	--	163.7	1.84×10^{-7}	--	--
Ammonium hydrogen carbonate	1066-33-7	−0.46	--	8.42×10^{5}	6.05×10^{-9}	--	--
Ammonium lactate	515-98-0	−0.65	−0.72	1.00×10^{6}	1.13×10^{-7}	--	8.13×10^{-8}
Anethole	104-46-1	3.39	--	98.68	2.56×10^{-4}	2.23×10^{-3}	--
Aniline	62-53-3	1.08	0.9	2.08×10^{4}	1.90×10^{-6}	2.18×10^{-6}	2.02×10^{-6}
Benactyzine hydrochloride	57-37-4	2.89	--	292.1	2.07×10^{-10}	--	--
Benzamorf	12068-08-5	4.71	--	0.8126	6.27×10^{-8}	--	--
Benzene	71-43-2	1.99	2.13	2,000	5.39×10^{-3}	5.35×10^{-3}	5.55×10^{-3}
Benzene, C10-16-alkyl derivatives	68648-87-3	8.43	9.36	0.0002099	1.78×10^{-1}	3.97×10^{-1}	--
Benzenesulfonic acid	98-11-3	−1.17	--	6.90×10^{5}	2.52×10^{-9}	--	--
Benzenesulfonic acid, (1-methylethyl)-,	37953-05-2	0.29	--	2.46×10^{4}	4.89×10^{-9}	--	--

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		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Benzenesulfonic acid, (1-methylethyl)-, ammonium salt	37475-88-0	0.29	--	2.46×10^{4}	4.89×10^{-9}	--	--
Benzenesulfonic acid, (1-methylethyl)-, sodium salt	28348-53-0	0.29	--	2.46×10^{4}	4.89×10^{-9}	--	--
Benzenesulfonic acid, C10-16-alkyl derivatives, compounds with cyclohexylamine	255043-08-4	4.71	--	0.8126	6.27×10^{-8}	--	--
Benzenesulfonic acid, C10-16-alkyl derivatives, compounds with triethanolamine	68584-25-8	5.2	--	0.255	8.32×10^{-8}	--	--
Benzenesulfonic acid, C10-16-alkyl derivatives, potassium salts	68584-27-0	5.2	--	0.255	8.32×10^{-8}	--	--
Benzenesulfonic acid, dodecyl-, branched, compounds with 2-propanamine	90218-35-2	4.49	--	1.254	6.27×10^{-8}	--	--
Benzenesulfonic acid, mono-C10-16-alkyl derivatives, sodium salts	68081-81-2	4.22	--	2.584	4.72×10^{-8}	--	--
Benzoic acid	65-85-0	1.87	1.87	2,493	1.08×10^{-7}	4.55×10^{-8}	3.81×10^{-8}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Benzyl chloride	100-44-7	2.79	2.3	1,030	2.09×10^{-3}	3.97×10^{-4}	4.12×10^{-4}
Benzyldimethyldodecylammonium chloride	139-07-1	2.93	--	36.47	7.61×10^{-12}	--	--
Benzylhexadecyldimethylammonium chloride	122-18-9	4.89	--	0.3543	2.36×10^{-11}	--	--
Benzyltrimethylammonium chloride	56-93-9	−2.47	--	1.00×10^{6}	3.37×10^{-13}	--	--
Bicine	150-25-4	−3.27	--	3.52×10^{5}	1.28×10^{-14}	--	--
Bis(1-methylethyl)naphthalenesulfonic acid, cyclohexylamine salt	68425-61-6	2.92	--	43.36	9.29×10^{-10}	--	--
Bis(2-chloroethyl) ether	111-44-4	1.56	1.29	6,435	1.89×10^{-4}	4.15×10^{-7}	1.70×10^{-5}
Bisphenol A	80-05-7	3.64	3.32	172.7	9.16×10^{-12}	--	--
Bronopol	52-51-7	−1.51	--	8.37×10^{5}	6.35×10^{-21}	--	--
Butane	106-97-8	2.31	2.89	135.6	9.69×10^{-1}	8.48×10^{-1}	9.50×10^{-1}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Butanedioic acid, sulfo-, 1,4-bis(1,3-dimethylbutyl) ester, sodium salt	2373-38-8	3.98	--	0.1733	1.61×10^{-12}	--	--
Butene	25167-67-3	2.17	2.4	354.8	2.03×10^{-1}	2.68×10^{-1}	2.33×10^{-1}
Butyl glycidyl ether	2426-08-6	1.08	0.63	2.66×10^{4}	4.37×10^{-6}	5.23×10^{-7}	2.47×10^{-5}
Butyl lactate	138-22-7	0.8	--	5.30×10^{4}	8.49×10^{-5}	--	1.92×10^{-6}
Butyryl trihexyl citrate	82469-79-2	8.21	--	5.56×10^{-5}	3.65×10^{-9}	--	--
C.I. Acid Red 1	3734-67-6	0.51	--	6.157	3.73×10^{-29}	--	--
C.I. Acid Violet 12, disodium salt	6625-46-3	0.59	--	3.379	2.21×10^{-30}	--	--
C.I. Pigment Red 5	6410-41-9	7.65	--	4.38×10^{-5}	4.36×10^{-21}	--	--
C.I. Solvent Red 26	4477-79-6	9.27	--	5.68×10^{-5}	5.48×10^{-13}	4.66×10^{-13}	--
C10-16-Alkyldimethylamines oxides	70592-80-2	2.87	--	89.63	1.14×10^{-13}	--	--
C10-C16 Ethoxylated alcohol	68002-97-1	4.99	--	4.532	1.25×10^{-6}	4.66×10^{-7}	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
C12-14 tert-Alkyl ethoxylated amines	73138-27-9	3.4	--	264.2	1.29×10^{-10}	--	--
Calcium dodecylbenzene sulfonate	26264-06-2	4.71	--	0.8126	6.27×10^{-8}	--	--
Camphor	76-22-2	3.04	2.38	339.1	7.00×10^{-5}	--	8.10×10^{-5}
Carbon dioxide	124-38-9	0.83	0.83	2.57×10^{4}	1.52×10^{-2}	--	1.52×10^{-2}
Carbonic acid, dipotassium salt	584-08-7	−0.46	--	8.42×10^{5}	6.05×10^{-9}	--	--
Choline bicarbonate	78-73-9	−5.16	--	1.00×10^{6}	2.03×10^{-16}	--	--
Choline chloride	67-48-1	−5.16	--	1.00×10^{6}	2.03×10^{-16}	--	--
Citric acid	77-92-9	−1.67	−1.64	1.00×10^{6}	8.33×10^{-18}	--	4.33×10^{-14}
Citronellol	106-22-9	3.56	3.91	105.5	5.68×10^{-5}	2.13×10^{-5}	--
Coconut trimethylammonium chloride	61789-18-2	1.22	--	2,816	9.42×10^{-11}	--	--
Coumarin	91-64-5	1.51	1.39	5,126	6.95×10^{-6}	--	9.92×10^{-8}
Cumene	98-82-8	3.45	3.66	75.03	1.05×10^{-2}	1.23×10^{-2}	1.15×10^{-2}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Cyclohexane	110-82-7	3.18	3.44	43.02	2.55×10^{-1}	1.94×10^{-1}	1.50×10^{-1}
Cyclohexanol	108-93-0	1.64	1.23	3.37×10^{4}	4.90×10^{-6}	3.70×10^{-6}	4.40×10^{-6}
Cyclohexanone	108-94-1	1.13	0.81	2.41×10^{4}	5.11×10^{-5}	1.28×10^{-5}	9.00×10^{-6}
Cyclohexylamine sulfate	19834-02-7	1.63	1.49	6.40×10^{4}	1.38×10^{-5}	--	4.16×10^{-6}
D&C Red no. 28	18472-87-2	9.62	--	1.64×10^{-8}	6.37×10^{-21}	--	--
D&C Red no. 33	3567-66-6	0.48	--	11.87	1.15×10^{-26}	--	--
Daidzein	486-66-8	2.55	--	568.4	3.91×10^{-16}	--	--
Dapsone	80-08-0	0.77	0.97	3,589	3.11×10^{-14}	--	--
Dazomet	533-74-4	0.94	0.63	1.94×10^{4}	2.84×10^{-3}	--	4.98×10^{-10}
Decyldimethylamine	1120-24-7	4.46	--	82.23	4.68×10^{-4}	2.45×10^{-3}	--
D-Glucitol	50-70-4	−3.01	−2.2	1.00×10^{6}	7.26×10^{-13}	2.94×10^{-29}	--
D-Gluconic acid	526-95-4	−1.87	--	1.00×10^{6}	4.74×10^{-13}	--	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
D-Glucopyranoside, methyl	3149-68-6	−2.5	--	1.00×10^{6}	1.56×10^{-14}	2.23×10^{-24}	--
D-Glucose	50-99-7	−2.89	−3.24	1.00×10^{6}	9.72×10^{-15}	1.62×10^{-26}	--
Di(2-ethylhexyl) phthalate	117-81-7	8.39	7.6	0.001132	1.18×10^{-5}	1.02×10^{-5}	2.70×10^{-7}
Dibromoacetonitrile	3252-43-5	0.47	--	9,600	4.06×10^{-7}	--	--
Dichloromethane	75-09-2	1.34	1.25	1.10×10^{4}	9.14×10^{-3}	3.01×10^{-3}	3.25×10^{-3}
Didecyldimethylammonium chloride	7173-51-5	4.66	--	0.9	6.85×10^{-10}	--	--
Diethanolamine	111-42-2	−1.71	−1.43	1.00×10^{6}	3.92×10^{-11}	3.46×10^{-15}	3.87×10^{-11}
Diethylbenzene	25340-17-4	4.07	3.72	58.86	1.16×10^{-2}	1.47×10^{-2}	2.61×10^{-3}
Diethylene glycol	111-46-6	−1.47	--	1.00×10^{6}	2.03×10^{-9}	1.20×10^{-13}	--
Diethylene glycol monomethyl ether	111-77-3	−1.18	--	1.00×10^{6}	6.50×10^{-10}	1.65×10^{-11}	--
Diethylenetriamine	111-40-0	−2.13	--	1.00×10^{6}	3.10×10^{-13}	1.09×10^{-14}	--
Diisobutyl ketone	108-83-8	2.56	--	528.8	2.71×10^{-4}	4.55×10^{-4}	1.17×10^{-4}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Diisopropanolamine	110-97-4	−0.88	−0.82	1.00×10^{6}	6.91×10^{-11}	1.90×10^{-14}	--
Diisopropylnaphthalene	38640-62-9	6.08	--	0.2421	1.99×10^{-3}	1.94×10^{-3}	--
Dimethyl adipate	627-93-0	1.39	1.03	7,749	9.77×10^{-7}	1.28×10^{-7}	2.31×10^{-6}
Dimethyl glutarate	1119-40-0	0.9	0.62	2.02×10^{4}	7.36×10^{-7}	9.09×10^{-8}	6.43×10^{-7}
Dimethyl succinate	106-65-0	0.4	0.35	3.96×10^{4}	5.54×10^{-7}	6.43×10^{-8}	--
Dimethylaminoethanol	108-01-0	−0.94	--	1.00×10^{6}	1.77×10^{-9}	1.77×10^{-9}	3.73×10^{-7}
Dimethyldiallylammonium chloride	7398-69-8	−2.49	--	1.00×10^{6}	7.20×10^{-12}	--	--
Diphenyl oxide	101-84-8	4.05	4.21	15.58	1.18×10^{-4}	2.81×10^{-4}	2.79×10^{-4}
Dipropylene glycol	25265-71-8	−0.64	--	3.11×10^{5}	3.58×10^{-9}	6.29×10^{-10}	--
Di-sec-butylphenol	31291-60-8	5.41	--	3.723	3.74×10^{-6}	6.89×10^{-6}	--
Disodium dodecyl(sulphonatophenoxy)benzenesulphonate	28519-02-0	5.05	--	0.0353	6.40×10^{-16}	--	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Disodium ethylenediaminediacetate	38011-25-5	−4.79	--	1.00×10^{6}	1.10×10^{-16}	--	--
Disodium ethylenediaminetetraacetate dihydrate	6381-92-6	−3.86	--	2.28×10^{5}	1.17×10^{-23}	--	5.77×10^{-16}
D-Lactic acid	10326-41-7	−0.65	−0.72	1.00×10^{6}	1.13×10^{-7}	--	8.13×10^{-8}
D-Limonene	5989-27-5	4.83	4.57	4.581	3.80×10^{-1}	--	3.19×10^{-2}
Docusate sodium	577-11-7	6.1	--	0.001227	5.00×10^{-12}	--	--
Dodecane	112-40-3	6.23	6.1	0.1099	9.35	1.34×10^{1}	8.18
Dodecylbenzene	123-01-3	7.94	8.65	0.001015	1.34×10^{-1}	2.81×10^{-1}	--
Dodecylbenzenesulfonic acid	27176-87-0	4.71	--	0.8126	6.27×10^{-8}	--	--
Dodecylbenzenesulfonic acid, monoethanolamine salt	26836-07-7	4.71	--	0.8126	6.27×10^{-8}	--	--
Epichlorohydrin	106-89-8	0.63	0.45	5.06×10^{4}	5.62×10^{-5}	2.62×10^{-6}	3.04×10^{-5}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Ethanaminium, N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]-, chloride	44992-01-0	−3.1	--	1.00×10^{6}	6.96×10^{-15}	--	--
Ethane	74-84-0	1.32	1.81	938.6	5.50×10^{-1}	4.25×10^{-1}	5.00×10^{-1}
Ethanol	64-17-5	−0.14	−0.31	7.92×10^{5}	5.67×10^{-6}	4.88×10^{-6}	5.00×10^{-6}
Ethanol, 2,2',2''-nitrilotris-, tris(dihydrogen phosphate) (ester), sodium salt	68171-29-9	−3.13	--	1.00×10^{6}	3.08×10^{-36}	--	--
Ethanol, 2-[2-[2-(tridecyloxy) ethoxy]ethoxy]-, hydrogen sulfate, sodium salt	25446-78-0	2.09	--	42	9.15×10^{-13}	--	--
Ethanolamine	141-43-5	−1.61	−1.31	1.00×10^{6}	3.68×10^{-10}	9.96×10^{-11}	--
Ethoxylated dodecyl alcohol	9002-92-0	4.5	--	14.19	9.45×10^{-7}	3.30×10^{-7}	--
Ethyl acetate	141-78-6	0.86	0.73	2.99×10^{4}	2.33×10^{-4}	1.58×10^{-4}	1.34×10^{-4}
Ethyl acetoacetate	141-97-9	−0.2	0.25	5.62×10^{4}	1.57×10^{-7}	--	1.20×10^{-6}
Ethyl benzoate	93-89-0	2.32	2.64	421.5	4.61×10^{-5}	2.45×10^{-5}	7.33×10^{-5}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Ethyl lactate	97-64-3	−0.18	--	4.73×10^{5}	4.82×10^{-5}	--	5.83×10^{-7}
Ethyl salicylate	118-61-6	3.09	2.95	737.1	6.04×10^{-6}	3.01×10^{-9}	--
Ethylbenzene	100-41-4	3.03	3.15	228.6	7.89×10^{-3}	8.88×10^{-3}	7.88×10^{-3}
Ethylene	74-85-1	1.27	1.13	3,449	9.78×10^{-2}	1.62×10^{-1}	2.28×10^{-1}
Ethylene glycol	107-21-1	−1.2	−1.36	1.00×10^{6}	1.31×10^{-7}	5.60×10^{-11}	6.00×10^{-8}
Ethylene oxide	75-21-8	−0.05	−0.3	2.37×10^{5}	1.20×10^{-4}	5.23×10^{-5}	1.48×10^{-4}
Ethylenediamine	107-15-3	−1.62	−2.04	1.00×10^{6}	1.03×10^{-9}	1.77×10^{-10}	1.73×10^{-9}
Ethylenediaminetetraacetic acid	60-00-4	−3.86	--	2.28×10^{5}	1.17×10^{-23}	--	5.77×10^{-16}
Ethylenediaminetetraacetic acid tetrasodium salt	64-02-8	−3.86	--	2.28×10^{5}	1.17×10^{-23}	--	5.77×10^{-16}
Ethylenediaminetetraacetic acid, disodium salt	139-33-3	−3.86	--	2.28×10^{5}	1.17×10^{-23}	--	5.77×10^{-16}
Ethyne	74-86-2	0.5	0.37	1.48×10^{4}	2.40×10^{-2}	2.45×10^{-2}	2.17×10^{-2}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Fatty acids, C18-unsaturated, dimers	61788-89-4	14.6	--	2.31×10^{-10}	4.12×10^{-8}	9.74×10^{-9}	--
FD&C Blue no. 1	3844-45-9	−0.15	--	0.2205	2.25×10^{-35}	--	--
FD&C Yellow no. 5	1934-21-0	−1.82	--	7.388	1.31×10^{-28}	--	--
FD&C Yellow no. 6	2783-94-0	1.4	--	242.7	3.26×10^{-23}	--	--
Formaldehyde	50-00-0	0.35	0.35	5.70×10^{4}	9.29×10^{-5}	6.14×10^{-5}	3.37×10^{-7}
Formamide	75-12-7	−1.61	−1.51	1.00×10^{6}	1.53×10^{-8}	--	1.39×10^{-9}
Formic acid	64-18-6	−0.46	−0.54	9.55×10^{5}	7.50×10^{-7}	5.11×10^{-7}	1.67×10^{-7}
Formic acid, potassium salt	590-29-4	−0.46	−0.54	9.55×10^{5}	7.50×10^{-7}	5.11×10^{-7}	1.67×10^{-7}
Fumaric acid	110-17-8	0.05	−0.48	1.04×10^{5}	1.35×10^{-12}	8.48×10^{-14}	--
Furfural	98-01-1	0.83	0.41	5.36×10^{4}	1.34×10^{-5}	--	3.77×10^{-6}
Furfuryl alcohol	98-00-0	0.45	0.28	2.21×10^{5}	2.17×10^{-7}	--	7.86×10^{-8}
Galantamine hydrobromide	69353-21-5	2.29	--	1,606	1.70×10^{-13}	--	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Gluconic acid	133-42-6	−1.87	--	1.00×10^{6}	4.74×10^{-13}	--	--
Glutaraldehyde	111-30-8	−0.18	--	1.67×10^{5}	1.10×10^{-7}	2.39×10^{-8}	--
Glycerol	56-81-5	−1.65	−1.76	1.00×10^{6}	6.35×10^{-9}	1.51×10^{-15}	1.73×10^{-8}
Glycine, N-(carboxymethyl)-N-(2-hydroxyethyl)-, disodium salt	135-37-5	−3.04	--	1.90×10^{5}	3.90×10^{-17}	--	--
Glycine, N-(hydroxymethyl)-, monosodium salt	70161-44-3	−3.41	--	7.82×10^{5}	1.80×10^{-12}	--	--
Glycine, N,N-bis(carboxymethyl)-, trisodium salt	5064-31-3	−3.81	--	7.39×10^{5}	1.19×10^{-16}	--	--
Glycine, N-[2-[bis(carboxymethyl)amino]ethyl]-N-(2-hydroxyethyl)-, trisodium salt	139-89-9	−4.09	--	4.31×10^{5}	3.81×10^{-24}	--	--
Glycolic acid	79-14-1	−1.07	−1.11	1.00×10^{6}	8.54×10^{-8}	6.29×10^{-11}	--
Glycolic acid sodium salt	2836-32-0	−1.07	−1.11	1.00×10^{6}	8.54×10^{-8}	6.29×10^{-11}	--
Glyoxal	107-22-2	−1.66	--	1.00×10^{6}	3.70×10^{-7}	--	3.33×10^{-9}

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		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Glyoxylic acid	298-12-4	−1.4	--	1.00×10^{6}	2.98×10^{-9}	--	--
Heptane	142-82-5	3.78	4.66	3.554	2.27	2.39	2.00
Hexadecyltrimethylammonium bromide	57-09-0	3.18	--	28.77	2.93×10^{-10}	--	--
Hexane	110-54-3	3.29	3.9	17.24	1.71	1.69	1.80
Hexanedioic acid	124-04-9	0.23	0.08	1.67×10^{5}	9.53×10^{-12}	8.10×10^{-13}	4.71×10^{-12}
Hydroxyvalerenic acid	1619-16-5	3.31	--	282.1	--	--	--
Indole	120-72-9	2.05	2.14	1,529	8.86×10^{-7}	1.99×10^{-6}	5.28×10^{-7}
Isoascorbic acid	89-65-6	−1.88	−1.85	1.00×10^{6}	4.07×10^{-8}	--	--
Isobutane	75-28-5	2.23	2.76	175.1	9.69×10^{-1}	1.02	1.19
Isobutene	115-11-7	2.23	2.34	399.2	2.40×10^{-1}	2.34×10^{-1}	2.18×10^{-1}
Isooctanol	26952-21-6	2.73	--	1,379	3.10×10^{-5}	4.66×10^{-5}	9.21×10^{-5}
Isopentyl alcohol	123-51-3	1.26	1.16	4.16×10^{4}	1.33×10^{-5}	1.65×10^{-5}	1.41×10^{-5}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Isopropanol	67-63-0	0.28	0.05	4.02×10^{5}	7.52×10^{-6}	1.14×10^{-5}	8.10×10^{-6}
Isopropanolamine dodecylbenzene	42504-46-1	7.94	8.65	0.001015	1.34×10^{-1}	2.81×10^{-1}	--
Isopropylamine	75-31-0	0.27	0.26	8.38×10^{5}	1.34×10^{-5}	--	4.51×10^{-5}
Isoquinoline	119-65-3	2.14	2.08	1,551	6.88×10^{-7}	4.15×10^{-7}	--
Isoquinoline, reaction products with benzyl chloride and quinoline	68909-80-8	2.14	2.08	1,551	6.88×10^{-7}	4.15×10^{-7}	--
Isoquinolinium, 2-(phenylmethyl)-, chloride	35674-56-7	4.4	--	6.02	1.19×10^{-6}	--	--
Lactic acid	50-21-5	−0.65	−0.72	1.00×10^{6}	1.13×10^{-7}	--	8.13×10^{-8}
Lactose	63-42-3	−5.12	--	1.00×10^{6}	4.47×10^{-22}	9.81×10^{-45}	--
Lauryl hydroxysultaine	13197-76-7	−1.3	--	7.71×10^{4}	1.04×10^{-21}	--	--
L-Dilactide	4511-42-6	1.65	--	3,165	1.22×10^{-5}	--	--
L-Glutamic acid	56-86-0	−3.83	−3.69	9.42×10^{5}	1.47×10^{-14}	--	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
L-Lactic acid	79-33-4	−0.65	−0.72	1.00×10^{6}	1.13×10^{-7}	--	8.13×10^{-8}
Methane	74-82-8	0.78	1.09	2,610	4.14×10^{-1}	6.58×10^{-1}	6.58×10^{-1}
Methanol	67-56-1	−0.63	−0.77	1.00×10^{6}	4.27×10^{-6}	3.62×10^{-6}	4.55×10^{-6}
Methenamine	100-97-0	−4.15	--	1.00×10^{6}	1.63×10^{-1}	--	1.64×10^{-9}
Methoxyacetic acid	625-45-6	−0.68	--	1.00×10^{6}	4.54×10^{-8}	8.68×10^{-9}	6.42×10^{-9}
Methyl salicylate	119-36-8	2.6	2.55	1,875	4.55×10^{-6}	2.23×10^{-9}	9.81×10^{-5}
Methyl vinyl ketone	78-94-4	0.41	--	6.06×10^{4}	2.61×10^{-5}	1.38×10^{-5}	4.65×10^{-5}
Methylcyclohexane	108-87-2	3.59	3.61	28.4	3.39×10^{-1}	3.30×10^{-1}	4.30×10^{-1}
Methylene bis(thiocyanate)	6317-18-6	0.62	--	2.72×10^{4}	2.61×10^{-8}	--	--
Methylenebis(5-methyloxazolidine)	66204-44-2	−0.58	--	1.00×10^{6}	1.07×10^{-7}	--	--
Morpholine	110-91-8	−0.56	−0.86	1.00×10^{6}	1.14×10^{-7}	3.22×10^{-9}	1.16×10^{-6}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Morpholinium, 4-ethyl-4-hexadecyl-, ethyl sulfate	78-21-7	4.54	--	0.9381	2.66×10^{-12}	--	--
N-(2-Acryloyloxyethyl)-N-benzyl-N,N-dimethylammonium chloride	46830-22-2	−1.39	--	4.42×10^{5}	5.62×10^{-16}	--	--
N-(3-Chloroallyl)hexaminium chloride	4080-31-3	−5.92	--	1.00×10^{6}	1.76×10^{-8}	--	--
N,N,N-Trimethyl-3-((1-oxooctadecyl)amino)-1-propanaminium methyl sulfate	19277-88-4	4.38	--	0.7028	2.28×10^{-16}	--	--
N,N,N-Trimethyloctadecan-1-aminium chloride	112-03-8	4.17	--	2.862	5.16×10^{-10}	--	--
N,N'-Dibutylthiourea	109-46-6	2.57	2.75	2,287	4.17×10^{-6}	--	--
N,N-Dimethyldecylamine oxide	2605-79-0	1.4	--	2,722	4.88×10^{-14}	--	--
N,N-Dimethylformamide	68-12-2	−0.93	−1.01	9.78×10^{5}	7.38×10^{-8}	--	7.39×10^{-8}
N,N-Dimethylmethanamine hydrochloride	593-81-7	0.04	0.16	1.00×10^{6}	3.65×10^{-5}	1.28×10^{-4}	1.04×10^{-4}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
N,N-Dimethyl-methanamine-N-oxide	1184-78-7	−3.02	--	1.00×10^{6}	3.81×10^{-15}	--	--
N,N-dimethyloctadecylamine hydrochloride	1613-17-8	8.39	--	0.008882	4.51×10^{-3}	3.88×10^{-2}	--
N,N'-Methylenebisacrylamide	110-26-9	−1.52	--	7.01×10^{4}	1.14×10^{-9}	--	--
Naphthalene	91-20-3	3.17	3.3	142.1	5.26×10^{-4}	3.70×10^{-4}	4.40×10^{-4}
Naphthalenesulfonic acid, bis(1-methylethyl)-	28757-00-8	2.92	--	43.36	9.29×10^{-10}	--	--
Naphthalenesulphonic acid, bis (1-methylethyl)-methyl derivatives	99811-86-6	4.02	--	3.45	1.13×10^{-9}	--	--
Naphthenic acid ethoxylate	68410-62-8	3.41	--	112.5	3.62×10^{-8}	2.74×10^{-9}	--
Nitrilotriacetamide	4862-18-4	−4.75	--	1.00×10^{6}	1.61×10^{-18}	--	--
Nitrilotriacetic acid	139-13-9	−3.81	--	7.39×10^{5}	1.19×10^{-16}	--	--
Nitrilotriacetic acid trisodium monohydrate	18662-53-8	−3.81	--	7.39×10^{5}	1.19×10^{-16}	--	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
N-Methyl-2-pyrrolidone	872-50-4	−0.11	−0.38	2.48×10^{5}	3.16×10^{-8}	--	3.20×10^{-9}
N-Methyldiethanolamine	105-59-9	−1.5	--	1.00×10^{6}	8.61×10^{-11}	2.45×10^{-14}	3.14×10^{-11}
N-Methylethanolamine	109-83-1	−1.15	−0.94	1.00×10^{6}	8.07×10^{-10}	2.50×10^{-10}	--
N-Methyl-N-hydroxyethyl-N-hydroxyethoxyethylamine	68213-98-9	−1.78	--	1.00×10^{6}	1.34×10^{-12}	5.23×10^{-17}	--
N-Oleyl diethanolamide	13127-82-7	6.63	--	0.1268	9.35×10^{-9}	1.94×10^{-12}	--
Oleic acid	112-80-1	7.73	7.64	0.01151	4.48×10^{-5}	1.94×10^{-5}	--
Pentaethylenehexamine	4067-16-7	−3.67	--	1.00×10^{6}	8.36×10^{-24}	2.56×10^{-27}	--
Pentane	109-66-0	2.8	3.39	49.76	1.29	1.20	1.25
Pentyl acetate	628-63-7	2.34	2.3	996.8	5.45×10^{-4}	4.45×10^{-4}	3.88×10^{-4}
Pentyl butyrate	540-18-1	3.32	--	101.9	9.60×10^{-4}	8.88×10^{-4}	--
Peracetic acid	79-21-0	−1.07	--	1.00×10^{6}	1.39×10^{-6}	--	2.14×10^{-6}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Phenanthrene	85-01-8	4.35	4.46	0.677	5.13×10^{-5}	2.56×10^{-5}	4.23×10^{-5}
Phenol	108-95-2	1.51	1.46	2.62×10^{4}	5.61×10^{-7}	6.58×10^{-7}	3.33×10^{-7}
Phosphonic acid (dimethylamino(methylene))	29712-30-9	−1.9	--	1.00×10^{6}	1.00×10^{-24}	--	--
Phosphonic acid, (((2-[(2-hydroxyethyl)(phosphonomethyl)amino)ethyl)imino]bis(methylene))bis-, compd. with 2-aminoethanol	129828-36-0	−6.73	--	1.00×10^{6}	5.29×10^{-42}	--	--
Phosphonic acid, (1-hydroxyethylidene) bis-, potassium salt	67953-76-8	−0.01	--	1.34×10^{5}	9.79×10^{-26}	--	--
Phosphonic acid, (1-hydroxyethylidene) bis-, tetrasodium salt	3794-83-0	−0.01	--	1.34×10^{5}	9.79×10^{-26}	--	--
Phosphonic acid, [[(phosphonomethyl) imino]bis[2,1-ethanediylnitrilobis (methylene)]]tetrakis-	15827-60-8	−9.72	--	1.00×10^{6}	--	--	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Phosphonic acid, [[(phosphonomethyl) imino]bis[2,1-ethanediylnitrilobis (methylene)]]tetrakis-, ammonium salt (1:x)	70714-66-8	−9.72	--	1.00×10^6	--	--	--
Phosphonic acid, [[(phosphonomethyl) imino]bis[2,1-ethanediylnitrilobis (methylene)]]tetrakis-, sodium salt	22042-96-2	−9.72	--	1.00×10^6	--	--	--
Phosphonic acid, [[(phosphonomethyl) imino]bis[6,1-hexanediylnitrilobis (methylene)]]tetrakis-	34690-00-1	−5.79	--	1.00×10^6	--	--	--
Phthalic anhydride	85-44-9	2.07	1.6	3,326	6.35×10^{-6}	--	1.63×10^{-8}
Poly(oxy-1,2-ethanediyl), .alpha.-(octylphenyl)-.omega.-hydroxy-, branched	68987-90-6	5.01	--	3.998	1.24×10^{-7}	1.07×10^{-6}	--
Potassium acetate	127-08-2	0.09	−0.17	4.76×10^5	5.48×10^{-7}	2.94×10^{-7}	1.00×10^{-7}
Potassium oleate	143-18-0	7.73	7.64	0.01151	4.48×10^{-5}	1.94×10^{-5}	--
Propane	74-98-6	1.81	2.36	368.9	7.30×10^{-1}	6.00×10^{-1}	7.07×10^{-1}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Propanol, 1(or 2)-(2-methoxymethylethoxy)-	34590-94-8	−0.27	--	4.27×10^{5}	1.15×10^{-9}	1.69×10^{-9}	--
Propargyl alcohol	107-19-7	−0.42	−0.38	9.36×10^{5}	5.88×10^{-7}	--	1.15×10^{-6}
Propylene carbonate	108-32-7	0.08	−0.41	2.58×10^{5}	3.63×10^{-4}	--	3.45×10^{-8}
Propylene pentamer	15220-87-8	6.28	--	0.05601	3.92×10^{-1}	1.09×10^{-3}	--
p-Xylene	106-42-3	3.09	3.15	228.6	6.56×10^{-3}	6.14×10^{-3}	6.90×10^{-3}
Pyrimidine	289-95-2	−0.06	−0.4	2.87×10^{5}	2.92×10^{-6}	--	--
Pyrrole	109-97-7	0.88	0.75	3.12×10^{4}	9.07×10^{-6}	7.73×10^{-6}	1.80×10^{-5}
Quaternary ammonium compounds, di-C8-10-alkyldimethyl, chlorides	68424-95-3	2.69	--	90.87	2.20×10^{-10}	--	--
Quinaldine	91-63-4	2.69	2.59	498.5	7.60×10^{-7}	2.13×10^{-6}	--
Quinoline	91-22-5	2.14	2.03	1,711	6.88×10^{-7}	1.54×10^{-6}	1.67×10^{-6}
Rhodamine B	81-88-9	6.03	--	0.0116	--	--	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Sodium 1-octanesulfonate	5324-84-5	1.06	--	5,864	9.15×10^{-8}	--	--
Sodium 2-mercaptobenzothiolate	2492-26-4	2.86	2.42	543.4	3.63×10^{-8}	--	--
Sodium acetate	127-09-3	0.09	−0.17	4.76×10^{5}	5.48×10^{-7}	2.94×10^{-7}	1.00×10^{-7}
Sodium benzoate	532-32-1	1.87	1.87	2,493	1.08×10^{-7}	4.55×10^{-8}	3.81×10^{-8}
Sodium bicarbonate	144-55-8	−0.46	--	8.42×10^{5}	6.05×10^{-9}	--	--
Sodium bis(tridecyl) sulfobutanedioate	2673-22-5	11.15	--	7.46×10^{-9}	8.51×10^{-11}	--	--
Sodium C14-16 alpha-olefin sulfonate	68439-57-6	4.36	--	2.651	4.95×10^{-7}	--	--
Sodium caprylamphopropionate	68610-44-6	−0.26	--	615.1	1.19×10^{-9}	2.45×10^{-10}	--
Sodium carbonate	497-19-8	−0.46	--	8.42×10^{5}	6.05×10^{-9}	--	--
Sodium chloroacetate	3926-62-3	0.34	0.22	1.95×10^{5}	1.93×10^{-7}	8.88×10^{-8}	9.26×10^{-9}
Sodium decyl sulfate	142-87-0	1.44	--	1,617	1.04×10^{-7}	--	--
Sodium D-gluconate	527-07-1	−1.87	--	1.00×10^{6}	4.74×10^{-13}	--	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Sodium diacetate	126-96-5	0.09	−0.17	4.76×10^{5}	5.48×10^{-7}	2.94×10^{-7}	1.00×10^{-7}
Sodium dichloroisocyanurate	2893-78-9	1.28	--	3,613	3.22×10^{-12}	--	--
Sodium dl-lactate	72-17-3	−0.65	−0.72	1.00×10^{6}	1.13×10^{-7}	--	8.13×10^{-8}
Sodium dodecyl sulfate	151-21-3	2.42	--	163.7	1.84×10^{-7}	--	--
Sodium erythorbate (1:1)	6381-77-7	−1.88	−1.85	1.00×10^{6}	4.07×10^{-8}	--	--
Sodium ethasulfate	126-92-1	0.38	--	1.82×10^{4}	5.91×10^{-8}	--	--
Sodium formate	141-53-7	−0.46	−0.54	9.55×10^{5}	7.50×10^{-7}	5.11×10^{-7}	1.67×10^{-7}
Sodium hydroxymethanesulfonate	870-72-4	−3.85	--	1.00×10^{6}	4.60×10^{-13}	--	--
Sodium l-lactate	867-56-1	−0.65	−0.72	1.00×10^{6}	1.13×10^{-7}	--	8.13×10^{-8}
Sodium maleate (1:x)	18016-19-8	0.05	−0.48	1.04×10^{5}	1.35×10^{-12}	8.48×10^{-14}	--
Sodium N-methyl-N-oleoyltaurate	137-20-2	4.43	--	0.4748	1.00×10^{-12}	--	--
Sodium octyl sulfate	142-31-4	0.46	--	1.58×10^{4}	5.91×10^{-8}	--	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Sodium salicylate	54-21-7	2.24	2.26	3,808	1.42×10^{-8}	5.60×10^{-12}	7.34×10^{-9}
Sodium sesquicarbonate	533-96-0	−0.46	--	8.42×10^{5}	6.05×10^{-9}	--	--
Sodium thiocyanate	540-72-7	0.58	--	4.36×10^{4}	1.46×10^{-4}	--	--
Sodium trichloroacetate	650-51-1	1.44	1.33	1.20×10^{4}	2.39×10^{-8}	--	1.35×10^{-8}
Sodium xylenesulfonate	1300-72-7	−0.07	--	5.89×10^{4}	3.06×10^{-9}	--	--
Sorbic acid	110-44-1	1.62	1.33	1.94×10^{4}	5.72×10^{-7}	4.99×10^{-8}	--
Sorbitan sesquioleate	8007-43-0	14.32	--	2.31×10^{-11}	7.55×10^{-12}	1.25×10^{-16}	--
Sorbitan, mono-(9Z)-9-octadecenoate	1338-43-8	5.89	--	0.01914	1.42×10^{-12}	5.87×10^{-20}	--
Sorbitan, monooctadecanoate	1338-41-6	6.1	--	0.01218	1.61×10^{-12}	2.23×10^{-19}	--
Sorbitan, tri-(9Z)-9-octadecenoate	26266-58-0	22.56	--	1.12×10^{-19}	4.02×10^{-11}	2.68×10^{-13}	--
Styrene	100-42-5	2.89	2.95	343.7	2.76×10^{-3}	2.81×10^{-3}	2.75×10^{-3}
Sucrose	57-50-1	−4.27	−3.7	1.00×10^{6}	4.47×10^{-22}	--	--

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Sulfan blue	129-17-9	−1.34	--	50.67	1.31×10^{-26}	--	--
Sulfuric acid, mono-C12-18-alkyl esters, sodium salts	68955-19-1	3.9	--	5.165	4.29×10^{-7}	--	--
Sulfuric acid, mono-C6-10-alkyl esters, ammonium salts	68187-17-7	0.46	--	1.58×10^{4}	5.91×10^{-8}	--	--
Symclosene	87-90-1	0.94	--	4,610	6.19×10^{-11}	--	--
tert-Butyl hydroperoxide	75-91-2	0.94	--	1.97×10^{4}	1.60×10^{-5}	--	--
tert-Butyl perbenzoate	614-45-9	2.89	--	159.2	2.06×10^{-4}	--	--
Tetradecane	629-59-4	7.22	7.2	0.009192	1.65×10^{1}	2.68×10^{1}	9.20
Tetradecyldimethylbenzylammonium chloride	139-08-2	3.91	--	3.608	1.34×10^{-11}	--	--
Tetraethylene glycol	112-60-7	−2.02	--	1.00×10^{6}	4.91×10^{-13}	5.48×10^{-19}	--
Tetraethylenepentamine	112-57-2	−3.16	--	1.00×10^{6}	2.79×10^{-20}	4.15×10^{-23}	--

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		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Tetrakis(hydroxymethyl)phosphonium sulfate	55566-30-8	−5.03	--	1.00×10^{6}	9.17×10^{-13}	--	--
Tetramethylammonium chloride	75-57-0	−4.18	--	1.00×10^{6}	4.17×10^{-12}	--	--
Thiamine hydrochloride	67-03-8	0.95	--	3,018	8.24×10^{-17}	--	--
Thiocyanic acid, ammonium salt	1762-95-4	0.58	--	4.36×10^{4}	1.46×10^{-4}	--	--
Thioglycolic acid	68-11-1	0.03	0.09	2.56×10^{5}	1.94×10^{-8}	--	--
Thiourea	62-56-6	−1.31	−1.08	5.54×10^{5}	1.58×10^{-7}	--	1.98×10^{-9}
Toluene	108-88-3	2.54	2.73	573.1	5.95×10^{-3}	5.73×10^{-3}	6.64×10^{-3}
Tributyl phosphate	126-73-8	3.82	4	7.355	3.19×10^{-6}	--	1.41×10^{-6}
Tributyltetradecylphosphonium chloride	81741-28-8	11.22	--	7.90×10^{-7}	2.61×10^{-1}	--	--
Tridecane	629-50-5	6.73	--	0.02746	1.24×10^{1}	1.90×10^{1}	2.88
Triethanolamine	102-71-6	−2.48	−1	1.00×10^{6}	4.18×10^{-12}	3.38×10^{-19}	7.05×10^{-13}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Triethanolamine hydrochloride	637-39-8	−2.48	−1	1.00×10^{6}	4.18×10^{-12}	3.38×10^{-19}	7.05×10^{-13}
Triethanolamine hydroxyacetate	68299-02-5	−2.97	--	1.00×10^{6}	6.28×10^{-11}	--	--
Triethyl citrate	77-93-0	0.33	--	2.82×10^{4}	6.39×10^{-10}	--	3.84×10^{-9}
Triethyl phosphate	78-40-0	0.87	0.8	1.12×10^{4}	5.83×10^{-7}	--	3.60×10^{-8}
Triethylene glycol	112-27-6	−1.75	−1.75	1.00×10^{6}	3.16×10^{-11}	2.56×10^{-16}	--
Triethylenetetramine	112-24-3	−2.65	--	1.00×10^{6}	9.30×10^{-17}	6.74×10^{-19}	--
Triisopropanolamine	122-20-3	−1.22	--	1.00×10^{6}	9.77×10^{-12}	4.35×10^{-18}	--
Trimethanolamine	14002-32-5	−3.95	--	1.00×10^{6}	1.42×10^{-8}	--	--
Trimethylamine	75-50-3	0.04	0.16	1.00×10^{6}	3.65×10^{-5}	1.28×10^{-4}	1.04×10^{-4}
Tripotassium citrate monohydrate	6100-05-6	−1.67	−1.64	1.00×10^{6}	8.33×10^{-18}	--	4.33×10^{-14}
Tripropylene glycol monomethyl ether	25498-49-1	−0.2	--	1.96×10^{5}	2.36×10^{-11}	4.55×10^{-13}	--
Trisodium citrate	68-04-2	−1.67	−1.64	1.00×10^{6}	8.33×10^{-18}	--	4.33×10^{-14}

Chemical name	CASRN	Log K_{ow}		Water solubility	Henry's law constant (atm-m^3/mol at 25°C)		
		Estimated	Measured	Estimate from log K_{ow} (mg/L at 25°C)	Bond method	Group method 25	Measured
Trisodium citrate dihydrate	6132-04-3	−1.67	−1.64	1.00×10^{6}	8.33×10^{-18}	--	4.33×10^{-14}
Trisodium ethylenediaminetetraacetate	150-38-9	−3.86	--	2.28×10^{5}	1.17×10^{-23}	--	5.77×10^{-16}
Trisodium ethylenediaminetriacetate	19019-43-3	−4.32	--	1.00×10^{6}	3.58×10^{-20}	--	--
Tromethamine	77-86-1	−1.56	--	1.00×10^{6}	8.67×10^{-13}	--	--
Undecane	1120-21-4	5.74	--	0.2571	7.04	9.52	1.93
Urea	57-13-6	−1.56	−2.11	4.26×10^{5}	3.65×10^{-10}	--	1.74×10^{-12}
Xylenes	1330-20-7	3.09	3.2	207.2	6.56×10^{-3}	6.14×10^{-3}	7.18×10^{-3}

"--" indicates no information available.

The EPI (Estimation Programs Interface) Suite™ (U.S. EPA, 2012a) is an open-source, Windows®-based suite of physicochemical property and environmental fate estimation programs developed by the EPA's Office of Pollution Prevention Toxics and Syracuse Research Corporation. More information on EPI Suite™ is available at http://www.epa.gov/oppt/exposure/pubs/episuite.htm.

Although only physicochemical properties from EPI Suite™ are provided here, other sources of information were also consulted. QikProp (Schrodinger, 2012) and LeadScope® (Inc., 2012) are commercial products designed primarily as drug development and screening tools. QikProp is specifically focused on drug discovery and provides predictions for physically significant descriptors and pharmaceutically (and toxicologically) relevant properties useful in predicting ADME (adsorption, distribution, metabolism, and excretion) characteristics of drug candidates. QikProp's use of whole-molecule descriptors that have a straightforward physical interpretation (as opposed to fragment-based descriptors).

LeadScope® is a program designed for interpreting chemical and biological screening data that can assist pharmaceutical scientists in finding promising drug candidates. The software organizes the chemical data by structural features familiar to medicinal chemists. Graphs are used to summarize the data, and structural classes are highlighted that are statistically correlated with biological activity. It incorporates chemically-based data mining, visualization, and advanced informatics techniques (e.g., prediction tools, scaffold generators). Note that properties generated by QikProp and LeadScope® are generally more relevant to drug development than to environmental assessment.

Physicochemical properties of chemicals were generated from the two-dimensional (2-D) chemical structures from the EPA National Center for Computational Toxicology's Distributed Structure-Searchable Toxicity (NCCT DSSTox) Database Network in structure-data file (SDF) format. For EPI Suite™ properties, both the desalted and non-desalted 2-D files were run using the program's batch mode (i.e., processing many molecules at once) to calculate environmentally-relevant, chemical property descriptors. The chemical descriptors in QikProp require 3-D chemical structures. For these calculations, the 2-D desalted chemical structures were converted to 3-D using the Rebuild3D function in the Molecular Operating Environment software (CCG, 2011). All computed physicochemical properties are added into the structure-data file prior to assigning toxicological properties.

Both LeadScope® and Qikprop software require input of desalted structures. Therefore, the structures were desalted, a process where salts and complexes are simplified to the neutral, uncomplexed form of the chemical, using "Desalt Batch" option in ACD Labs ChemFolder. All LeadScope® general chemical descriptors (Parent Molecular Weight, AlogP, Hydrogen Bond Acceptors**,** Hydrogen Bond Donors, Lipinski Score, Molecular Weight, Parent Atom Count, Polar Surface Area, and Rotatable Bonds) were calculated by default.

All physicochemical properties generated from EPI Suite™, QikProp, and LeadScope® will be made available to the public in an electronic format in 2015.

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Appendix D

Designing, Constructing, and Testing Wells for Integrity

Appendix D. Designing, Constructing, and Testing Wells for Integrity

This appendix presents the goals for the design and construction of oil and gas production wells, the well components used to achieve those goals, and methods for testing well integrity to help verify that the goals for well performance are achieved. This information provides additional background for the well component discussions presented in Chapter 6. Information on the pathways associated with the well that can cause fluid movement into drinking water resources is presented in Chapter 6.

D.1. Design Goals for Well Construction

Simply stated, production wells are designed to move oil and gas from the production zone (within the oil and gas reservoir) into the well and then through the well to the surface. There are typically a variety of goals for well design (Renpu, 2011), but the main purposes are facilitating the flow of oil and gas from the hydrocarbon reservoirs to the well (production management) while isolating that oil and gas and the hydrocarbon reservoirs from nearby ground water resources (zonal isolation).

To achieve these goals, operators design and construct wells to have and maintain mechanical integrity throughout the life of the well. A properly designed and constructed well has two types of mechanical integrity: internal and external. Internal mechanical integrity refers to the absence of significant leakage within the production tubing, casing, or packer. External mechanical integrity refers to the absence of significant leakage along the well outside of the casing.

Achieving mechanical integrity involves designing the well components to resist the stresses they will encounter. Each well component must be designed to withstand all of the stresses to which the well will be subjected, including burst pressure, collapse, tensile, compression (or bending), and cyclical stresses (see Section 6.2.1 for additional information on these stresses). Well materials should also be compatible with the fluids (including liquids or gases) with which they come into contact to prevent leaks caused by corrosion.

These goals are accomplished by the use of one or more layers of casing, cement, and mechanical devices (such as packers), which provide the main barrier preventing migration of fluids from the well into drinking water sources.

D.2. Well Components

Casing and cement are used in the design and construction of wells to achieve the goals of mechanical integrity and zonal isolation. Several industry-developed specifications and best practices for well construction have been established to guide well operators in the construction process; see Text Box D-1. (Information is not available to determine how often these practices are used or how well they prevent the development of pathways for fluid movement to drinking water resources.) The sections below describe options available for casing, cement, and other well components.

Text Box D-1. Selected Industry-Developed Specifications and Recommended Practices for Well Construction in North America.

American Petroleum Institute (API)

- API Guidance Document HF1—Hydraulic Fracturing Operations—Well Construction and Integrity Guidelines (API, 2009a)
- API RP 10B-2—Recommended Practice for Testing Well Cements (API, 2013)
- API RP 10D-2—Recommended Practice for Centralizer Placement and Stop Collar Testing (API, 2004)
- API RP 5C1—Recommended Practices for Care and Use of Casing and Tubing (API, 1999)
- API RP 65-2—Isolating Potential Flow Zones during Well Construction (API, 2010a)
- API Specification 10A—Specification on Cements and Materials for Well Cementing (API, 2010b)
- API Specification 11D1—Packers and Bridge Plugs (API, 2009b)
- API Specification 5CT—Specification for Casing and Tubing (API, 2011)

Canadian Association of Petroleum Producers (CAPP) and Enform

- Hydraulic Fracturing Operating Practices: Wellbore Construction and Quality Assurance (CAPP, 2013)
- Interim Industry Recommended Practice Volume #24—Fracture Stimulation: Inter-wellbore Communication (Enform, 2013)

Marcellus Shale Coalition (MSC)

- Recommended Practices—Drilling and Completions (MSC, 2013)

D.2.1. Casing

Casing is steel pipe that is placed into the wellbore (the cylindrical hole drilled through the subsurface rock formation) 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. Up to four types of casing may be present in a well, including (from largest to smallest-diameter): conductor casing, surface casing, intermediate casing, and production casing. Each is described below.

The **conductor casing** is the largest diameter string of casing. It is typically in the range of 30 in. (76 cm) to 42 in. (107 cm) in diameter (Hyne, 2012). Its main purpose is to prevent unconsolidated material, such as sand, gravel, and soil, from collapsing into the wellbore. Therefore, the casing is typically installed from the surface to the top of the bedrock or other consolidated formations. The conductor casing may or may not be cemented in place.

The next string of casing is the **surface casing**. A typical surface casing diameter is 13.75 in. (34.93 cm), but diameter can vary (Hyne, 2012). The surface casing's main purposes are to isolate any ground water resources that are to be protected by preventing fluid migration along the wellbore

once the casing is cemented and to provide a sturdy structure to which blow-out prevention equipment can be attached. For these reasons, the surface casing most commonly extends from the surface to some distance beneath the lowermost geologic formation containing ground water resources to be protected. The specific depth to which the surface casing is set is often governed by the depth of the ground water resource as defined and identified for protection in state regulations.

Intermediate casing is typically used in wells to control pressure in an intermediate-depth formation. It may be used to reduce or prevent exposure of weak formations to pressure from the weight of the drilling fluid or cement or to allow better control of over-pressured formations. The intermediate casing extends from the surface through the formation of concern. There may be more than one string of concentric intermediate casing present or none at all, depending on the subsurface geology. Intermediate casing may be cemented, especially through over-pressured zones; however, it is not always cemented to the surface. Intermediate casing, when present, is often 8.625 in. (21.908 cm) in diameter but can vary (Hyne, 2012).

Production casing extends from the surface into the production zone. The main purposes of the production casing are to isolate the hydrocarbon product from fluids in surrounding formations and to transport the product to the surface. It can also be used to inject fracturing fluids, receive flowback during hydraulic fracturing operations (e.g., if tubing or a temporary fracturing string is not present), and prevent other fluids from mixing with and diluting the produced hydrocarbons. The production casing is generally cemented to some point above the production zone. Production casing is often 5.5 in. (14.0 cm) in diameter but can vary (Hyne, 2012).

Liners are another type of metal tubular (casing-like) well component that can be used to fulfill the same purposes as intermediate and production casing in the production zone. Like casing, they are steel pipe, but differ in that they do not extend from the production zone to the surface. Rather, they are connected to the next largest string of casing by a hanger that is attached to the casing. A frac sleeve is a specialized type of liner that is used during fracturing. It has plugs that can be opened and closed by dropping balls from the surface (see the discussion of well completions below for additional information on the use of frac sleeves).

Production tubing is the smallest, innermost steel pipe in the well and is distinguished from casing by not being cemented in place. It is used to transport the hydrocarbons to the surface. Fracturing may be done through the tubing if present, or through the production casing. Because casing cannot be replaced, tubing is often used, especially if the hydrocarbons contain corrosive substances such as hydrogen sulfide or carbon dioxide. Tubing may not be used in high-volume production wells. Typical tubing diameter is between 1.25 in. (3.18 cm) and 4.5 in. (11.4 cm) (Hyne, 2012).

D.2.2. Cement

Cement is the main barrier preventing fluid movement along the wellbore outside the casing. It also lends mechanical strength to the well and protects the casing from corrosion by naturally occurring formation fluids. Cement is placed in the annulus, which is the space between two adjacent casings or the space between the outermost casing and the rock formation through which the wellbore was

drilled. The sections below describe considerations for selecting cement and additives, as well as cementing procedures and techniques.

D.2.2.1. Considerations for Cementing

The length and location of the casing section to be cemented and the composition of the cement can vary based on numerous factors, including the presence and locations of weak formations, over- or under-pressured formations, or formations containing fluids; formation permeability; and temperature. State requirements for oil and gas production well construction and the relative costs of well construction options are also factors.

Improper cementing can lead to the formation of channels (small connected voids) in the cement, which can—if they extend across multiple formations or connect to other existing channels or fractures—present pathways for fluid migration. This section describes some of the considerations and concerns for proper cement placement and techniques and materials that are available to address these concerns. Careful selection of cements (and additives) and design of the cementing job can avoid integrity problems related to cement.

To select the appropriate cement type, properties, and additives, operators consider the required strength needed to withstand downhole conditions and compatibility with subsurface chemistry, as described below:

- The cement design needs to **achieve the strength** required under the measured or anticipated downhole conditions. Factors that are taken into account to achieve proper strength can include density, thickening time, the presence of free water, compressive strength, and formation permeability (Renpu, 2011). Commonly, cement properties are varied during the process, with a "weaker" (i.e., less dense) lead cement, followed by a "stronger" (denser) tail cement. The lead cement is designed with a lower density to reduce pressure on the formation and better displace drilling fluid without a large concern for strength. The stronger tail cement provides greater strength for the deeper portions of the well the operator considers as requiring greater strength.
- The **compatibility of the cement** with the chemistry of formation fluids, hydrocarbons, and hydraulic fracturing fluids is important for maintaining well integrity through the life of the well. Most oil and gas wells are constructed using some form of Portland cement. Portland cement is a specific type of cement consisting primarily of calcium silicates with additional iron and aluminum. Industry specifications for recommended cements are determined by the downhole pressure, temperature, and chemical compatibility required.

There are a number of considerations in the design and execution of a cement job. Proper centralization of the casing within the wellbore is one of the more important considerations. Others include the potential for lost cement, gas invasion, cement shrinkage, incomplete removal of drilling mud, settling of solids in the wellbore, and water loss into the formation while curing. These concerns, and techniques available to address them, include the following:

- **Improper centralization of the casing within the wellbore** can lead to preferential flow of cement on the side of the casing with the larger space and little to no cement on the side closest to the formation. If the casing is not centered in the wellbore, cement will flow unevenly during the cement job, leading to the formation of cement channels. Kirksey (2013) notes that, if the casing is off-center by just 25%, the cement job is almost always inadequate. Centralizers are used to keep the casing in the center of the hole and allow an even cement job. To ensure proper centralization, centralizers are placed at regular intervals along the casing (API, 2010a). Centralizer use is especially key in horizontal wells, as the casing will tend to settle (due to gravity) to the bottom of the wellbore if the casing is not centered (Sabins, 1990), leading to inadequate cement on the lower side.
- **Lost cement** (sometimes referred to as lost returns) refers to cement that moves out of the wellbore and into the formation instead of filling up the annulus between the casing and the formation. Lost cement can occur in weak formations that fail (fracture) under pressure of the cement or in particularly porous, permeable, or naturally fractured formations. Lost cement can result in lack of adequate cement across a water- or brine-bearing zone. To avoid inadequate placement of cement due to lost cement, records of nearby wells can be examined to determine zones where lost cement returns occur (API, 2009a). If records from nearby wells are not available, cores and logs may be used to identify any high-permeability or mechanically weak formations that might lead to lost cement. Steps can then be taken to eliminate or reduce loss of cement to the formation. Staged cementing (see below) can reduce the hydrostatic pressure on the formation and may avoid fracturing weak formations (Lyons and Pligsa, 2004). Additives are also available that will lessen the flow of cement into highly porous formations (API, 2010a; Ali et al., 2009).
- **Gas invasion and cement shrinkage** during cement setting can also cause channels and poor bonding. During the cementing process, the hydrostatic pressure from the cement column keeps formation gas from entering the cement. As the cement sets (hardens), the hydrostatic pressure decreases; if it becomes less than the formation pressure, gas can enter the cement, leading to channels. Cement also shrinks as it sets, which can lead to poor bonding and formation of microannuli. These problems can be avoided by using cement additives that increase setting time or expand to offset shrinkage (McDaniel et al., 2014; Wojtanowicz, 2008; Dusseault et al., 2000). Foamed cement can help alleviate problems with shrinkage, although care needs to be taken in cement design to ensure the proper balance of pressure between the cement column and formation (API, 2010a). Cement additives are also available that will expand upon contact with certain fluids such as hydrocarbons. These cements, termed self-healing cements, are relatively new but have shown early promise in some fields (Ali et al., 2009). Rotating the casing during cementing will also delay cement setting. Another technique called pulsation, where pressure pulses are applied to the cement while it is setting, also can delay cement setting and loss of hydrostatic pressure until the cement is strong enough to resist gas penetration (Stein et al., 2003).

- Another important issue is **removal of drilling mud**. If drilling mud is not completely removed, it can gather on one side of the wellbore and prevent that portion of the wellbore from being adequately cemented. The drilling mud can then be eroded away after the cement sets, leaving a channel. Drilling mud can be removed by circulating a denser fluid (spacer fluid) to flush the drilling mud out (Kirksey, 2013; Brufatto et al., 2003). Mechanical devices called scratchers can also be attached to the casing and the casing rotated or reciprocated to scrape drilling mud from the wellbore (Hyne, 2012; Crook, 2008). The spacer fluid, which is circulated prior to the cement to wash the drilling fluid out of the wellbore, must be designed with the appropriate properties and pumped in such a way that it displaces the drilling fluid without mixing with the cement (Kirksey, 2013; API, 2010a; Brufatto et al., 2003).
- Also of concern in horizontal wells is the possibility of **solids settling** at the bottom of the wellbore and free water collecting at the top of the wellbore. This can lead to channels and poor cement bonding. The cement slurry must be properly designed for horizontal wells to minimize free water and solids settling.
- If there is free water in the cement, pressure can cause **water loss into the formation,** leaving behind poor cement or channels (Jiang et al., 2012). In horizontal wells, free water can also accumulate at the top of the wellbore, forming a channel (Sabins, 1990). Minimizing free water in the cement design and using fluid loss control additives can help control loss of water (Ross and King, 2007).

D.2.2.2. Cement Placement Techniques

The primary cement job is most commonly conducted by pumping the cement down the inside of the casing, then out the bottom of the casing where it is then forced up the space between the outside of the casing and the formation. (The cement can also be placed in the space between two casings.) If **continuous cement** (i.e., a sheath of cement placed along the entire wellbore) is desired, cement is circulated through the annulus until cement that is pumped down the central casing flows out of the annulus at the surface. A spacer fluid is often pumped ahead of cement to remove any excess drilling fluid left in the wellbore; even if the operator does not plan to circulate cement to the surface, the spacer fluid will still return to the surface, as this is necessary to remove the drilling mud from the annulus. If neither the spacer fluid nor the cement returns to the surface, this indicates that fluids are being lost into the formation.

Staged cementing is a technique that reduces pressure on the formation by decreasing the height (and therefore the weight) of the cement column. This may be necessary if the estimated weight and pressure associated with standard cement emplacement could damage zones where the formation intersected is weak. The reduced hydrostatic pressure at the bottom of the cement column can also reduce the loss of water to permeable formations, improving the quality of the cement job. In multiple-stage cementing, cement is circulated to just below a cement collar placed between two sections of casing. A cement collar will have been placed between two sections of casing, just above, with ports that can be opened by dropping a weighted tool. Two plugs—which are often referred to as bombs or darts because of their shape—are then dropped. The first plug is

dropped, once the desired cement for the first stage has been pushed out of the casing by a spacer fluid. It closes the section of the well below the cement collar and stops cement from flowing into the lower portion of the well. The second plug (or opening bomb) opens the cement ports in the collar, allowing cement to flow into the annulus between the casing and formation. Cement is then circulated down the wellbore, out the cement ports, into the annulus, and up to the surface. Once cementing is complete, a third plug is dropped to close the cement ports, preventing the newly pumped cement from flowing back into the well (Lyons and Pligsa, 2004); see Figure D-1.

Another less commonly used primary cementing technique is **reverse circulation cementing.** This technique has been developed to decrease the force exerted on weak formations. In reverse circulation cementing, the cement is pumped down the annulus directly between the outside of the outermost casing and the formation. This essentially allows use of lower density cement and lower pumping pressures. With reverse circulation cementing, greater care must be taken in calculating the required cement, ensuring proper cement circulation, and locating the beginning and end of the cemented portion.

Another method used to cement specific portions of the well without circulating cement along the entire wellbore length is to use a **cement basket**. A cement basket is a device that attaches to the well casing. It is made of flexible material such as canvas or rubber that can conform to the shape of the wellbore. The cement basket acts as a one-way barrier to cement flow. Cement can be circulated up the wellbore past the cement basket, but when circulation stops the basket prevents the cement from falling back down the wellbore. Cement baskets can be used to isolate weak formations or formations with voids. They can also be placed above large voids such as mines or caverns with staged cementing used to cement the casing above the void.

If any deficiencies are identified, **remedial cementing** may be performed. The techniques available to address deficiencies in the primary cement job including cement squeezes or top-job cementing. A cement squeeze injects cement under high pressure to fill in voids or spaces in the primary cement job caused by high pressure, failed formations, or improper removal of drilling mud. Although cement squeezes can be used to fix deficiencies in the primary cement job, they require the well to be perforated, which can weaken the well and make it susceptible to degradation by pressure and temperature cycling as would occur during fracturing (Crescent, 2011). Another method of secondary cementing is the top job. In a top job, cement is pumped down the annulus directly to fill the remaining uncemented space when cement fails to circulate to the surface.

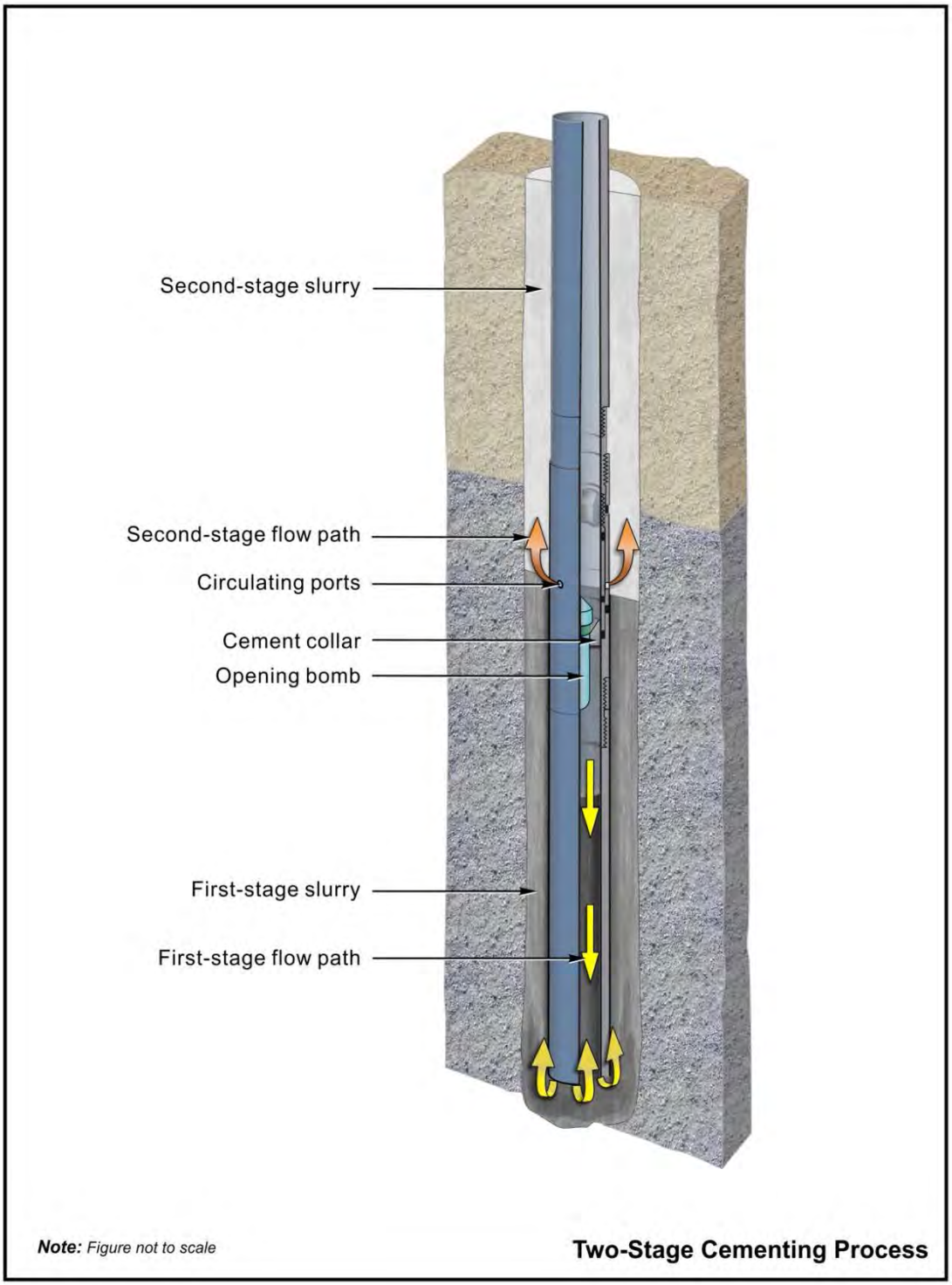

Figure D-1. A typical staged cementing process.

D.3. Well Completions

Completion refers to how the well is prepared for production and how flow is established between the formation and the surface. Figure D-2 presents examples of well completion types, including cased, formation packer, and open hole completion.

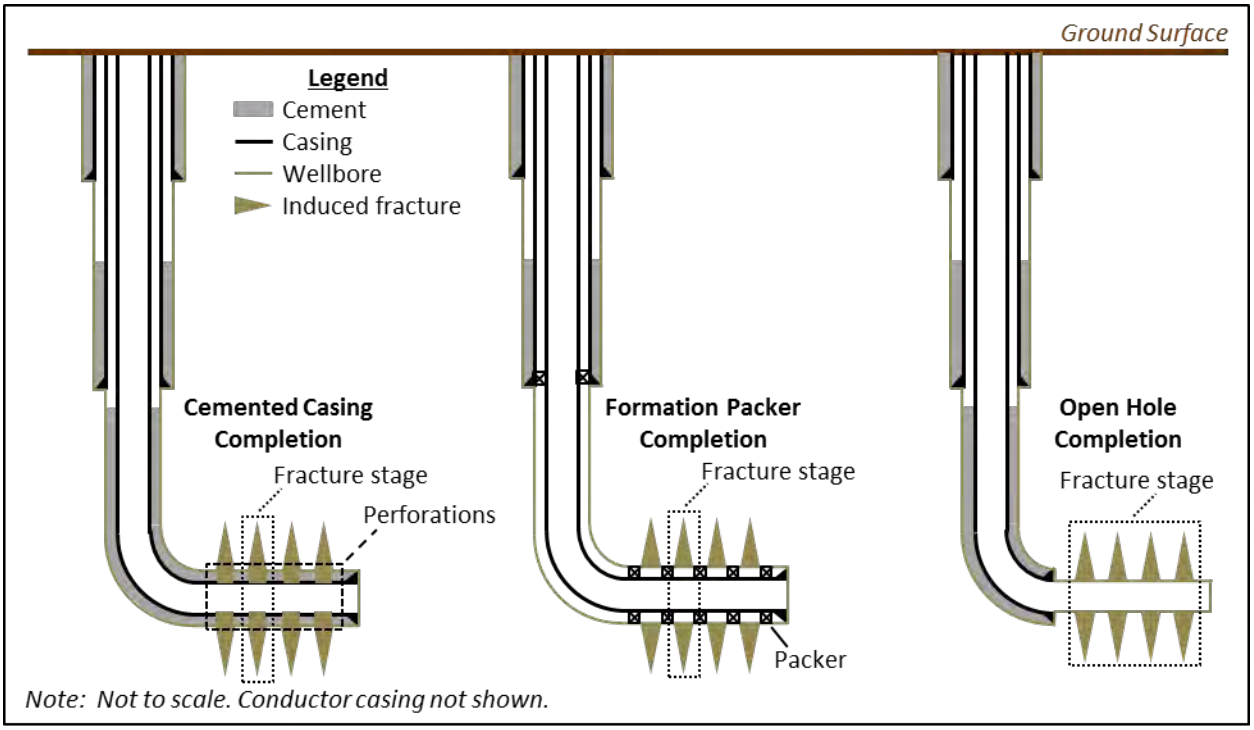

Figure D-2. Examples of well completion types.

Configurations shown include cased, formation packer, and open hole completion. From U.S. EPA (2015f).

A **cased completion**, where the casing extends to the end of the wellbore and is cemented in place, is the most common configuration of the well in the production zone (U.S. EPA, 2015f). Perforations are made through the casing and cement and into the formation using small explosive charges called "perf guns" or other devices, such as sand jets. Hydraulic fracturing then is conducted through the perforations. This is a common technique in wells that produce from several different depths and in low-permeability formations that are fractured (Renpu, 2011). While perforations do control the initiation point of the fracture, this can be a disadvantage if the perforations are not properly aligned with the local stress field. If the perforations are not aligned, the fractures will twist to align with the stress field, leading to tortuosity in the fractures and making fluid movement through them more difficult (Cramer, 2008). Fracturing stages can be isolated from each other using various mechanisms such as plugs or baffle rings, which close off a section of the well when a ball of the correct size is dropped down the well.

A packer is a mechanical device used to selectively seal off certain s ections of the wellbore. Packers can be used to seal the space between the tubing and casing, between two casings, or between the production casing and formation. The packer has one or more rubber elements that can be manipulated downhole to increase in diameter and make contact with the inner wall of the next-largest casing or the formation, effectively sealing the annulus created between the outside of the tubing and the inside of the casing. Packers vary in how they are constructed and how they are set, based on the downhole conditions in which they are used. There are two types of packers: internal packers and formation packers. Internal packers are used to seal the space between the casing and tubing or between two different casings. They isolate the outer casing layers from produced fluids and prevent fluid movement into the annulus. Formation packers seal the space between the casing and the formation and are often used to isolate fracture stages; they can be used to separate an open hole completion into separate fracture stages. Packers can seal an annulus by several different mechanisms. Mechanical packers expand mechanically against the formation and can exert a significant force on the formation. Swellable packers have elastomer sealing elements that swell when they come into contact with a triggering fluid such as water or hydrocarbons. They exert less force on the formation and can seal larger spaces but take some time to fully swell (McDaniel and Rispler, 2009). Internal mechanical integrity tests such as pressure tests can verify that the packer is functioning as designed and has not corroded or deteriorated.

In an **open hole completion**, the production casing extends just into the production zone and the entire length of the wellbore through the production zone is left uncased. This is only an option in formations where the wellbore is stable enough to not collapse into the wellbore. In formations that are unstable, a slotted liner may be used in open hole completions to control sand production (Renpu, 2011). Perforations are not needed in an open hole completion, since the production zone is not cased. An open hole completion can be fractured in a single stage or in multiple stages.

If formations are to be fractured in stages, additional completion methods are needed to separate the stages from each other and control the location of the fractures. One possibility is use of a liner with formation packers to isolate each stage. The liner is equipped with sliding sleeves that can be opened by dropping balls down the casing to open each stage. Fracturing typically occurs from the end of the well and continues toward the beginning of the production zone.

D.4. Mechanical Integrity Testing

While proper design and construction of the well's casing and cement are important, it is also important to verify the well was constructed and is performing as designed. Mechanical integrity tests (MITs) can verify that the well was constructed as planned and can detect damage to the production well that occurs during operations, including hydraulic fracturing activities. Verifying that a well has mechanical integrity can prevent potential impacts to drinking water resources by providing early warning of a problem with the well or cement and allowing repairs.

It is important to note that if a well fails an MIT, this does not mean the well has failed or that an impact on drinking water resources has occurred. An MIT failure is a warning that one or more components of the well are not performing as designed and is an indication that corrective actions

are necessary. If well remediation is not performed, a loss of well integrity could occur, which could result in fluid movement from the well.

D.4.1. Internal Mechanical Integrity

Internal mechanical integrity is an absence of significant leakage in the tubing, casing, or packers within the well system. Loss of internal mechanical integrity is usually due to corrosion or mechanical failure of the well's tubular and mechanical components.

Internal mechanical integrity can be tested by the use of pressure testing, annulus pressure monitoring, ultrasonic monitoring, and casing inspection logs or caliper logs:

- **Pressure testing** involves raising the pressure in the wellbore to a set level and shutting in the well. If the well has internal mechanical integrity, the pressure should remain constant with only small changes due to temperature fluctuation. Typically, the well is shut in (i.e., production is stopped and the wellhead valves closed) for half an hour, and if the pressure remains within 5% of the original reading, the well is considered to have passed the test. Usually, the well is pressure tested to the maximum expected pressure; for a well to be used for hydraulic fracturing this would be the pressure applied during hydraulic fracturing. Pressure tests, however, can cause debonding of the cement from the casing, so test length is often limited to reduce this effect (API, 2010a).
- If the annulus between the tubing and casing is sealed by a packer, **annulus pressure monitoring** can give an indication of the integrity of the tubing and casing. If the tubing, casing, and packer all have mechanical integrity, the pressure in the annulus should not change except for small changes in response to temperature fluctuations. The annulus can be filled with a non-corrosive liquid and the level of the liquid can be used as another indication of the integrity of the casing, tubing, and packer. The advantage of monitoring the tubing/production casing annulus is it can give a continuous, real-time indication of the internal integrity of the well. Even if the annulus is not filled with a fluid, monitoring its pressure can indicate leaks. If pressure builds up in the annulus and then recovers quickly after having bled off, that condition is referred to as sustained casing pressure or surface casing vent flow and is a sign of a leak in the tubing or casing (Watson and Bachu, 2009). Monitoring of annuli between other sets of casings can also provide information on the integrity of those casings. It can also provide information on external mechanical integrity for annuli open to the formation (see Section D.4.2 for additional information on external MITs). Jackson et al. (2013) also note that monitoring annular pressure allows the operator to vent gas before it accumulates enough pressure to cause migration into drinking water resources. Measuring annulus flow rate also allows detection of gas flowing into the annulus (Arthur, 2012).
- A newer tool uses **ultrasonic monitors** to detect leaks in casing and other equipment. It measures the attenuation of an ultrasonic signal as it is transmitted through the wellbore. The tool measures transmitted ultrasonic signals as it is lowered down the wellbore. The tool can pick up ultrasonic signals created by the leak, similar to noise logs. The tool only

has a range of a few feet but is claimed to detect leaks as small as half a cup per minute (Julian et al., 2007).

- **Caliper logs** have mechanical fingers that extend from a central tool and measure the distance from the center of the wellbore to the side of the casing. Running a caliper log can identify areas where corrosion has altered the diameter of the casing or where holes have formed in the casing. Caliper logs may also detect debris or obstructions in the well. Casing inspection and caliper logs are primarily used to determine the condition of the casing. Regular use of them may identify problems such as corrosion and allow mitigation before they cause of loss of integrity to the casing. To run these logs in a producing well, the tubing must first be pulled.
- **Casing inspection logs** are instruments lowered into the casing to inspect the casing for signs of wear or corrosion. One type of casing log uses video equipment to detect corrosion or holes. Another type uses electromagnetic pulses to detect variations in metal thickness. Running these logs in a producing well requires the tubing to be pulled.

If an internal mechanical integrity problem is detected, first, the location of the problem must be found. Caliper or casing inspection logs can detect locations of holes in casing. Locations of leaks can also be detected by sealing off different sections of the well using packers and performing pressure tests on each section until the faulty section is located. If the leaks are in the tubing or a packer, the problem may be remedied by replacing the well component. Casing leaks may be remedied by performing a cement squeeze (see the section on cementing).

D.4.2. External Mechanical Integrity

External well mechanical integrity is demonstrated by establishing the absence of significant fluid movement along the outside of the casing, either between the outer casing and cement or between the cement and the wellbore. Failure of an external MIT can indicate improper cementing or degradation of the cement emplaced in the annular space between the outside of the casing and the wellbore. This type of failure can lead to movement of fluids out of intended production zones and toward drinking water resources.

Several types of logs are available to evaluate external mechanical integrity, including temperature logs, noise logs, oxygen activation logs, radioactive tracer logs, and cement evaluation logs.

- **Temperature logs** measure the temperature in the wellbore. They are capable of measuring small changes in temperature. They can be performed using instruments that are lowered down the well on a wireline or they can be done using fiber optic sensors permanently installed in the well. When performed immediately after cementing, they can detect the heat from the cement setting and determine the location of the top of cement. After the cement has set, temperature logs can sense the difference in temperatures between formation fluids and injected or produced fluids. They may also detect temperature changes due to cooling or warming caused by flow. In this way temperature logs may detect movement of fluid outside the casing in the wellbore (Arthur, 2012).

Temperature logs require interpretation of the causes of temperature changes and are therefore subject to varying results among different users.

- **Noise logs** are sensitive microphones that are lowered down the well on a wireline. They are capable of detecting small noises caused by flowing fluids, such as fluids flowing through channels in the cement (Arthur, 2012). They are most effective at detecting fast-moving gas leaks and less successful with more slowly moving liquid migration.
- **Oxygen activation logs** consist of a neutron source and one or more detectors that are lowered on a wireline. The neutron source bombards oxygen molecules surrounding the wellbore and converts them into unstable nitrogen molecules that rapidly decay back to oxygen, emitting gamma radiation in the process. Gamma radiation detectors above or below the neutron source measure how quickly the oxygen molecules are moving away from the source, thereby determining flow associated with water.
- **Radioactive tracer logs** involve release of a radioactive tracer and then passing a detector up or down the wellbore to measure the path the tracers have taken. They can be used to determine if fluid is flowing up the wellbore. Tracer logs can be very sensitive but may be limited in the range over which leaks can be detected.
- **Cement evaluation logs** (also known as cement bond logs) are acoustic logs consisting of an instrument that sends out acoustic signals along with receivers, separated by some distance, that record the acoustic signals. As the acoustic signals pass through the casing they will be attenuated to an extent, depending on whether the pipe is free or is bonded to cement. By analyzing the return acoustic signal, the degree of cement bonding with the casing can be determined. The cement evaluation log measures the sound attenuation as sound waves passing through the cement and casing. There are different types of cement evaluation logs available. Some instruments can only return an average value over the entire wellbore. Other instruments are capable of measuring the cement bond radially. Cement logs do not actually determine whether fluid movement through the annulus is occurring. They only can determine whether cement is present in the annulus and in some cases can give a qualitative assessment of the quality of the cement in the annulus. Cement evaluation 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.

If the well fails an external MIT, damaged or missing cement may be repaired using a cement squeeze (Wojtanowicz, 2008). A cement squeeze involves injection of cement slurry into voids behind the casing or into permeable formations. Different types of cement squeezes are available depending on the location of the void needing to be filled and well conditions (Kirksey, 2013). Cement squeezes are not always successful, however, and may need to be repeated to successfully seal off flow (Wojtanowicz, 2008).

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Appendix E

Flowback and Produced Water Supplemental Tables and Information

Appendix E. Flowback and Produced Water Supplemental Tables and Information

E.1. Flowback and Long-Term Produced Water Volumes

The EPA (2015g) estimates of flowback volumes and long-term produced water volumes used to generate the summaries appearing in Table 7-3 of Chapter 7 appear below in Table E-1.

Table E-1. Flowback and long-term produced water characteristics for wells in unconventional formations, formation-level data.

Source: U.S. EPA (2015g).

Basin	Resource Type	Unconventional Formation	Drill Type	Fracturing Fluid (Mgal)			Flowback (% of Fracturing Fluid Returned)			Long-Term Produced Water Rates (gpd)		
				Median	Range	Number of Data Points	Median	Range[a]	Number of Data Points	Median	Range[b]	Number of Data Points
Anadarko	Shale	Woodford	H	4.7	1.0-12	2,239	34	20-50	3	5,500	3,200-6,400	198
	Tight	Cleveland	H	0.81	0.2-4.0	144	--	12-40	2	82	20-300	571
			V	0.69	0.11-3	4	--	--	2	32	6.6-170	390
		Granite Wash	H	6.2	0.2-9.4	77	--	7-22	2	1,300	0-2,200	273
			V	0.56	0.05-3	26	--	--	2	500	170-1,300	2,413
		Mississippi Lime	H	1.8	0.82-2.4	428	--	50	1	--	37,000-120,000	4
Appalachian	Shale	Marcellus	H	4.4	0.9-11	14,010	7	4-47	4,374	860	54-13,000	4,984
			V	2.6	0.53-6.6	66	40	21-60	7	230	100-1,200	714
		Utica	H	4.0	1.0-11	150	4	2-27	73	510	210-1,200	82
Arkoma	Shale	Fayetteville	H	5.1	1.7-11	1,668	--	10-20	2	430	150-2,300	2,305
Denver-Julesburg	Shale	Niobrara	H	2.6	0.73-3.4	69	13	6-25	16	680	260-810	250
			V	0.32	0.27-3.3	367	11	7-35	9	340	240-600	5,474
	Tight	Codell	D	0.28	0.21-0.46	78	--	--	0	--	--	0
			V	0.27	0.13-0.46	185	--	--	0	--	--	0
		Codell-Niobrara	H	2.6	0.15-2.7	62	7	--	32	34	19-140	32
			D	0.45	0.21-0.47	116	--	--	0	--	--	0
			V	0.30	0.13-0.46	592	--	--	0	29	13-65	1,677

Basin	Resource Type	Unconventional Formation	Drill Type	Fracturing Fluid (Mgal)			Flowback (% of Fracturing Fluid Returned)			Long-Term Produced Water Rates (gpd)		
				Median	Range	Number of Data Points	Median	Range[a]	Number of Data Points	Median	Range[b]	Number of Data Points
Denver-Julesburg, cont.	Tight cont.	Muddy J	D	0.59	.025-0.62	162	--	--	0	230	64-390	3
			V	0.28	0.16-0.62	292	--	--	0	55	9.3-500	129
Fort Worth	Shale	Barnett	H	3.6	1-7.3	23,917	30	21-40	11	920	160-4,200	10,349
			V	1.3	0.4-1.9	3,589	--	--	0	250	170-580	3,318
Green River	Shale	Hilliard-Baxter-Mancos	H	1.7	1.0-5.6	2	--	--	0	37	15-58	7
	Tight	Lance	V	1.3	0.81-3.5	29	3	1-50	31	410	250-580	1,050
			D	1.2	0.76-1.9	180	6	1-17	170	860	360-1,200	1,140
Green River, cont.		Mesaverde	D	0.23	0.16-0.31	73	8	0-37	61	190	150-440	445
			V	0.17	0.081-0.29	14	21	6-83	11	290	140-610	1,081
Illinois	Shale	New Albany	H	--	--	0	--	--	0	--	2,900	2
Michigan	Shale	Antrim	V	--	0.05	1	--	25-75	2	--	4,600	1
Permian	Shale	Avalon & Bone Spring	D	2.2	0.94-4.5	20	13	5-31	16	950	220-2,400	183
			H	1.1	0.73-2.8	17	--	--	0	0	0-2,300	37
		Barnett-Woodford	H	2.1	0.5-4.5	2	--	--	0	--	--	0

Basin	Resource Type	Unconventional Formation	Drill Type	Fracturing Fluid (Mgal)			Flowback (% of Fracturing Fluid Returned)			Long-Term Produced Water Rates (gpd)		
				Median	Range	Number of Data Points	Median	Range[a]	Number of Data Points	Median	Range[b]	Number of Data Points
Permian, cont.	Shale, cont.	Devonian (TX)	H	0.32	0.13-0.89	10	--	--	0	880	310-1,800	381
			V	0.27	0.12-1.0	16	--	--	0	400	150-3,000	162
		Wolfcamp	H	1.4	1.1-3.9	55	--	--	0	3,000	210-19,000	104
			D	1.3	0.26-1.7	12	16	15-20	3	310	22-8,700	259
			V	0.81	0.078-1.7	60	--	--	0	910	130-1,700	926
	Tight	Spraberry	V	--	1.0	1	--	--	0	870	100-4,000	66
San Juan	Tight	Mesaverde (San Juan)	D	--	--	0	--	--	0	18	12-260	48
		Dakota	V	0.2	0.063-0.22	19	--	--	0	65	29-120	6
			D	0.12	0.07-0.3	52	4	1-40	30	160	41-370	379
TX-LA-MS	Shale	Bossier	H	2.7	1.7-3.6	2	--	--	0	750	610-1,200	25
			V	0.4	0.19-1.7	16	--	--	0	470	180-1,100	1,203
			D	0.28	0.13-0.8	21	--	--	0	320	130-1,300	253
		Haynesville	H	5.3	0.95-15	3,222	5	5-30	3	1,700	84-1,800	1,249
			V	0.61	.14-3.5	9	--	--	0	210	56-850	263
	Tight	Cotton Valley	H	4.2	.25-6.0	30	--	<60	2	770	130-2,700	335
			D	.48	.084-4.0	24	--	<60	2	950	630-1,800	1801
			V	.28	.019-.94	76	--	<60	2	640	370-1,800	10,717

Basin	Resource Type	Unconventional Formation	Drill Type	Fracturing Fluid (Mgal)			Flowback (% of Fracturing Fluid Returned)			Long-Term Produced Water Rates (gpd)		
				Median	Range	Number of Data Points	Median	Range[a]	Number of Data Points	Median	Range[b]	Number of Data Points
TX-LA-MS, cont.	Tight, cont.	Travis Peak	H	3.0	0.25-6	2	--	--	0	200	39-1,700	5
			V	0.9	0.2-4	2	--	--	0	980	330-1,800	1,380
Western Gulf	Shale	Eagle Ford	H	5.0	1.0-14	2,485	4	2-8	1,800	110	9.1-250	498
			V	2.9	2.0-4.1	9	--	--	0	--	--	0
		Pearsall	H	3.7	3.3-4.1	2	--	--	0	200	54-370	12
	Tight	Austin Chalk	H	0.94	0.58-1.3	15	--	--	0	720	290-2,400	1,097
		Vicksburg	V	.016	0.084-0.6	20	--	--	0	1,000	650-1,900	937
			D	0.11	0.1-0.13	4	--	--	0	--	--	0
		Wilcox Lobo	H	2.1	0.66-2.6	4	--	--	0	330	62-740	77
			V	0.21	0.06-0.6	14	--	--	0	620	330-1,400	1,514
			D	.058	.056-.076	3	--	--	0	--	--	0
		Olmos	V	--	0.15	2	--	--	0	--	--	0
Williston		Bakken	H	2.0	0.35-10	2,203	19	5-47	206	680	380-1,500	1,739
			V	1.1	.35-2.9	12	--	--	0	1,000	340-3,100	222

"--" indicates no data; H, horizontal well; D, directional well; V, vertical well.

[a] For some formations, if only one data point was reported, the EPA reported it in the range column and did not report a median value.

[b] For some formations, the number of data points was not reported in the data source. In these instances, the EPA reported the number of data points as equal to one, even if the source reported a range and median value.

E.2. Produced Water Content

E.2.1. Introduction

In the main text of Chapter 7, we describe aspects of flowback and produced water composition, including temporal changes in water quality parameters of flowback (Section 7.5) and major classes of compounds in produced water (Section 7.6). In section 7.7 we describe variability as occurring on three levels: between different rock types (e.g., coal vs. sandstone), between formations composed of the same rock types (e.g., Barnett Shale vs. Bakken Shale), and within formations of the same rock type (e.g., northeastern vs. southwestern Marcellus Shale). In this appendix we present data from the literature which illustrates the differences among these three variability levels.

E.2.2. General Water Quality Parameters

As noted in Chapter 7, the EPA identified data characterizing the content of unconventional flowback and produced water in a total of 12 shale and tight formations and coalbed methane (CBM) basins. These formations and basins span 18 states. Note that in this subsection we treat all fluids as produced water. As a consequence, the variability of reported concentrations is likely higher than if the data could be standardized to a specific point on the flowback-to-produced water continuum. Table E-2 and Table E-3 provide supporting data on general water quality parameters of produced water for 12 formations.

Table E-2. Reported concentrations of general water quality parameters in produced water for unconventional shale and tight formations, presented as: average (minimum–maximum) or *median* (minimum–maximum).

Parameter	Units	Shales					Tight formations			
		Bakken[a]	Barnett[b]	Fayetteville[c]	Marcellus		Cotton Valley Group[f]	Devonian Sandstone[g]	Mesaverde[f]	Oswego[f]
States	**n/a**	**MT, ND**	**TX**	**AR**	**PA[d]**	**PA, WV[e]**	**LA, TX**	**PA**	**CO, NM, UT, WY**	**OK**
Acidity	mg/L	-	NC (ND–ND)	-	NC (<5–473)	***162*** (5–925)	-	-	-	-
Alkalinity	mg/L	-	***725*** (215–1,240)	1,347 (811–1,896)	165 (8–577)	***99.8*** (7.5–577)	-	99 (43–194)	-	582 (207–1,220)
Ammonium	mg/L	-	-	-	-	-	89 (40–131)	-	-	-
Bicarbonate	mg/L	291 (122–610)	-	-	-	-	-	524 (ND–8,440)	2,230 (1,281–13,650)	-
Biochemical oxygen demand (BOD)	mg/L	-	***582*** (101–2,120)	-	-	***141*** (2.8–12,400)	-	-	-	-
Carbonate	mg/L	-	-	-	-	-	-	-	227 (ND–1,680)	-
Chloride	mg/L	119,000 (90,000–133,000)	***34,700*** (9,600–60,800)	9,156 (5,507–12,287)	57,447 (64–196,000)	***49,000*** (64.2–196,000)	101,332 (3,167–221,498.7)	132,567 (58,900–207,000)	4,260 (8–75,000)	44,567 (23,000–75,000)
Chemical oxygen demand	mg/L	-	***2,945*** (927–3,150)	-	15,358 (195–36,600)	***4,670*** (195–36,600)	-	-	-	-

Parameter	Units	Shales					Tight formations			
		Bakken[a]	Barnett[b]	Fayetteville[c]	Marcellus		Cotton Valley Group[f]	Devonian Sandstone[g]	Mesaverde[f]	Oswego[f]
States	**n/a**	**MT, ND**	**TX**	**AR**	**PA[d]**	**PA, WV[e]**	**LA, TX**	**PA**	**CO, NM, UT, WY**	**OK**
DO	mg/L	-	-	-	-	-	-	0.8 (0.2–2.5)	-	-
DOC	mg/L	-	***11.2*** (5.5–65.3)	-	-	***117*** (3.3–5,960)	-	-	-	-
Hardness as $CaCO_3$	mg/L	-	***5,800*** (3,500–21,000)	-	34,000 (630–95,000)	***25,000*** (156–106,000)	-	-	-	-
Oil and grease	mg/L	-	***163.5*** (88.2–1,430)	-	74 (5–802)	***16.85*** (4.7–802)	-	-	-	-
pH	SU	5.87 (5.47–6.53)	***7.05*** (6.5–7.2)	-	6.6 (5.1–8.4)	***6.5*** (4.9–7.9)	-	6.3 (5.5–6.8)	8 (5.8–11.62)	6.3 (6.1–6.4)
Specific conductivity	µS/cm	213,000 (205,000–220,800)	***111,500*** (34,800–179,000)	-	-	***183,000*** (479–763,000)	-	184,800 (118,000–211,000)	-	-
Specific gravity	--	1.13 (1.0961–1.155)	-	-	-	-	-	-	-	-
TDS	mg/L	196,000 (150,000–219,000)	***50,550*** (16,400–97,800)	13,290 (9,972–15,721)	106,390 (680–345,000)	***87,800*** (680–345,000)	164,683 (5,241–356,666)	235,125 (106,000–354,000)	15,802 (1,032–125,304)	73,082 (56,541–108,813)
Total Kjeldahl nitrogen	mg/L	-	***171*** (26–298)	-	-	***94.9*** (5.6–312)	-	-	-	-

Parameter	Units	Shales					Tight formations			
		Bakken[a]	Barnett[b]	Fayetteville[c]	Marcellus		Cotton Valley Group[f]	Devonian Sandstone[g]	Mesaverde[f]	Oswego[f]
States	**n/a**	**MT, ND**	**TX**	**AR**	**PA[d]**	**PA, WV[e]**	**LA, TX**	**PA**	**CO, NM, UT, WY**	**OK**
TOC	mg/L	-	***9.75*** (6.2–36.2)	-	160 (1.2–1,530)	***89.2*** (1.2–5,680)	198 (184–212)	-	-	-
Total suspended solids	mg/L	-	***242*** (120–535)	-	352 (4–7,600)	***127*** (6.8–3,220)	-	-	-	-
Turbidity	NTU	-	***239*** (144–314)	-	-	***126*** (2.3–1,540)	-	-	-	-

n/a, not applicable; -, no value available; NC, not calculated; ND, not detected., SU= standard units, ***bolded italic*** numbers are medians

[a] Stepan et al. (2010). *n* = 3. Concentrations were calculated based on Stepan et al.'s raw data. Samples had charge balance errors of 1.74, -0.752, and -0.220%

[b] Hayes and Severin (2012b). *n* = 16. This data source reported concentrations without direct presentation of raw data.

[c] Warner et al. (2013). *n* = 6. Concentrations were calculated based on Warner et al.'s raw data. Both flowback and produced water included.

[d] Barbot et al. (2013). n = 134–159. This data source reported concentrations without direct presentation of raw data.

[e] Hayes (2009). *n* = 31-67. Concentrations were calculated based on Hayes's raw data. Both flowback and produced water included. Non-detects and contaminated blanks omitted.

[f] Blondes et al. (2014). Cotton Valley Group, *n*=2; Mesa Verde, *n* = 1–407; Oswego, *n* = 4–30. Concentrations were calculated based on raw data presented in the U.S. Geological Survey (USGS) National Produced Water Database v2.0.

[g] Dresel and Rose (2010). *n* = 3–15. Concentrations were calculated based on Dresel and Rose's raw data.

Table E-3. Reported concentrations of general water quality parameters in produced water for unconventional coalbed basins, presented as: average (minimum–maximum).

Parameter	Units	Black Warrior[a]	Powder River[b]	Raton[b]	San Juan[b]
States	n/a	AL, MS	MT, WY	CO, NM	AZ, CO, NM, UT
Alkalinity	mg/L	355 (3–1,600)	1,384 (653–2,672)	1,107 (130–2,160)	3,181 (51–11,400)
Ammonium	mg/L	3.60 (0.16–8.91)	-	-	-
Bicarbonate	mg/L	427 (2–1,922)	1,080 (236–3,080)	1,124 (127–2,640)	3,380 (117–13,900)
Carbonate	mg/L	3 (0–64)	2.17 (0.00–139.0)	51.30 (1.30–316.33)	40.17 (0.00–1,178)
Chloride	mg/L	9,078 (11–42,800)	21 (BDL–282)	787 (4.8–8,310)	624 (BDL–20,100)
Chemical oxygen demand	mg/L	830 (0–10,500)	-	-	-
Dissolved oxygen	mg/L	-	1.07 (0.11–3.48)	0.39 (0.01–3.52)	0.51 (0.04–1.69)
DOC	mg/L	3.37 (0.53–61.41)	3.18 (1.09–8.04)	1.26 (0.30–8.54)	3.21 (0.89–11.41)
Hardness as $CaCO_3$	mg/L	871 (3–6,150)	-	-	-
Hydrogen sulfide	mg/L	-	-	4.41 (BDL–190.0)	23.00 (23.00–23.00)
Oil and grease	mg/L	-	-	9.10 (0.60–17.6)	-
pH	SU	7.5 (5.3–9.0)	7.71 (6.86–9.16)	8.19 (6.90–9.31)	7.82 (5.40–9.26)
Phosphate	mg/L	0.435 (0.026–3.570)	BDL (BDL–BDL)	0.04 (BDL–1.00)	1.89 (BDL–9.42)
Specific conductivity	µS/cm	20,631 (718–97,700)	1,598 (413–4,420)	3,199 (742–11,550)	5,308 (232–18,066)
TDS	mg/L	14,319 (589–61,733)	997 (252–2,768)	2,512 (244–14,800)	4,693 (150–39,260)
Total Kjeldahl nitrogen	mg/L	6.08 (0.15–38.40)	0.48 (BDL–4.70)	2.61 (BDL–26.10)	0.46 (BDL–3.76)
TOC	mg/L	6.03 (0.00–103.00)	3.52 (2.07–6.57)	1.74 (0.25–13.00)	2.91 (0.95–9.36)
Total suspended solids	mg/L	78 (0–2,290)	11.0 (1.4–72.7)	32.3 (1.0–580.0)	47.2 (1.4–236.0)
Turbidity	NTU	74 (0–539)	8.2 (0.7–57.0)	4.5 (0.3–25.0)	61.6 (0.8–810.0)

n/a, not applicable; -, no value available; BDL, below detection limit.

[a] DOE (2014). *n* = 206. Concentrations were calculated based on raw data presented in the reference.

[b] Dahm et al. (2011). Powder River, *n* = 31; Raton, *n* = 40; San Juan, *n* = 20. This data source reported concentrations without presentation of raw data.

E.2.3. Salinity and Inorganics

Table E-4 and Table E-5 provide supporting data on salinity and inorganic constituents of produced water for 12 formations.

E.2.3.1. Processes Controlling Salinity and Inorganics Concentrations

Multiple mechanisms likely control elevated salt concentrations in flowback and produced water and are largely dependent upon post-injection fluid interactions and the formation's stratigraphic and hydrogeologic environment (Barbot et al., 2013). High inorganic ionic loads observed in flowback and produced water are expressed as TDS.

Subsurface brines or formation waters are saline fluids associated with the targeted formation. Shale and sandstone brines are typically much more saline than coalbed waters. After hydraulic fracturing fluids are injected into the subsurface, the injected fluids (which are typically not sources of high TDS) mix with in situ brines, which typically contain high ionic loads (Haluszczak et al., 2013).

Deep brines, present in over- or underlying strata, may naturally migrate into targeted formations over geologic time or artificially intrude if a saline aquifer is breached during hydraulic fracturing (Chapman et al., 2012; Maxwell, 2011; Blauch et al., 2009). Whether it is through natural or induced intrusion, saline fluids may contact the producing formation and introduce novel salinity sources to the produced water (Chapman et al., 2012).

The dissolution salts associated with formation solids both increases TDS concentrations and alters formation porosity and permeability (Blauch et al., 2009). Additionally, the mobilization of connate fluids (deposition-associated pore fluids) and formation fluids during hydraulic fracturing likely contributes to increased TDS levels (Dresel and Rose, 2010; Blauch et al., 2009). Despite the general use of fresh water for hydraulic fracturing fluid, some elevated salts in produced water may result from the use of reused saline flowback or produced water as a hydraulic fracturing base fluid (Hayes, 2009).

Table E-4. Reported concentrations (mg/L) of inorganic constituents contributing to salinity in unconventional shale and tight formations produced water, presented as: average (minimum–maximum) or *median* (minimum–maximum).

Parameter	Shale					Tight Formations			
	Bakken[a]	Barnett[b]	Fayetteville[c]	Marcellus		Cotton Valley Group[f]	Devonian Sandstone[g]	Mesaverde[f]	Oswego[f]
States	MT, ND	TX	AR	PA[d]	PA,WV[e]	LA, TX	PA	CO, NM, UT, WY	OK
Bromide	-	**589** (117–798)	111 (96–144)	511 (0.2–1,990)	***512*** (15.8–1,990)	498 (32–1,338)	1,048 (349–1,350)	-	-
Calcium	9,680 (7,540–13,500)	***1,600*** (1,110–6,730)	317 (221–386)	7,220 (38–41,000)	***7,465*** (173-33,000)	19,998 (181–51,400)	20,262 (8,930–34,400)	212 (1.01–4,580)	5,903 (3,609–8,662)
Chloride	119,000 (90,000–133,000)	***34,700*** (9,600–60,800)	9,156 (5,507–12,287)	57,447 (64–196,000)	***49,000*** (64.2–196,000)	101,332 (3,167–221,498.7)	132,567 (58,900–207,000)	4,260 (8–75,000)	44,567 (23,000–75,000)
Fluoride	-	***3.8*** (3.5–12.8)	-	-	***0.975*** (0.077–32.9)	-	-	-	-
Iodine	-	-	-	-	-	20 (1–36)	39 (11–56)	1.01 (1.01–1.01)	-
Nitrate as N	-	-	NC (ND–ND)	-	***1.7*** (0.65–15.9)	-	-	0.6 (0.6–0.6)	-
Nitrite as N	-	***4.7*** (3.5–38.1)	-	-	***11.8*** (1.1–146)	-	-	-	-
Phosphorus	NC (ND–0.03)	***0.395*** (0.19–0.7)	-	-	***0.3*** (0,08–21.8)	-	-	-	-
Potassium	2,970 (0–5,770)	***316*** (80–750)	-	-	***337*** (38–3,950)	1,975 (8–7,099)	858 (126–3,890)	160 (4–2,621)	-

Parameter	Shale					Tight Formations			
	Bakken[a]	Barnett[b]	Fayetteville[c]	Marcellus		Cotton Valley Group[f]	Devonian Sandstone[g]	Mesaverde[f]	Oswego[f]
States	MT, ND	TX	AR	PA[d]	PA,WV[e]	LA, TX	PA	CO, NM, UT, WY	OK
Silica	7 (6.41–7)	-	52 (13–160)	-	-	4 (4–4)	-	-	-
Sodium	61,500 (47,100–74,600)	***18,850*** (4,370–28,200)	3,758 (3,152–4,607)	21,123 (69–117,000)	***21,650*** (63.8–95,500)	39,836 (1,320–85,623.24)	58,160 (24,400–83,300)	5,828 (132–48,817)	19,460 (13,484–31,328)
Sulfate	660 (300–1,000)	***709*** (120–1,260)	NC (ND–3)	71 (0–763)	***58.9*** (2.4–348)	407 (ND–2,200.46)	20 (1–140)	837 (ND–14,612)	183 (120–271)
Sulfide	-	NC (ND–ND)	-	-	***3.2*** (1.6–5.6)	-	0.7 (0.1–2.5)	-	-
Sulfite	-	-	-	-	***12.4*** (5.2–73.6)	-	-	-	-
TDS	196,000 (150,000–219,000)	*50,550* (16,400–97,800)	13,290 (9,972–15,721)	106,390 (680–345,000)	***87,800*** (680–345,000)	164,683 (5,241–356,666)	235,125 (106,000–354,000)	15,802 (1,032–125,304)	73,082 (56,541–108,813)

-, no value available; NC, not calculated; ND, not detected. ***Bolded italic*** numbers are medians.

[a] Stepan et al. (2010). *n* = 3. Concentrations were calculated based on Stepan et al.'s raw data. Samples had charge balance errors of 1.74, -0.752, and -0.220%

[b] Hayes and Severin (2012b). *n* = 16. This data source reported concentrations without presentation of raw data.

[c] Warner et al. (2013). *n* = 6. Concentrations were calculated based on Warner et al.'s raw data. Both flowback and produced water included.

[d] Barbot et al. (2013). *n* = 134–159. This data source reported concentrations without presentation of raw data.

[e] Hayes (2009). *n* = 8-65. Concentrations were calculated based on Hayes's raw data. Both flowback and produced water included. Non-detects and contaminated blanks omitted.

[f] Blondes et al. (2014) Cotton Valley Group, *n* = 2; Mesa Verde, *n* = 1–407; Oswego, *n* = 4–30. Concentrations were calculated based on raw data presented in the USGS National Produced Water Database v2.0.

[g] Dresel and Rose (2010). *n* = 3–15. Concentrations were calculated based on Dresel and Rose's raw data.

Table E-5. Reported concentrations (mg/L) of inorganic constituents contributing to salinity in produced water for unconventional CBM basins, presented as: average (minimum–maximum).

Parameter	Black Warrior[a]	Powder River[b]	Raton[b]	San Juan[b]
State	AL, MS	MT, WY	CO, NM	AZ, CO, NM, UT
Barium	45.540 (0.136–352)	0.61 (0.14–2.47)	1.67 (BDL–27.40)	10.80 (BDL–74.0)
Boron	0.185 (0–0.541)	0.17 (BDL–0.39)	0.36 (BDL–4.70)	1.30 (0.21–3.45)
Bromide	-	0.09 (BDL–0.26)	4.86 (0.04–69.60)	9.77 (BDL–43.48)
Calcium	218 (0–1,640)	32.09 (2.00–154.0)	14.47 (0.81–269.0)	53.29 (1.00–5,530)
Chloride	9,078 (11–42,800)	21 (BDL–282)	787 (4.8–8,310)	624 (BDL–20,100)
Fluoride	6.13 (0.00–22.60)	1.57 (0.40–4.00)	4.27 (0.59–20.00)	1.76 (0.58–10.00)
Magnesium	68.12 (0.18–414.00)	14.66 (BDL–95.00)	3.31 (0.10–56.10)	15.45 (BDL–511.0)
Nitrate	8.70 (0.00–127.50)	-	-	-
Nitrite	0.03 (0.00–2.08)	-	-	-
Phosphorus	0.32 (0.00–5.76)	-	-	-
Potassium	12.02 (0.46–74.00)	11.95 (BDL–44.00)	6.37 (BDL–29.40)	26.99 (BDL–970.0)
Silica	8.66 (1.04–18.10)	6.46 (4.40–12.79)	7.05 (4.86–10.56)	12.37 (3.62–37.75)
Sodium	4,353 (126–16,700)	356 (12–1,170)	989 (95–5,260)	1,610 (36–7,834)
Strontium	11.354 (0.015–142.000)	0.60 (0.10–1.83)	5.87 (BDL–47.90)	5.36 (BDL–27.00)
Sulfate	5.83 (0.00–302.00)	5.64 (BDL–300.0)	14.75 (BDL–253.00)	25.73 (BDL–1,800)
TDS	14,319 (589–61,733)	997 (252–2,768)	2,512 (244–14,800)	4,693 (150–39,260)

-, no value available; BDL, below detection limit.

[a] DOE (2014). *n* = 206. Concentrations were calculated based on the authors' raw data.

[b] Dahm et al. (2011). Powder River, *n* = 31; Raton, *n* = 40; San Juan, *n* = 20. This data source reported concentrations without presentation of raw data.

E.2.4. Metals and Metalloids

Table E-6 and Table E-7 provide supporting data on metal constituents of produced water for 12 formations.

Table E-6. Reported concentrations (mg/L) of metals and metalloids from unconventional shale and tight formation produced water, presented as: average (minimum–maximum) or *median* (minimum–maximum).

Note that calcium, potassium, and sodium appear in Table E-4.

Parameter	Shale					Tight Formation			
	Bakken[a]	Barnett[b]	Fayetteville[c]	Marcellus		Cotton Valley Group[f]	Devonian Sandstone[g]	Mesaverde[f]	Oswego[f]
States	MT, ND	TX	AR	PA[d]	PA, WV[e]	LA, TX	PA	CO, NM, UT, WY	OK
Aluminum	-	***0.43*** (0.37–2.21)	-	-	***2.5***7 (0.22–47.2)	-	-	-	-
Antimony	-	NC (ND–ND)	-	-	***0.028*** (0.018–0.038)	-	-	-	-
Arsenic	-	NC (ND–ND)	-	-	***0.101*** (0.013–0.124)	-	-	-	-
Barium	10 (0–24.6)	***3.6*** (0.93–17.9)	4 (3–5)	2,224 (0.24–13,800)	***542.5*** (2.590–13,900)	160 (ND–400.52)	1,488 (7–4,370)	139 (4–257)	
Beryllium	-	NC (ND–ND)	-	-	-	-	-	-	-
Boron	116 (39.9–192)	***30.3*** (7.0–31.9)	4.800 (2.395–21.102)	-	***12.2*** (0.808–145)	37 (2–100)	-	10 (1–14.2)	-
Cadmium	-	NC (ND–ND)	-	-	-	-	-	-	-
Chromium	-	***0.03*** (0.01–0.12)	-	-	***0.079*** (0.011–0.567)	-	-	-	-
Cobalt	-	***0.01*** (0.01–0.01)	-	-	-	-	-	-	-

Parameter	Shale					Tight Formation			
	Bakken[a]	Barnett[b]	Fayetteville[c]	Marcellus		Cotton Valley Group[f]	Devonian Sandstone[g]	Mesaverde[f]	Oswego[f]
States	MT, ND	TX	AR	PA[d]	PA, WV[e]	LA, TX	PA	CO, NM, UT, WY	OK
Copper	NC (ND–0.21)	***0.29*** (0.06–0.52)	-	-	***0.506*** (0.253–4.150)	0.7 (0.48–1)	0.04 (0.01–0.13)	-	-
Iron	96 (ND–120)	***24.9*** (12.1–93.8)	7 (1–13)	-	***53.65*** (2.68–574)	-	188 (90–458)	9 (1–29)	61 (41–78)
Lead	-	***0.02*** (0.01–0.02)	-	-	***0.066*** (0.003–0.970)	-	0.02 (0.01–0.04)	-	-
Lithium	-	***19.0*** (2.56–37.4)	9.825 (2.777–28.145)	-	***53.85*** (3.410–323)	23 (1–53)	97.8 (20.2–315)	3 (1–33)	-
Magnesium	1,270 (630–1,750)	***255*** (149–755)	61 (47–75)	632 (17–2,550)	***678*** *(40.8–2,020)*	1,363 (27–3,712.98)	2,334 (797–3,140)	74 (1–2,394)	753 (486–1,264)
Manganese	7 (4–10.2)	***0.86*** (0.25–2.20)	2 (2–3)	-	***2.825*** (0.369–18.600)	30.33 (30.33–30.33)	19 (5.6–68)	-	-
Mercury	-	NC (ND–ND)	-	-	*0.00024*	-	-	-	-
Molybdenum	NC (ND–<0.2)	***0.02*** (0.02–0.03)	-	-	-	-	-	-	-
Nickel	-	***0.04*** (0.03–0.05)	-	***0.1815*** (0.007–0.137)	***0.419*** (0.068–0.769)	-	-	-	-
Selenium	-	***0.03*** (0.03–0.04)	-	-	*0.004*	-	-	-	-
Silver	-	-	-	-	***4*** *(3-6)*	-	-	-	-

Parameter	Shale					Tight Formation			
	Bakken[a]	Barnett[b]	Fayetteville[c]	Marcellus		Cotton Valley Group[f]	Devonian Sandstone[g]	Mesaverde[f]	Oswego[f]
States	MT, ND	TX	AR	PA[d]	PA, WV[e]	LA, TX	PA	CO, NM, UT, WY	OK
Strontium	764 (518–1,010)	***529*** (48–1,550)	27 (14–49)	1,695 (0.6–8,460)	***1,240*** (0.580–8,020)	2,312 (39–9,770)	3,890 (404–13,100)	-	-
Thallium	-	NC (ND–0.14)	-	-	*0.168*	-	-	-	-
Tin	-	NC (ND–ND)	-	-	-	-	-	-	-
Titanium	-	***0.02*** (0.02–0.03)	-	-	-	-	-	-	-
Zinc	7 (2–11.3)	***0.15*** (0.10–0.36)	-	-	***0.391*** (0.087–247)	-	0.20 (0.03–1.26)	-	-

-, no value available; NC, not calculated; ND, not detected; BDL, below detection limit. ***Bolded italic*** numbers are medians.

[a] Stepan et al. (2010). *n* = 3. Concentrations were calculated based on Stepan et al.'s raw data.

[b] Hayes and Severin (2012b). *n* = 16. This data source reported concentrations without presentation of raw data.

[c] Warner et al. (2013). *n* = 6. Concentrations were calculated based on Warner et al.'s raw data. Both flowback and produced water included.

[d] Barbot et al. (2013). *n* = 134–159. This data source reported concentrations without presentation of data.

[e] Hayes (2009). *n* = 48. Concentrations were calculated based on Hayes's raw data. Both flowback and produced water included. Non-detects and contaminated blanks omitted.

[f] Blondes et al. (2014). Cotton Valley Group, *n* = 2; Mesa Verde, *n* = 1–407; Oswego, *n* = 4–30. Concentrations were calculated based on raw data presented in the USGS National Produced Water Database v2.0.

[g] Dresel and Rose (2010). *n* = 3–15. Concentrations were calculated based on Dresel and Rose's raw data.

Table E-7. Reported concentrations (mg/L) of metals and metalloids from unconventional coalbed produced water, presented as: average (minimum–maximum).

Parameter	Black Warrior[a]	Powder River[b]	Raton[b]	San Juan[b]
States	AL, MS	MT, WY	CO, NM	AZ, CO, NM, UT
Aluminum	0.037 (0–0.099)	0.018 (BDL–0.124)	0.193 (BDL–2,900)	0.069 (BDL–0.546)
Antimony	0.006 (0.00–0.022)	BDL (BDL–BDL)	BDL (BDL–BDL)	BDL (BDL–BDL)
Arsenic	0.002 (0.0–0.085)	0.001 (BDL–0.004)	0.010 (BDL–0.060)	0.001 (BDL–0.020)
Barium	45.540 (0.136–352)	0.61 (0.14–2.47)	1.67 (BDL–27.40)	10.80 (BDL–74.0)
Beryllium	0.0 (0.0–0.008)	BDL (BDL–BDL)	BDL (BDL–BDL)	BDL (BDL–BDL)
Boron	0.185 (0–0.541)	0.17 (BDL–0.39)	0.36 (BDL–4.70)	1.30 (0.21–3.45)
Cadmium	0.001 (0.00–0.015)	BDL (BDL–0.002)	0.002 (BDL–0.003)	0.002 (BDL–.006)
Calcium	218 (0–1,640)	32.09 (2.00–154.0)	14.47 (0.81–269.0)	53.29 (1.00–5,530)
Cesium	0.011 (0.0–0.072)	-	-	-
Chromium	0.002 (0.0–0.351)	0.012 (BDL–0.250)	0.105 (BDL–3.710)	0.002 (BDL–0.023)
Cobalt	0.023 (0.00–0.162)	BDL (BDL–BDL)	0.001 (BDL–0.018)	0.001 (BDL–0.017)
Copper	0.001 (0.0–0.098)	0.078 (BDL–1.505)	0.091 (BDL–4.600)	0.058 (BDL–0.706)
Iron	8.956 (0.045–93.100)	1.55 (BDL–190.0)	7.18 (0.09–95.90)	6.20 (BDL–258.0)
Lead	0.008 (0.00–0.250)	BDL (BDL–BDL)	0.023 (BDL–0.233)	0.023 (BDL–0.390)
Lithium	1.157 (0–8.940)	0.13 (BDL–0.34)	0.32 (0.01–1.00)	1.61 (0.21–4.73)
Magnesium	68.12 (0.18–414.00)	14.66 (BDL–95.00)	3.31 (0.10–56.10)	15.45 (BDL–511.0)
Manganese	0.245 (0.006–4.840)	0.02 (BDL–0.16)	0.11 (0.01–2.00)	0.19 (BDL–1.34)
Mercury	0.000 (0.000–0.000)	-	-	-
Molybdenum	0.002 (0–0.083)	0.005 (BDL–0.029)	0.002 (BDL–0.035)	0.020 (BDL–0.040)
Nickel	0.015 (0.0–0.358)	0.141 (BDL–2.61)	0.015 (0.004–0.11)	0.020 (BDL–0.13)
Potassium	12.02 (0.46–74.00)	11.95 (BDL–44.00)	6.37 (BDL–29.40)	26.99 (BDL–970.0)
Rubidium	0.013 (0.0–0.114)	-	-	-
Selenium	0.002 (0.00–0.063)	0.006 (BDL–0.046)	0.017 (BDL–0.100)	0.018 (BDL–0.067)
Silver	0.015 (0.0–0.565)	0.003 (0.003–0.003)	0.015 (BDL–0.140)	BDL (BDL–BDL)
Sodium	4,353 (126–16,700)	356 (12–1,170)	989 (95–5,260)	1,610 (36–7,834)
Strontium	11.354 (0.015–142.000)	0.60 (0.10–1.83)	5.87 (BDL–47.90)	5.36 (BDL–27.00)
Thallium	-	-	-	-
Tin	0.00 (0.00–0.009)	0.006 (BDL–0.028)	0.008 (BDL–0.021)	0.017 (BDL–0.039)
Titanium	0.003 (0.0–0.045)	BDL (BDL–0.002)	BDL (BDL–0.002)	0.004 (BDL–0.020)

Parameter	Black Warrior[a]	Powder River[b]	Raton[b]	San Juan[b]
States	AL, MS	MT, WY	CO, NM	AZ, CO, NM, UT
Vanadium	0.001 (0.0–0.039)	BDL (BDL–BDL)	0.001 (BDL–0.013)	BDL (BDL–BDL)
Zinc	0.024 (0.0–0.278)	0.063 (BDL–0.390)	0.083 (0.010–3.900)	0.047 (0.005–0.263)

-, no value available; BDL, below detection limit.

[a] DOE (2014). *n* = 206. Concentrations were calculated based on the authors' raw data.

[b] Dahm et al. (2011). Powder River, *n* = 31; Raton, *n* = 40; San Juan, *n* = 20. This data source reported concentrations without presentation of raw data.

E.2.4.1. Processes Controlling Mineral Precipitation and Dissolution

Hydraulic fracturing treatments introduce fluids into the subsurface that are not in equilibrium with respect to formation mineralogy. Subsurface geochemical equilibrium modeling and saturation indices are therefore used to assess the solution chemistry of unconventional produced water and the subsequent likelihood of precipitation and dissolution reactions (Engle and Rowan, 2014; Barbot et al., 2013). Dissolution and precipitation reactions between fracturing fluids, formation solids, and formation water contribute to the chemistry of flowback and produced water.

For example, early flowback fluids may be under-saturated with respect to certain constituents or minerals associated with formation solids. Through time, as fluid-rock geochemistry returns to equilibrium, formation minerals will dissolve into solution and return in flowback.

Depending upon the formation chemistry and composition of the hydraulic fracturing fluid, the hydraulic fracturing fluid may initially have a lower ionic strength than existing formation fluids. Consequently, salts, carbonate, sulfate, and silicate minerals may undergo dissolution or precipitation. Proppants may also undergo dissolution or serve as nucleation sites for precipitation (McLin et al., 2011).

Currently, relatively little literature quantitatively explores subsurface dissolution and precipitation reactions between hydraulic fracturing fluids and formation solids and water. However, the processes that take place will likely be a function of the solubilities of the minerals, the chemistry of the fluid, pH, redox conditions, and temperature.

Documented dissolution processes in unconventional resources include the dissolution of feldspar followed by sodium enrichment in coalbed produced water (Rice et al., 2008). Dissolution of barium-rich minerals (barite ($BaSO_4$) and witherite ($BaCO_3$)), and strontium-rich minerals (celestite ($SrSO_4$) and strontianite ($SrCO_3$)) are known to enrich shale produced waters in barium and strontium (Chapman et al., 2012).

Known precipitation processes in unconventional resources include the precipitation of carbonate and subsequent reduction of calcium and magnesium concentrations in coalbed produced water (Rice et al., 2008). Additionally, calcium carbonate precipitation is suspected to cause declines in pH and alkalinity levels in shale produced water (Barbot et al., 2013).

The subsurface processes associated with fluid-rock interactions take place over a scale of weeks to months through the generation of flowback and produced water. Note that the types and extent of subsurface dissolution and precipitation reactions change with time, from injection through flowback and production. For instance, Engle and Rowan (2014) found that early Marcellus Shale flowback was under-saturated with respect to gypsum ($CaSO_4 \cdot 2H_2O$), halite (NaCl), celestite, strontianite, and witherite, indicating that these minerals would dissolve in the subsurface. Fluids were oversaturated with respect to barite. Saturation indices for gypsum, halite, celestite, and barite all increased during production. Knowing when dissolution and precipitation will likely occur is important, because dissolution and precipitation of minerals change formation permeability and porosity, which can affect production (André et al., 2006).

Additionally, pyrite (FeS_2) is an important minor mineral in reduced sedimentary rocks. Pyrite is the primary form of sulfur and iron occurrence in shales (Leventhal and Hosterman, 1982) and is also a common mineral phase generated in coals in which organic matter is closely associated (Ward, 2002). Pyrite content in shales can vary from less than 1% to several percent (Chermak and Schreiber, 2014; Vulgamore et al., 2007). Researchers have found a strong association of trace metals (i.e., nickel, copper, cadmium, chromium, cobalt, lead, selenium, vanadium, and zinc) with pyrite in shales (Chermak and Schreiber, 2014; Tuttle et al., 2009; Leventhal and Hosterman, 1982).

Although studies considering pyrite oxidation within the context of hydraulic fracturing are currently lacking, it is likely that the introduction of oxygenated fluids to freshly exposed surfaces in the subsurface during hydraulic fracturing can initiate limited, short-term pyrite oxidation or dissolution. Pyrite dissolution may increase iron and trace element concentrations and acidity in produced waters (Nordstrom and Alpers, 1999; Moses and Herman, 1991).

The extent to which the oxidative dissolution of pyrite would exert a control on post-injection subsurface fluid chemistry is unknown, although an ongoing U.S. Geological Survey (USGS) study anticipates it may be more significant than previously hypothesized (Li and Brantley, 2011). Regardless, relative to other reactions contributing to the composition of flowback and produced water (i.e., dissolution of salts), pyrite oxidation appears to be less significant. Ultimately, reactions resulting from temporary changes in subsurface redox conditions will be less important relative to other reactions that are less redox-dependent.

E.2.5. Naturally Occurring Radioactive Material (NORM) and Technically Enhanced Naturally Occurring Radioactive Material (TENORM)

E.2.5.1. Formation Solids Levels of NORM

Elevated uranium levels in formation solids have been used to identify potential areas of natural gas production for decades (Fertl and Chilingar, 1988). Marine black shales are estimated to contain an average of 5–20 ppm uranium depending on depositional conditions, compared to an average of less than 5 ppm among all shales (USGS, 1961). Shales that bear 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).

Bank et al. (2012) identified Marcellus samples with uranium ranging from 4–72 ppm, with an average of 30 ppm. Additionally, shale samples taken from three counties within the Marcellus Shale had uranium concentrations ranging from 8 to 84 ppm (BTGS, 2011; Hatch and Leventhal, 1981). Chermak and Schreiber (2014) compiled mineralogy and trace element data available in the literature for nine U.S. hydrocarbon-producing shales. In this combined data set, uranium levels among different shale plays were found to vary over three orders of magnitude, with samples of the Utica Shale containing approximately 0–5 ppm uranium and samples of the Woodford Shale containing uranium in the several-hundred-ppm range.

Vine (1956) reported that the principal uranium-bearing coal deposits of the United States are found in Cretaceous and Tertiary formations in the northern Great Plains and Rocky Mountains; in some areas of the West, coal deposits have been found with uranium concentrations in the range of thousands of ppm or greater. In contrast, most Mississippian, Pennsylvanian, and Permian coals in the north-central and eastern United States contain less than 10 ppm uranium, rarely containing 50 ppm or more.

E.2.5.2. Produced Water Levels of TENORM

Background data on NORM in the Marcellus Shale and Devonian sandstones are given in Table E-8.

Table E-8. Reported concentrations (in pCi/L) of radioactive constituents in unconventional shale and sandstone produced water, presented as: average (minimum–maximum) or *median* (minimum–maximum).

Parameter	Marcellus				Devonian Sandstone[a]
		PA NORM STUDY (PA DEP, 2015)			
States	NY, PA[b]	Flowback[c]	Conventional Produced Water[d]	Unconventional Produced Water[e]	PA
Gross alpha	***6,845*** (ND–123,000)	***10,700*** (288–71,000)	***1,835*** (465–2,570)	***11,300*** (2,240–41,700)	-
Gross beta	***1,170*** (ND–12,000)	***2,400*** (742–21,300)	***909*** (402–1,140)	***3.445*** (1.5–7,600)	-
Radium-226	***1,869*** (ND–16,920)	***4,500*** (551-25,500)	***243*** (81 – 819)	***6,300*** (1,700–26,600)	***2,367*** (200–5,000)
Radium-228	***557*** (ND–2,589)	***633*** (248–1,740)	***128*** (26 – 896)	***941*** (366–1,900)	-
Total Radium	***2,530*** (0.192-18,045)	-	***371*** (107 – 1,715)	***7,180*** (2,336–28,500)	-
Uranium^{235}	1 (ND–20)	-	-	-	-
Uranium^{238}	42 (ND–497)	-	-	-	-

n/a, not applicable; -, no value available; BDL, below detection limit. ***Bolded italic*** numbers are medians.

[a] Dresel and Rose (2010). *n* = 3. Concentrations presented were calculated based on Dresel and Rose's raw data.

[b] Rowan et al. (2011). *n* = 51. Concentrations presented were calculated based on Rowan et al.'s raw data for Marcellus samples. Uranium data from Barbot et al. (2013) *n* = 14.

[c] PA DEP (2015). n = 9. Data reported in Table 3-14.

[d] PA DEP (2015). n = 9. Values calculated from Table 3-15 for unfiltered samples.

[e] PA DEP (2015). n = 4. Values calculated from Table 3-15 for unfiltered samples.

E.2.5.3. Mobilization of Naturally Occurring Radioactive Material

Similar to conventional oil and gas production, in unconventional oil and gas production, radionuclides native to the targeted formation return to the surface with produced water. The principal radionuclides found in oil and gas produced waters include radium-226 of the uranium-238 decay series and radium-228 of the thorium-232 decay series (White, 1992). Levels of TENORM in produced water are controlled by geologic and geochemical interactions between injected and formation fluids, and the targeted formation (Bank, 2011). Mechanisms controlling NORM mobilization into produced water include (1) the TENORM content of the targeted formation; (2) factors governing the release of radionuclides, particularly radium, from the reservoir matrix; and (3) the geochemistry of the produced water (Choppin, 2007, 2006; Fisher, 1998).

Organic-rich shales and coals are enriched in uranium, thorium, and other trace metals in concentrations several times above those seen in typical shales or sedimentary rocks (Diehl et al., 2004; USGS, 1997; Wignall and Myers, 1988; Tourtelot, 1979; Vine and Tourtelot, 1970). Unlike shales and coals, sandstones are generally not organic-rich source rocks themselves. Instead, hydrocarbons migrate into these formations over long periods of time (Clark and Veil, 2009). Since TENORM and organic contents are typically positively correlated due to the original, reduced depositional environment (Fertl and Chilingar, 1988), it is unlikely that sandstones would be enriched in TENORM to the same extent as oil- and gas-bearing shales and coals. Therefore, concern related to TENORM within produced water is focused on operations targeting shales and coalbeds.

Radium is most soluble and mobile in chloride-rich, high-TDS, reducing environments (Sturchio et al., 2001; Zapecza and Szabo, 1988; Langmuir and Riese, 1985). In formation fluids with high TDS, calcium, potassium, magnesium, and sodium compete with dissolved radium for sorption sites, limiting radium sorption onto solids and allowing it to accumulate in solution at higher concentrations (Fisher, 1998; Webster et al., 1995). The positive correlation between TDS and radium is well established and TDS is a useful indicator of radium and TENORM activity within produced water, especially in lithologically homogenous reservoirs (Rowan et al., 2011; Sturchio et al., 2001; Fisher, 1998; Kraemer and Reid, 1984).

Uranium and thorium are poorly soluble under reducing conditions and are therefore more concentrated in formation solids than in solution (Fisher, 1998; Kraemer and Reid, 1984; Langmuir and Herman, 1980). However, because uranium becomes more soluble in oxidizing environments, the introduction of relatively oxygen-rich fracturing fluids may promote the temporary mobilization of uranium during hydraulic fracturing and early flowback. In addition, the physical act of hydraulic fracturing creates fresh fractures and exposes organic-rich and highly reduced surfaces from which radionuclides could be released from the rock into formation fluids.

Produced water geochemistry determines, in part, the fate of subsurface radionuclides, particularly radium. Radium may remain in the host mineral or it may be released into formation fluids, where it can remain in solution as the dissolved Ra^{2+} ion, be adsorbed onto oxide grain coatings or clay particles by ion exchange, substitute for other cations during the precipitation of minerals, or form

complexes with chloride, sulfate, and carbonate ions (Rowan et al., 2011; Sturchio et al., 2001; Langmuir and Riese, 1985). Uranium- and thorium-containing materials with a small grain size, a large surface-to-volume ratio, and the presence of uranium and thorium near grain surfaces promote the escape of radium into formation fluids. Vinson et al. (2009) point to alpha decay along fracture surfaces as a primary control on radium mobilization in crystalline bedrock aquifers. Radium may also occur in formation fluids due to other processes, such as the decay of dissolved parent isotopes and adsorption-desorption reactions on formation surfaces (Sturchio et al., 2001).

Preliminary results from fluid-rock interaction studies (Bank, 2011) indicate that a significant percentage of uranium in the Marcellus Shale may be subject to mobilization by hydrochloric acid, which is used as a fracturing fluid additive. Understanding these processes will determine the extent to which such processes might influence the TENORM content of flowback and produced water.

E.2.6. Organics

Background data on organics in seven formations is given in Table E-9.

Table E-9. Concentrations of select organic parameters from unconventional shale, a tight formation, and coalbed produced water, presented as: average (minimum–maximum) or *median* (minimum–maximum).

		Shale			Tight Formation	Coal			
Parameter	**Unit**	**Barnett[a]**	**Marcellus**		**Cotton Valley Group[d]**	**Powder River[e]**	**Raton[e]**	**San Juan[e]**	**Black Warrior[f]**
States	**n/a**	**TX**	**PA[b]**	**PA, WV[c]**	**LA, TX**	**MT, WY**	**CO, NM**	**AZ, CO, NM, UT**	**AL, MS**
TOC	mg/L	***9.75*** (6.2–36.2)	160 (1.2–1,530)	***89.2*** (1.2–5680)	198 (184–212)	3.52 (2.07–6.57)	1.74 (0.25–13.00)	2.91 (0.95–9.36)	6.03 (0.00–103.00)
DOC	mg/L	***11.2*** (5.5–65.3)	*43* (5–695)	***117*** (3.3–5,960)	-	3.18 (1.09–8.04)	1.26 (0.30–8.54)	3.21 (0.89–11.41)	3.37 (0.53–61.41)
BOD	mg/L	***582*** (101–2,120)	-	***141*** (2.8–12,400)	-	-	-	-	-
Oil and grease	mg/L	***163.5*** (88.2–1,430)	74 (5–802)	***16.9*** (4.7–802)	-	-	9.10 (0.60–17.6)	-	-
Benzene	µg/L	680 (49–5,300)	-	***220*** (5.8–2,000)	-	-	4.7 (BDL–220.0)	149.7 (BDL–500.0)	-
Toluene	µg/L	760 (79–8,100)	-	***540*** (5.1–6,200)	-	-	4.7 (BDL–78.0)	1.7 (BDL–6.2)	-
Ethylbenzene	µg/L	29 (2.2–670)	-	***42*** (7.6–650)	-	-	0.8 (BDL–18.0)	10.5 (BDL–24.0)	-

Parameter	Unit	Shale			Tight Formation	Coal			
		Barnett[a]	Marcellus		Cotton Valley Group[d]	Powder River[e]	Raton[e]	San Juan[e]	Black Warrior[f]
States	**n/a**	**TX**	**PA[b]**	**PA, WV[c]**	**LA, TX**	**MT, WY**	**CO, NM**	**AZ, CO, NM, UT**	**AL, MS**
Xylenes	µg/L	360 (43–1,400)	-	***300*** (15–6,500)	-	-	9.9 (BDL–190.0)	121.2 (BDL–327.0)	-
Average total BTEX[g]	µg/L	1,829	2,910	1,102	-	-	20.1	283.1	-

n/a, not applicable; -, no value available; BDL, below detection limit. ***Bolded italic*** numbers are medians.

[a] Hayes and Severin (2012b). *n* = 16. This data source reported concentrations without presentation of raw data.

b Barbot et al. (2013). *n* = 55; no presentation of raw data.

[c] Hayes (2009) *n* = 13-67. Concentrations were calculated based on Hayes' raw data. Both flowback and produced water included. Non-detects and contaminated blanks omitted.

[d] Blondes et al. (2014). *n* = 2. Concentrations were calculated based on raw data presented in the USGS National Produced Water Database v2.0.

[e] Dahm et al. (2011). Powder River, *n* = 31; Raton, *n* = 40; San Juan, *n* = 20. This data source reported concentrations without presentation of raw data.

[f] DOE (2014). n = 206. Concentrations were calculated based on the authors' raw data.

[g] Average total BTEX was calculated by summing the average/median concentrations of benzene, toluene, ethylbenzene, and xylenes for a unique formation or basin. Minimum to maximum ranges were not calculated due to inaccessible raw data.

Several classes of naturally occurring organic chemicals are present in conventional and unconventional produced waters, with large concentration ranges (Lee and Neff, 2011). These organic classes include total organic carbon (TOC); saturated hydrocarbons; BTEX (benzene, toluene, ethylbenzene, and xylenes); and polyaromatic hydrocarbons (PAHs) (see Table E-9). While TOC concentrations in produced water are detected at the milligrams to grams per liter level, concentrations of individual organic compounds are typically detected at the micrograms to milligrams per liter level.

TOC indicates the level of dissolved and undissolved organics in produced water, including non-volatile and volatile organics (Acharya et al., 2011). TOC concentrations in conventional produced water vary widely from less than 0.1 mg/L to more than 11,000 mg/L. Average TOC concentrations in unconventional produced water range from less than 2.00 mg/L in the Raton CBM basin to approximately 200 mg/L in the Cotton Valley Group sandstones, although individual measurements have exceeded 5,000 mg/L in the Marcellus Shale (see Table E-9).

Dissolved organic carbon (DOC) is a general indicator of organic loading and is the fraction of organic carbon available for complexing with metals and supporting microbial growth. DOC values in unconventional produced water range from less than 1.50 mg/L (average) in the Raton Basin to more than 115 mg/L (median) in the Marcellus Shale (see Table E-9). Individual DOC concentrations in the Marcellus Shale produced water approach 6,000 mg/L. For comparison, DOC levels in fresh water systems are typically below 5 mg/L, while raw wastewater can exceed 50 mg/L (Katsoyiannis and Samara, 2007; Muylaert et al., 2005).

Biochemical oxygen demand (BOD) is a conventional pollutant under the U.S. Clean Water Act. It is an indirect measure of biodegradable organics in produced water and an estimate of the oxygen demand on a receiving water. Median BOD levels for Barnett and Marcellus Shales produced water exceed 30 mg/L, and both reported maximum concentrations exceeding 12,000 mg/L (Table E-9). In some circumstances wide variation in produced water median BOD levels may be reflective of flowback reuse in fracturing fluids (Hayes, 2009).

Lastly, BTEX is associated with petroleum. Benzene was found in produced water from several basins: average produced water benzene concentration from the Barnett Shale was 680 μg/L, from the Marcellus Shale was 220 μg/L (median), and from the San Juan Basin was 150 μg/L (see Table E-9). Total BTEX concentrations for conventional produced water vary widely from less than 100 μg/L to nearly 580,000 μg/L. For comparison, average total BTEX concentrations in unconventional produced water range from 20 μg/L in the Raton Basin to nearly 3,000 μg/L in the Marcellus play (see Table E-9). From these data, average total BTEX levels in shale produced water are one to two orders of magnitude higher than those in CBM produced water.

In addition to abundant BTEX, a variety of volatile and semi-volatile organic compounds VOCs and SVOCs have been detected in shale and coalbed produced water. Shale produced water contains naphthalene, alkylated toluenes, and methylated aromatics in the form of several benzene and phenol compounds, as shown in Table E-10. Like BTEX, naphthalene, methylated phenols, and acetophenone are associated with petroleum. Detected shale produced water organics such as

acetone, 2-butanone, carbon disulfide, and pyridine are potential remnants of chemical additives used as friction reducers or industrial solvents (Hayes, 2009).

Table E-10. Reported concentrations (µg/L) of organic constituents in produced water for two unconventional shale formations, presented as: average (minimum–maximum) or *median* (minimum–maximum).

Parameter	Barnett[a]	Marcellus[b]
States	TX	MD, NY, OH, PA, VA, WY
Acetone	145 (27–540)	***83*** (14–5,800)
Carbon disulfide	-	***400*** (19–7,300)
Chloroform	-	28
Isopropylbenzene	35 (0.8–69)	***120*** (86–160)
Naphthalene	238 (4.8–3,100)	***195*** (14–1,400)
Phenolic compounds	***119.65*** (9.3–230)	-
1,2,4-Trimethylbenzene	173 (6.9–1,200)	***66.5*** (7.7–4,000)
1,3,5-Trimethylbenzene	59 (6.4–300)	***33*** (5.2–1,900)
1,2-Diphenylhydrazine	4.2 (0.5–7.8)	-
1,4-Dioxane	6.5 (3.1–12)	-
2-Methylnaphthalene	1,362 (5.4–20,000)	***3.4*** (2–120)
2-Methylphenol	28.3 (5.8–76)	***13*** (11–15)
2,4-Dichlorophenol	(ND–15)	-
2,4-Dimethylphenol	14.5 (8.3–21)	12
3-Methylphenol and 4-Methylphenol	41 (7.8–100)	***11.5*** (0.35-16)
Acetophenone	(ND–4.6)	***13*** (10–22)
Benzidine	(ND–35)	-
Benzo(a)anthracene	(ND–17.0)	-
Benzo(a)pyrene	(ND–130.0)	6.7
Benzo(b)fluoranthene	42.2 (0.5–84.0)	10
Benzo(g,h,i)perylene	42.3 (0.7–84.0)	6.9
Benzo(k)fluoranthene	32.8 (0.6–65.0)	5.9
Benzyl alcohol	81.5 (14.0–200)	***41*** (17–750)
Bis(2-Ethylhexyl) phthalate	210 (4.8–490)	***20*** (9.6–870)
Butyl benzyl phthalate	34.3 (1.9–110)	-

Parameter	Barnett[a]	Marcellus[b]
States	TX	MD, NY, OH, PA, VA, WY
Chrysene	120 (0.57–240)	-
Di-n-octyl phthalate	(ND–270)	15
Di-n-butyl phthalate	41 (1.5–120)	***14*** (11–130)
Dibenz(a,h)anthracene	77 (3.2–150)	***3.2*** (2.3–11)
Diphenylamine	5.3 (0.6–10.0)	-
Fluoranthene	(ND–0.18)	6.1
Fluorene	0.8 (0.46–1.3)	8.4
Indeno(1,2,3-cd)pyrene	71 (2.9–140)	***3.1*** (2.4–9.5)
N-Nitrosodiphenylamine	8.9 (7.8–10)	2.7
N-Nitrosomethylethylamine	(ND–410)	-
Phenanthrene	107 (0.52–1,400)	***9.75*** (3–22)
Phenol	63 (17–93)	***10*** (2.4–21)
Pyrene	0.2 (ND–0.18)	13
Pyridine	413 (100–670)	***250*** (10–2,600)

-, no value available; ND, not detected.

[a] Hayes and Severin (2012b). *n* = 16. Data from days 1–23 of flowback. This data source reported concentrations without presentation of raw data.

[b] Hayes (2009). *n* = 1-35. Data from days 1–90 of flowback. Concentrations were calculated from Hayes' raw data. Non-detects and contaminated blanks omitted.

The organic profile of CBM produced water is characterized by high levels of aromatic and halogenated compounds compared to other unconventional produced waters (Sirivedhin and Dallbauman, 2004). PAHs and phenols are the most common organic compounds found in coalbed produced water. Produced water from coalbeds in the Black Warrior Basin mainly contains phenols, multiple naphthalic PAHs, and various decanoic and decenoic fatty acids (see Table E-11). CBM-associated organics are also known to include biphenyls, alkyl aromatics, hydroxypyridines, aromatic amines, and nitrogen-, oxygen-, and sulfur-bearing heterocyclics (Orem et al., 2014; Pashin et al., 2014; Benko and Drewes, 2008; Orem et al., 2007; Fisher and Santamaria, 2002).

Table E-11. Reported concentrations of organic constituents in 65 samples of produced water from the Black Warrior CBM Basin, presented as average (minimum–maximum).

Parameter	Number of observations	Concentration (μg/L)[a]
States	-	AL, MS
Benzothiazole	45	0.25 (0.01–3.04)
Caprolactam	10	0.75 (0.02–2.39)
Cyclic octaatomic sulfur	29	1.06 (0.10–9.63)
Dimethyl-naphthalene	39	0.79 (0.01–9.51)
Dioctyl phthalate	57	0.21 (0.01–2.30)
Dodecanoic acid	30	1.13 (0.67–2.52)
Hexadecanoic acid	50	1.58 (1.17–3.02)
Hexadecenoic acid	25	1.69 (1.13–8.37)
Methyl-biphenyl	18	0.25 (0.01–2.13)
Methyl-naphthalene	52	0.77 (0.01–15.55)
Methyl-quinoline	31	0.96 (0.03–3.75)
Naphthalene	49	0.41 (0.01–6.57)
Octadecanoic acid	32	1.95 (1.62–3.73)
Octadecenoic acid	29	1.87 (1.60–3.47)
Phenol, 2,4-bis(1,1-dimethyl)	21	0.45 (0.01–4.94)
Phenol, 4-(1,1,3,3-tetramethyl)	17	1.65 (0.01–18.34)
Phenolic compounds	-	19.06 (ND–192.00)
Tetradecanoic acid	53	1.51 (0.94–5.32)
Tributyl phosphate	23	0.26 (0.01–2.66)
Trimethyl-naphthalene	23	0.65 (0.01–4.49)
Triphenyl phosphate	6	1.18 (0.01–6.77)

-, no value available.

[a] DOE (2014). Concentrations were calculated based on the authors' raw data.

Hayes (2009) characterized the content of Marcellus Shale produced water including organics (see Table E-10). The author tested for the majority of VOCs and SVOCs, pesticides and PCBs, based on the recommendation of the Pennsylvania and West Virginia Departments of Environmental Protection. Only 0.5% of VOCs and 0.03% of SVOCs in the produced water were detected above 1 mg/L. Approximately 96% of VOCs, 98% of SVOCs, and virtually all pesticides and PCBs were at nondetectable levels.

E.2.7. Chemical Reactions

Section E.2.7.1 describes general aspects of subsurface chemical reactions that might occur during hydraulic fracturing operations. Here we augment the discussion by describing subsurface chemical processes.

E.2.7.1. Injected Chemical Processes

Hydraulic fracturing injects relatively oxygenated fluids into a reducing environment, which may mobilize trace or major constituents into solution. Injection of oxygenated fluids may lead to short-term changes in the subsurface redox state, as conditions may shift from reducing to oxidizing. The chemical environment in hydrocarbon-rich unconventional reservoirs, such as black shales, is generally reducing, as evidenced by the presence of pyrite and methane (Engle and Rowan, 2014; Dresel and Rose, 2010). For black shales, reducing conditions are a product of original accumulations of organic matter whose decay depleted oxygen to create rich organic sediments within oil- and gas-producing formations (Tourtelot, 1979; Vine and Tourtelot, 1970). Yet reactions resulting from temporary redox shifts are likely to be less important than those resulting from other longer-term physical and geochemical processes. Temporary subsurface redox shifts may be due to the short timeframe for fluid injection (a few days to a few weeks) and the use of oxygen scavengers to prevent downhole equipment corrosion.

Hydraulic fracturing fluid injection introduces novel chemicals into the subsurface.[1] As such, the geochemistry of injected and native fluids will not be in equilibrium. Over the course of days to months, a complex series of reactions will equilibrate disparate fluid chemistries. The evolution of flowback and produced water geochemistry are dependent upon the exposure of formation solids and fluids to novel chemicals within hydraulic fracturing fluid. Chemical additives interact with reservoir solids and either mobilize constituents or themselves become adsorbed to solids. Such additives include metallic salts, elemental complexes, salts of organic acids, organometallics, and other metal compounds (Montgomery, 2013; House of Representatives, 2011).

The salts, elemental complexes, organic acids, organometallics, and other metal-containing compounds may interact with metals and metalloids in the target formation through processes such as ion exchange, adsorption, desorption, chelation, and complexation. For instance, natural organic ligands (e.g., citrate) are molecules that can form coordination compounds with heavy metals such as cadmium, copper, and lead (Martinez and McBride, 2001; Stumm and Morgan, 1981; Bloomfield et al., 1976). Citrate-bearing compounds are used in hydraulic fracturing fluids as surfactants, iron control agents, and biocides. Studies of the additives' interactions with formation solids at concentrations representative of hydraulic fracturing fluids are lacking.

Furthermore, pH will likely play a role in the nature and extent of these processes, as the low pH of hydraulic fracturing fluids may mobilize trace constituents. The pH of injected fluids may differ from existing subsurface conditions due to the use of dilute acids (e.g., hydrochloric or acetic) used for cleaning perforations and fractures during hydraulic fracturing treatments (Montgomery, 2013;

[1] For more information on chemical additive usage, refer to Chapter 5 (Chemical Mixing).

GWPC and ALL Consulting, 2009). Metals within formation solids may be released through the dissolution of acid-soluble phases such as iron and manganese oxides or hydroxides (Yang et al., 2009; Kashem et al., 2007; Filgueiras et al., 2002). Thus, the pH of hydraulic fracturing fluids, or changes in system pH that may occur as fluid recovery begins, may influence which metals and metalloids are likely to be retained within the formation and which may be recovered in flowback. Ultimately, more research is needed to fully understand how the injection of hydraulic fracturing fluids affects subsurface geochemistry and resultant flowback and produced water chemistry.

E.2.8. Microbial Community Processes and Content

By design, hydraulic fracturing releases hydrocarbons and other reduced mineral species from freshly fractured shale, sandstone, and coal, resulting in saltier in situ fluids, the release of formation solids, and increased interconnected fracture networks with rich colonization surfaces that are ideal for microbial growth (Wuchter et al., 2013; Curtis, 2002). Depending upon the formation, microorganisms may be native to the subsurface and/or introduced from non-sterile equipment and fracturing fluids. Additionally, microorganisms compete for novel organics in the form of chemical additives (Wuchter et al., 2013; Arthur et al., 2009). Since large portions of hydraulic fracturing fluid can remain emplaced in the targeted formation, long-term microbial activity is supported through these novel carbon and energy resources (Orem et al., 2014; Murali Mohan et al., 2013a; Struchtemeyer and Elshahed, 2012; Bottero et al., 2010). Such physical and chemical changes to the environment at depth stimulate microbial activity and influence flowback and produced water content in important ways.

Several studies characterizing produced water from unconventional formations (i.e., the Barnett, Marcellus, Utica, and Antrim Shales) indicate that taxa with recurring physiologies compose shale flowback and produced water microbial communities (Murali Mohan et al., 2013b; Wuchter et al., 2013). Such physiologies include sulfur cyclers (e.g., sulfidogens: sulfur , sulfate , and thiosulfate reducers); fermenters; acetogens; hydrocarbon oxidizers; methanogens; and iron, manganese, and nitrate reducers (Davis et al., 2012).

Based on their physiologies, microorganisms cycle substrates at depth by mobilizing or sequestering constituents in and out of solution. Mobilization can occur through biomethylation, complexation, and leaching. Sequestration can occur through intracellular sequestration, precipitation, and sorption to biomass.

The extent to which constituents are mobilized or sequestered depends upon the prevailing geochemical environment after hydraulic fracturing and through production. Significant environmental factors that influence the extent of microbially mediated reactions are increases in ionic content (i.e., salinity, conductivity, total nitrogen, bromide, iron, and potassium); decreases in acidity, and organic and inorganic carbon; the availability of diverse electron acceptors and donors; and the availability of sulfur-containing compounds (Cluff et al., 2014; Murali Mohan et al., 2013b; Davis et al., 2012). Examples follow that illustrate how subsurface microbial activity influences the content of produced water.

Under prevailing anaerobic and reducing conditions, microorganisms can mobilize or sequester metals found in unconventional produced water (Gadd, 2004). Microbial enzymatic reduction carried out by chromium-, iron-, manganese-, and uranium-reducing bacteria can both mobilize and sequester metals (Vanengelen et al., 2008; García et al., 2004; Mata et al., 2002; Gauthier et al., 1992; Myers and Nealson, 1988; Lovley and Phillips, 1986). For instance, iron and manganese species go into solution when reduced, while chromium and uranium species precipitate when reduced (Gadd, 2004; Newman, 2001; Ahmann et al., 1994).

Metals can also be microbially solubilized by complexing with extracellular metabolites, siderophores (metal-chelating compounds), and microbially generated bioligands (e.g., organic acids) (Glorius et al., 2008; Francis, 2007; Gadd, 2004; Hernlem et al., 1999). For example, *Pseudomonas* spp. secrete acids that act as bioligands to form complexes with uranium(VI) (Glorius et al., 2008).

Many sulfur-cycling taxa have been found in hydraulic fracturing flowback and produced water communities (Murali Mohan et al., 2013b; Mohan et al., 2011). Immediately following injection, microbial sulfate reduction is stimulated by diluting high-salinity formation waters with fresh water (high salinities inhibit sulfate reduction). Microbial sulfate reduction oxidizes organic matter and decreases aqueous sulfate concentrations, thereby increasing the solubility of barium (Cheung et al., 2010; Lovley and Chapelle, 1995).

Sulfidogens also reduce sulfate, as well as elemental sulfur and other sulfur species (e.g., thiosulfate) prevalent in the subsurface, contributing to biogenic sulfide or hydrogen sulfide gas in produced water (Alain et al., 2002; Ravot et al., 1997). Sulfide can also sequester metals in sulfide phases (Ravot et al., 1997; Lovley and Chapelle, 1995). Sources of sulfide also include formation solids (e.g., pyrite in shale) and remnants of drilling muds (e.g., barite and sulfonates), or other electron donor sources (Davis et al., 2012; Kim et al., 2010; Collado et al., 2009; Grabowski et al., 2005).

Additionally, anaerobic hydrocarbon oxidizers associated with shale produced water can readily degrade simple and complex carbon compounds across a considerable salinity and redox range (Murali Mohan et al., 2013b; Fichter et al., 2012; Timmis, 2010; Lalucat et al., 2006; Yakimov et al., 2005; McGowan et al., 2004; Hedlund et al., 2001; Cayol et al., 1994; Gauthier et al., 1992; Zeikus et al., 1983).

Lastly, microbial fermentation produces organic acids, alcohols, and gases under anaerobic conditions, as is the case during methanogenesis. Some nitrogen-cycling genera have been identified in unconventional shale gas systems. These include genera involved in nitrate reduction and denitrification (Kim et al., 2010; Yoshizawa et al., 2010; Yoshizawa et al., 2009; Lalucat et al., 2006). These genera likely couple sugar, organic carbon, and sulfur species oxidation to nitrate reduction and denitrification processes.

Consequently, using a variety of recurring physiologies, microorganisms mobilize and sequester constituents in and out of solution to influence the content of flowback and produced water in important ways.

E.3. Produced Water Content Spatial Trends

E.3.1. Variability between Plays of the Same Rock Type

E.3.1.1. Shale Formation Variability

The content of shale produced water varies geographically, as shown by data from four formations (the Bakken, Barnett, Fayetteville, and Marcellus Shales; see Table E-2, Table E-4, Table E-6, Table E-9, Table E-10). For several constituents, variability between shale formations is common. The average/median TDS concentrations in the Marcellus (87,800 to 106,390 mg/L) and Bakken (196,000 mg/L) Shales are one order of magnitude greater than the average TDS concentrations reported for the Barnett and Fayetteville Shales (see Table E-2). As Fayetteville produced water contains the lowest reported average TDS concentration (13,290 mg/L), average concentrations for many inorganics (i.e., bromide, calcium, chloride, magnesium, sodium, and strontium) that contribute to dissolved solids loads are the lowest compared to average concentrations for the same inorganics in Bakken, Barnett, and Marcellus produced water (see Table E-4 and Table E-6). Average concentrations for metals reported within Bakken and Marcellus produced water are also higher than those within the Barnett or Fayetteville formations (see Table E-6).

Additionally, Marcellus produced water is enriched in barium (average concentration of 2,224 mg/l in Barbot et al. (2013) or median calculated from Hayes (2009) of 542.5 mg/L) and strontium (average concentration of 1,695 mg/L (Barbot et al., 2013) or median calculated from Hayes (2009)of 1,240 mg/L) by one to three orders of magnitude compared to Bakken, Barnett, and Fayetteville produced water (see Table E-6). Subsequently, radionuclide variability expressed as isotopic ratios (e.g., radium-228/radium-226, strontium-87/strontium-86) are being used to determine the reservoir source for produced water (Chapman et al., 2012; Rowan et al., 2011; Blauch et al., 2009). Lastly, Barnett and Bakken produced waters are enriched in sulfate.

Although organic data are limited, average BTEX concentrations are higher in Marcellus compared to Barnett produced water by one order of magnitude, whereas concentrations of benzene alone are marginally higher in Barnett compared to Marcellus produced water (see Table E-9 and Table E-10).

E.3.1.2. Tight Formation Variability

The average concentrations for various constituents in tight formation produced water vary geographically between sandstone formations (the Cotton Valley Group, Devonian sandstone, and the Mesaverde and Oswego), as shown in Table E-2, Table E-4, and Table E-6. The average TDS concentrations in the Devonian sandstone (235,125 mg/L) and Cotton Valley Group (164,683 mg/L) are one to two orders of magnitude greater than the average TDS concentrations reported for the Mesaverde (15,802 mg/L) and Oswego Formations (73,082 mg/L) (see Table E-2).

Mesaverde produced water also contained the lowest average concentrations for many of the inorganic components of TDS (i.e., calcium, chloride, iron, magnesium, and sodium; see Table E-4 and Table E-6).

Little variability was reported in pH between these four tight formations (see Table E-2). Mesaverde produced water was enriched in sulfate, with an average concentration of 837 mg/L (see Table E-4), whereas Devonian produced water was enriched in barium, which had an average concentration of 1,488 mg/L (see Table E-6).

E.3.1.3. Coalbed Variability

Geochemical analysis showed that the Powder River Basin is predominately characterized by bicarbonate water types with a large intrusion of sodium-type waters across a large range of magnesium and calcium concentrations (Dahm et al., 2011).[1] In contrast, the Raton Basin is typified by sodium-type waters with low calcium and magnesium concentrations. A combination of Powder River and Raton produced water compositional characteristics typifies the San Juan Basin (Dahm et al., 2011). Lastly, Black Warrior Basin produced water is differentiated based upon its sodium bicarbonate- or sodium chloride-type waters (DOE, 2014; Pashin et al., 2014).

Regional variability is observed in average produced water concentrations for various constituents of four CBM basins (Powder River, Raton, San Juan, and Black Warrior; see Table E-3, Table E-5, Table E-7, Table E-9, and Table E-11), but particularly between produced water of the Black Warrior Basin and the others. As the average TDS concentration in Black Warrior Basin produced water (14,319 mg/L) is one to two orders of magnitude higher than that of the other three presented in Table E-3, average concentrations for TDS contributing ions (i.e., calcium, chloride, and sodium) were also higher than in the Powder River, Raton, and San Juan Basins. These high levels follow from the marine depositional environment of the Black Warrior Basin (Horsey, 1981).

Powder River Basin produced water has the lowest average TDS concentration (997 mg/L), which is consistent with Dahm et al. (2011) reporting that nearly a quarter of all the produced water sampled from the Powder River Basin meets the U.S. drinking water secondary standard for TDS (less than 500 mg/L).[2] In addition, the Black Warrior Basin appears to be slightly enriched in barium, compared to the other three CBM basins (see Table E-5). Lastly, the three western CBM basins (Powder River, Raton, and San Juan) are much more alkaline and enriched in bicarbonate than their eastern counterpart (the Black Warrior Basin; see Table E-3).

[1] Water is classified as a "type" if the dominant dissolved ion is greater than 50% of the total. A sodium-type water contains more that 50% of the cation milliequivalents (mEq) as sodium. Similarly, a sodium-bicarbonate water contains 50% of the cation mEq as sodium, and 50% of the anion mEq as bicarbonate (USGS, 2002).

[2] MCL refers to the highest level of a contaminant that is allowed in drinking water. MCLs are enforceable standards. These include primary MCLs for barium, cadmium, chromium, lead, mercury, and selenium. National Secondary Drinking Water Regulations (NSDWRs or secondary standards) are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. Secondary MCLs are recommended for aluminum, chloride, copper, iron, manganese, pH, silver, sulfate, TDS, and others. See http://water.epa.gov/drink/contaminants/index.cfm#Primary for more information.

Average concentrations of benzene, ethylbenzene, and xylenes are higher in San Juan compared to Raton produced water by two orders of magnitude, whereas concentrations of toluene are marginally higher in Raton compared to San Juan produced water (see Table E-9).

E.3.2. Local Variability

Spatial variability of produced water content frequently exists within a single producing formation. For instance, Marcellus Shale barium levels increase along a southwest to northeast transect (Barbot et al., 2013). Additionally, produced water from the northern and southern portions of the San Juan Basin differ in TDS, due to ground water recharge in the northern basin leading to higher chloride concentrations than in the southern portion (Dahm et al., 2011; Van Voast, 2003).

Spatial variability of produced water content also exists at a local level due to the stratigraphy surrounding the producing formation. For example, deep saline aquifers, if present in the over- or underlying strata, may over geologic time encroach upon shales, coals, and sandstones via fluid intrusion processes (Blauch et al., 2009). Evidence of deep brine migration from adjacent strata into shallow aquifers via natural faults and fractures has been noted previously in the Michigan Basin and the Marcellus Shale (Vengosh et al., 2014; Warner et al., 2012; Weaver et al., 1995). By extension, in situ hydraulic connectivity, which is stimulated by design during hydraulic fracturing, may lead to the migration of brine-associated constituents in under- and overlying strata into producing formations, as discussed in Chapter 6.

As hydrocarbon source rocks often form repeating sedimentary sequences, contact between these layers presents opportunities for an exchange of organics and inorganics (Fredrickson and Balkwill, 2006; U.S. EPA, 2004). For instance, diffusion of carbon sources and electron donors occurs at subsurface shale-sandstone interfaces, suggesting a stratigraphic role in the exchange of constituents between formations (Fredrickson and Balkwill, 2006).

E.4. Example Calculation for Roadway Transport

This section provides background information for the roadway transport calculation appearing in Chapter 7.

E.4.1. Estimation of Transport Distance

In a study of wastewater management for the Marcellus Shale, Rahm et al. (2013) used data reported to the Pennsylvania Department of Environmental Protection (PA DEP) to estimate the average distance wastewater was transported. For the period from 2008 to 2010, the distance transported was approximately 100 km, but it was reduced by 30% for 2011. The reduction was attributed to increased treatment infrastructure in Lycoming County, an area of intensive hydraulic fracturing operations in northeastern Pennsylvania. For the part of Pennsylvania within the Susquehanna River Basin, Gilmore et al. (2013) estimated the likely transport distances for drilling waste to landfills (256 km or 159 mi); produced water to disposal wells (388 km or 241 mi); and commercial wastewater treatment plants (CWTPs) (158 km or 98 mi). These distances are longer

than the values from Rahm et al. (2013), in part, because wells in the Susquehanna Basin are further to the east of Ohio disposal wells and some CWTPs.

E.4.2. Estimation of Wastewater Volumes

In an example water balance calculation, Gilmore et al. (2013) used 380,000 gal of flowback as the volume transported to CWTPs, 450,000 gal of flowback transported to injection wells, and 130,000 gal of un-reusable treated water also transported to injection wells for a total estimated wastewater volume of 960,000 gal per well.

E.4.3. Estimation of Roadway Accidents

The U.S. Department of Transportation (DOT) published statistics on roadway accidents (U.S. Department of Transportation, 2012) which indicate that the combined total of combination truck crashes in 2012 was 179,736, or 110 per 100 million vehicle miles (1.77 million km) (see Table E-12). As an indicator of the uncertainty of these data, DOT reported 122,240 large truck crashes from a differing set of databases (see Table E-13), with a rate of 75 per 100 million vehicle miles, which is 68% of the number of combination truck crashes.

Table E-12. Combination truck crashes in 2012 for the 2,469,094 registered combination trucks, which traveled 163,458 million miles (U.S. Department of Transportation, 2012).[a]

Type of crash	Combination trucks involved in crashes	Rates per 100 million vehicle miles traveled by combination trucks
Property damage only	135,000	82.8
Injury	42,000	25.5
Fatal	2,736	1.74
Total	179,736	110

[a] A combination truck is defined as a truck tractor pulling any number of trailers (U.S. Department of Transportation, 2012).

Table E-13. Large truck crashes in 2012 (U.S. Department of Transportation, 2012).[a]

Type of crash	Total crashes	Large trucks with cargo tanks	
		Number	Percentage
Towaway crashes	72,644	4,364	6.0%
Injury	45,794	3,245	7.1%
Fatal	3,802	360	9.5%
Totals	122,240	7,969	6.5%

[a] A large truck is defined as a truck with a gross vehicle weight rating greater than 10,000 pounds (U.S. Department of Transportation, 2012).

E.4.4. Estimation of Material Release Rates in Crashes

Estimates ranging from 5.6% to 36% have been made for the probability of material releases from crashed trucks. Craft (2004) used data from three databases to estimate the probability of spills in fatality accidents at 36%, which may overestimate the probability for all types of accidents (Rozell and Reaven, 2012).[1] The U.S. Department of Transportation (2012) provides estimates of hazardous materials releases from large truck crashes. For all types of hazardous materials carried, 408 of 2,903 crashes, or 14%, were known to have hazardous materials releases. The occurrence of a release was unknown for 18% of the crashes. These crashes were not distinguished by truck type, so they likely overestimated the number of tanker crashes. Harwood et al. (1993) used accident data from three states (California, Illinois, and Michigan) to develop hazardous materials release rate estimates for different types of roadways, accidents, and settings (urban or rural). For roadways in rural settings the probability of release ranged from 8.1% to 9.0%, while in urban settings the probability ranged from 5.6% to 6.9%.

E.4.5. Estimation of Volume Released in Accidents

Based on the estimated volume (960,000 gal (3.63 million L) per well) and disposal distances used by Rahm et al. (2013) and Gilmore et al. (2013), and an assumed 20,000 L (5,300 gal)-containing truck (Gilmore et al., 2013), the total travel distance by trucks ranges from 9,620 miles (14,900 km) to 17,760 miles (28,570 km) per well (see Table E-14).

[1] The three databases were the Trucks Involved in Fatal Accidents developed by the Center for National Truck Statistics at the University of Michigan, the National Automotive Sampling System's General Estimates System (GES) produced by the National Highway Transportation Safety Agency, and the Motor Carrier Management Information System (MCMIS) Crash File produced by the Federal Motor Carrier Safety Administration.

Table E-14. Estimate of total truck-travel miles per well in the Susquehanna River Basin based on the transport analysis performed by Gilmore et al. (2013).

Action	Waste per well (million gal)	Trucks (20 m^3/truck)	Miles traveled per truck	Total miles traveled (per well)	Material release rate bounds			
					5.6%		36%	
					Crashes per 100 million miles			
					75	110	75	110
Gilmore et al. (2013) distance estimates								
Produced water to CWTP	0.38	72	26.9	1,937				
Produced water to disposal well	0.45	85	147	12,495				
CWTP effluent to disposal well	0.13	25	133	3,325				
Total	0.96	182		17,757	3	4	18	27
Rahm et al. (2013) distance estimates								
Transport 100 km	0.96	182	62.1	11,300	2	3	12	17
Transport 70 km	0.96	182	43.5	9,620	1	2	8	12

The Susquehanna River Basin Commission reported 1,928 well pads permitted within the basin (SRBC, 2012). Assuming two wells per pad, the total distance traveled to haul hydraulic fracturing wastewater is 68.4 million miles (110 million km).

Combining these data with the DOT crash data gives an estimated 76 crashes per year using the combination truck crash rate or 52 per year using the DOT large truck crash rate. Based on the various assumptions of travel distances, crash rates, and estimated minimum and maximum material release rates, the number of crashes with releases ranges from 1 to 27 (see Table E-14).

Several limitations are inherent in this analysis, including differing rural road accident rates and highway rates, differing wastewater endpoints, and differing amounts of produced water transport. Further, the estimates present an upper bound on impacts, because not all releases of wastewater would reach or impact drinking water resources.

E.5. References for Appendix E

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Appendix F

Wastewater Treatment and Waste Disposal Supplemental Information

Appendix F. Wastewater Treatment and Waste Disposal Supplemental Information

This appendix provides additional information for context and background to support the discussions of hydraulic fracturing wastewater management and treatment in Chapter 8 of the Hydraulic Fracturing Drinking Water Assessment. Information in this appendix includes: estimates compiled for several states for volumes of wastewater generated in regions where hydraulic fracturing is occurring; an overview of the technologies that can be used to treat hydraulic fracturing wastewater; calculations of estimated treatment process effluent concentrations for example constituents; a description of the different discharge options for centralized waste treatment plants; and the water quality needed for wastewater to be reused for hydraulic fracturing. Discussion is also provided on difficulties that can arise during treatment of hydraulic fracturing wastewaters: the potential impacts of hydraulic fracturing wastewater on biological treatment processes; and an overview of the formation of disinfection byproducts.

F.1. Estimates of Wastewater Production in Regions where Hydraulic Fracturing is Occurring

Table F-1 presents estimated wastewater volumes for several states in areas with hydraulic fracturing activity. These data were compiled from production data available on state databases and were tabulated by year. For California, data were compiled for Kern County, where about 95% of hydraulic fracturing is taking place (CCST, 2015). Production records from Colorado, Utah, and Wyoming include the producing formation for each well reported; data from these states were filtered to select data from formations indicated in the literature as targets for hydraulic fracturing. Data presented for these three states include statewide estimates as well as estimates for selected basins. Data from New Mexico are available from the states in files for three basins as well as for the state; these data were not filtered further.

Results in Table F-1 illustrate some of the challenges associated with obtaining estimates of hydraulic fracturing wastewater volumes, especially using publicly available data. Some of the values likely include reported values from conventional wells (wells that may not be hydraulically fractured, and are typically not subject to modern, high volume hydraulic fracturing). For example, the well counts for California, Colorado, Utah, and Wyoming were in the thousands or tens of thousands at least as early as 2000, several years before the surge of modern hydraulic fracturing began in the mid-2000s. The data used for California were from Kern County but are not specific to hydraulic fracturing activity. Where producing formations are provided, the accuracy of the estimates will depend upon correct selection of hydraulically fractured formations. Thus, both underestimation and overestimation may be possible because of a lack of clear indication of which wells were hydraulically fractured.

Table F-1. Estimated volumes (millions of gallons) 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
California	San Joaquin[a]	Shale, unconsoli-dated sands	Produced water	46,000	48,000	58,000	65,000	71,000	75,000	74,000	-	Data from CA Department of Conservation, Oil and Gas Division.[a] Produced water data compiled for Kern County. Data may also represent contributions from production without hydraulic fracturing.
			Wells	*33,695*	*39,088*	*46,519*	*49,201*	*51,031*	*51,567*	*52,763*	-	
Colorado	All basins with hy-draulically fractured formations	-	Produced water	7,300	11,000	21,000	14,000	12,000	12,000	7,700	-	Data from CO Oil and Gas Conservation Commission.[b] Produced water includes flowback. Data filtered for formations indicated in literature as undergoing hydraulic fracturing and matched to corresponding basins. Example counties selected for presentation as well as estimated state total.
			Wells	*11,264*	*14,934*	*28,282*	*33,929*	*35,999*	*38,371*	*37,618*	-	
	Denver	Sandstone, shale	Produced water	140	160	170	160	160	150	110	-	
			Wells	*1,829*	*1,511*	*1,277*	*1,204*	*1,193*	*1,131*	*1,072*	-	
	Piceance	Sandstone	Produced water	3,500	5,800	9,300	6,900	6,500	6,800	4,300	-	
			Wells	*1,134*	*2,478*	*6,486*	*9,105*	*10,057*	*10,868*	*10,954*	-	

State	Basin	Principal lithologies	Data type	2000	2004	2008	2010	2011	2012	2013	2014	Comments
Colorado, cont.	Raton	Coalbed methane	Produced water	2,400	4,100	8,900	4,300	3,200	2,700	2,100	-	
			Wells	*681*	*1,634*	*2,795*	*2,734*	*2,778*	*2,710*	*2,545*	-	
	San Juan	Coalbed methane	Produced water	1,000	1,100	1,300	2,000	1,200	1,100	650	-	
			Wells	*1,183*	*1,605*	*1,975*	*2,220*	*2,308*	*2,328*	*2,333*	-	
New Mexico	Permian	Shale, sandstone	Produced water	-	-	-	-	-	31,000	31,000	20,000	Data from New Mexico Oil Conservation Division.[c] Data provided by the state by basin and for the entire state. Unclear how much contribution from production without hydraulic fracturing. Produced water includes flowback.
			Wells	-	-	-	-	-	*29,839*	*30,386*	*30,287*	
	Raton	Coalbed methane	Produced water	-	-	-	-	-	510	540	310	
			Wells	-	-	-	-	-	*1,495*	*1,502*	*1,526*	
	San Juan	Coalbed methane	Produced water	-	-	-	-	-	1,700	2,000	1,100	
			Wells	-	-	-	-	-	*22,492*	*22,349*	*22,076*	
	Total	-	Produced water	-	-	-	-	-	33,000	34,000	22,000	
			Wells	-	-	-	-	-	*53,826*	*54,237*	*53,889*	

State	Basin	Principal lithologies	Data type	2000	2004	2008	2010	2011	2012	2013	2014	Comments
Utah	All basins with hydraulically fractured formations	-	Produced water	1,200	1,200	2,300	2,400	2,700	2,900	3,400	2,800	Data from State of Utah Oil and Gas Program.[d] Produced water includes flowback. Data filtered by formation indicated in the literature as hydraulically fractured and matched to basins. Data presented for selected basins as well as for all formations likely to be hydraulically fractured.
			Wells	*3,080*	*4,377*	*7,409*	*8,432*	*9,101*	*10,075*	*10,661*	*10,900*	
	Kaiparowits/ Uinta	Coalbed methane	Produced water	860	740	1,300	1,400	1,800	2,000	2,400	1,900	
			Wells	*1,718*	*2,517*	*3,761*	*4,329*	*4,838*	*5,538*	*6,046*	*6,334*	
	San Juan/ Uinta	Coalbed methane	Produced water	2	49	350	270	240	230	190	120	
			Wells	*62*	*223*	*910*	*933*	*959*	*951*	*867*	*870*	
	Uinta	Shale/sandstone	Produced water	350	420	560	680	700	640	830	790	
			Wells	*1,067*	*1,396*	*2,282*	*2,745*	*2,888*	*3,115*	*3,257*	*3,223*	
Wyoming	All basins with hydraulically fractured formations	-	Produced water	1,300	1,400	1,300	1,500	1,600	1,700	1,600	1,800	Data from Wyoming Oil and Gas Conservation Commission.[e] Produced water may include flowback. Data filtered by formation indicated in the literature as hydraulically fractured and matched to basins. Data presented for selected basins as well as for all formations likely to be hydraulically fractured.

State	Basin	Principal lithologies	Data type	2000	2004	2008	2010	2011	2012	2013	2014	Comments
Wyoming, cont.			*Wells*	*3,470*	*3,378*	*3,585*	*3,620*	*3,728*	*3,843*	*4,030*	*4,213*	
	Big Horn	Sandstone	Produced water	380	350	350	380	430	440	420	440	
			Wells	*365*	*359*	*387*	*397*	*412*	*414*	*407*	*403*	
	Denver	Sandstone	Produced water	54	44	49	59	76	90	97	170	
			Wells	*142*	*118*	*124*	*140*	*167*	*204*	*230*	*278*	
	Green River	Sandstone/ shale	Produced water	0	1	2	8	5	5	9	15	
			Wells	*44*	*44*	*60*	*67*	*67*	*59*	*64*	*67*	
	Powder River	Coalbed methane	Produced water	690	630	620	660	700	840	970	1,100	
			Wells	*1,953*	*1,900*	*2,001*	*2,028*	*2,119*	*2,207*	*2,352*	*2,565*	
	Wind River/ Powder River	Sandstone/ shale	Produced water	130	330	330	400	420	290	110	41	
			Wells	*966*	*957*	*1,013*	*988*	*963*	*959*	*977*	*900*	

[a] California Department of Conservation, Oil and Gas Division. Oil & Gas – Online Data. Monthly Production and Injection Databases: ftp://ftp.consrv.ca.gov/pub/oil/new_database_format/.

[b] Colorado Oil and Gas Conservation Commission. Data: Downloads: Production Data: http://cogcc.state.co.us/data2.html#/downloads.

[c] New Mexico Oil Conservation Division. Production Data. Production Summaries: All Wells Data: http://gotech.nmt.edu/gotech/Petroleum_Data/allwells.aspx.

[d] Utah Department of Natural Resources. Division of Oil, Gas, and Mining. Data Research Center. Database Download Files: http://oilgas.ogm.utah.gov/Data_Center/DataCenter.cfm#production.

[e] Wyoming Oil and Gas Conservation Commission. Production files by county and year: http://wogcc.state.wy.us/productioncountyyear.cfm?Oops=#oops#&RequestTimeOut=6500.

F.2. Overview of Treatment Processes for Treating Hydraulic Fracturing Wastewater

Treatment technologies discussed in this appendix are classified as basic or advanced. Basic treatment technologies are ineffective for reducing total dissolved solids (TDS) and are typically not labor intensive. Advanced treatment technologies can remove TDS and/or are complex in nature (e.g., energy- and labor-intensive).

F.2.1. Basic Treatment

Basic treatment technologies include physical separation, coagulation/oxidation, electrocoagulation, sedimentation, and disinfection. These technologies are effective at removing total suspended solids (TSS), oil and grease, scale-forming compounds, and metals, and they can minimize microbial activity. Basic treatment is typically incorporated in a permanent treatment facility (i.e., fixed location) but can also be part of a mobile unit for onsite treatment applications.

F.2.1.1. Physical Separation

The most basic treatment need for oil and gas wastewaters, including those from hydraulic fracturing operations, is separation to remove suspended solids, and oil and grease. The separation method largely depends on the type of resource(s) targeted by the hydraulic fracturing operation. Down-hole separation techniques, including mechanical blocking devices and water shut-off chemicals to prevent or minimize water flow to the well, may be used during production in shale plays containing greater amounts of liquid hydrocarbons. To treat water at the surface, separation technologies such as hydrocyclones, dissolved air or induced gas flotation systems, media (sand) filtration, and biological aerated filters can remove suspended solids and some organics from hydraulic fracturing wastewater.

Media filtration can also remove hardness and some metals if chemical precipitation (i.e., coagulation, lime softening) is also employed (Boschee, 2014). An example of a centralized waste treatment facility (CWT) that uses chemical precipitation and media filtration to treat hydraulic fracturing waste is the Water Tower Square Gas Well Wastewater Processing Facility in Pennsylvania (see Table 8-7). One or more of these technologies is typically used prior to advanced treatment such as reverse osmosis (RO) because advanced treatment processes foul, scale, or otherwise do not operate effectively in the presence of TSS, certain organics, and/or some metals and metalloid compounds (Boschee, 2014; Drewes et al., 2009). The biggest challenge associated with use of these separation technologies is solids disposal from the resulting sludge (Igunnu and Chen, 2014).

F.2.1.2. Coagulation/Oxidation

Coagulation is the process of agglomerating small, unsettleable particles into larger particles to promote settling. Chemical coagulants such as alum, iron chloride, and polymers can be used to precipitate TSS, some dissolved solids (except monovalent ions such as sodium and chloride), and metals from hydraulic fracturing wastewater. Adjusting the pH using chemicals such as lime or caustic soda can increase the potential for some constituents, including dissolved metals, to form precipitates. Chemical precipitation is often used in industrial wastewater treatment as a

pretreatment step to decrease the pollutant loading on subsequent advanced treatment technologies; this strategy can save time, money, energy consumption and the lifetime of the infrastructure.

Processes using advanced oxidation and precipitation have been applied to hydraulic fracturing wastewaters in on-site and mobile systems. Hydroxyl radicals generated by cavitation processes and the addition of ozone can degrade organic compounds and inactivate micro-organisms. The process can also aid in the precipitation of elements, which cause hardness and scaling in the treated water (e.g. calcium, magnesium). The process can also reduce sulfate and carbonate concentrations in the treated water. This type of treatment can be very effective for on-site reuse of wastewater (Ely et al., 2011).

The produced solid residuals from coagulation/oxidation processes typically require further treatment, such as de-watering (Duraisamy et al., 2013; Hammer and VanBriesen, 2012).

F.2.1.3. Electrocoagulation

Electrocoagulation (EC) (Figure F-1) combines the principles of coagulation and electrochemistry into one process (Gomes et al., 2009). An electrical current added to the wastewater produces coagulants that then neutralize the charged particles, causing them to destabilize, precipitate, and settle. EC may be used in place of, or in addition to, chemical coagulation. EC can be effective for removal of organics, TSS, and metals, but it is less effective for removing TDS and sulfate. Although it is still considered an emerging technology for unconventional oil and gas wastewater treatment, EC has been used in mobile treatment systems to treat hydraulic fracturing wastewaters (Halliburton, 2014; Igunnu and Chen, 2014). Limitations with this technology are the potential for scaling, corrosion, and bacterial growth (Gomes et al., 2009).

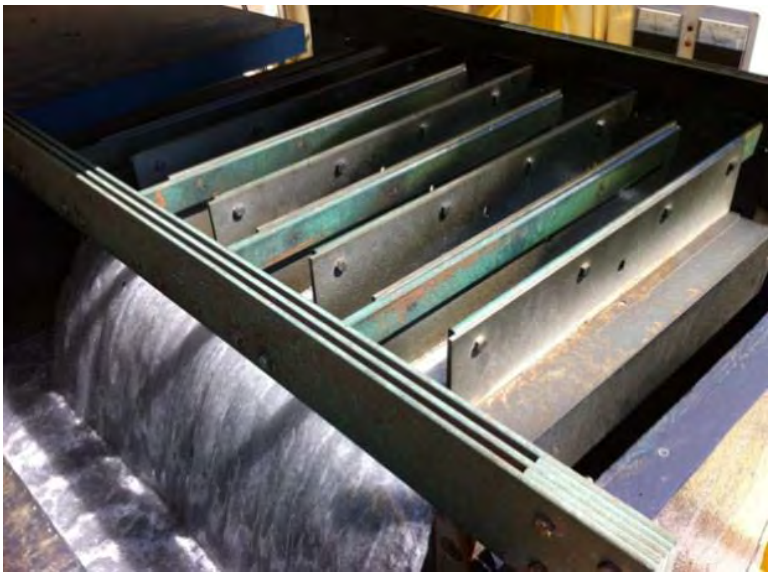

Figure F-1. Electrocoagulation unit.

Source: Dunkel (2013).

F.2.1.4. Sedimentation

Treatment plants may include sedimentation tanks, clarifiers, or some other form of settling basin to allow larger particles to settle out of the water where they can eventually be collected, dewatered, and disposed of. These types of tanks/basins all serve the same purpose – to reduce the amount of solids going to subsequent processes (i.e., overload the media filters).

F.2.1.5. Disinfection

Some hydraulic fracturing applications may require disinfection to kill bacteria after treatment and prior to reuse. Chlorine is a common disinfectant. Chlorine dioxide, ozone, or ultraviolet light can also be used. This is an important step for reused water because bacteria can cause problems for further hydraulic fracturing operations by multiplying rapidly and causing build-up in the well bore, which decreases gas extraction efficiency.

F.2.2. Advanced Treatment

Advanced treatment technologies consist of membranes (reverse osmosis (RO), nanofiltration, ultrafiltration, microfiltration, electrodialysis, forward osmosis, and membrane distillation), thermal distillation technologies, crystallizers, ion exchange, and adsorption. These technologies are effective for removing TDS and/or targeted compounds. They typically require pretreatment to remove solids and other constituents that may damage or otherwise impede the technology from operating as designed. Advanced treatment technologies can be energy intensive and are typically employed when a purified water effluent is necessary for direct discharge, indirect discharge, or reuse. In some instances, these water treatment technologies can make use of methane generated by the gas well as an energy source. Some advanced treatment technologies can be made mobile for on-site treatment.

F.2.2.1. Membranes

Pressure-driven membrane processes including microfiltration, ultrafiltration, nanofiltration, and RO (Figure F-2) are being used in some settings to treat oil and gas wastewater. These processes use hydraulic pressure to overcome the osmotic pressure of the influent waste stream, forcing clean water through the membrane (Drewes et al., 2009). Microfiltration and ultrafiltration processes do not reduce TDS but can remove TSS and some metals and organics (Drewes et al., 2009). RO and nanofiltration are capable of removing TDS, including anions and radionuclides. RO, however, may be limited to treating TDS levels of approximately 40,000 mg/L TDS (Shaffer et al., 2013; Younos and Tulou, 2005).

Figure F-2. Photograph of reverse osmosis system.

Source: Thinkstock.

F.2.2.2. Electrodialysis

Electrodialysis relies on positively and negatively charged particles and coated membranes to separate contaminants from the water (Figure F-3). Electrodialysis has been considered for use by the shale gas industry, but it is not currently widely utilized (ALL Consulting, 2013). TDS concentrations above 15,000 mg/L are difficult to treat by electrodialysis (ALL Consulting, 2013), and oil and divalent cations (e.g. Ca, Fe, Mg) can foul the membranes (Hayes and Severin, 2012b; Guolin et al., 2008).

Figure F-3. Picture of mobile electrodialysis units in Wyoming.

Source: DOE (2006). Permission: ALL Consulting.

F.2.2.3. Forward Osmosis/Membrane Distillation

Forward osmosis, an emerging technology for treating hydraulic fracturing wastewater, uses an osmotic pressure gradient across a membrane to draw the contaminants from a low osmotic solution (the feed water) to a high osmotic solution (Drewes et al., 2009). The selection of the constituents for the draw solution is very important as the constituents should be more easily removed from solution than the compounds (e.g. salts) in the feed. Alternatively, draw solutions can contain components that are more easily reused or recycled. Another emerging technology, membrane distillation, relies on a thermal gradient across a membrane surface to volatilize pure water and capture it in the distillate (Drewes et al., 2009).

F.2.2.4. Thermal Distillation

Thermal distillation technologies, such as mechanical vapor recompression (MVR) (Figure F-4) and dewvaporation, use liquid-vapor separation by applying heat to the waste stream, vaporizing the water to separate out impurities, and condensing the vapor into distilled water (Drewes et al., 2009; LEau LLC, 2008; Hamieh and Beckman, 2006). MVR and dewvaporation can treat high-TDS waters and have been proven in the field as effective for treating oil and gas wastewater (Hayes and Severin, 2012b; Drewes et al., 2009). Like RO, these processes are energy intensive and are used when the objective is very clean water (i.e., TDS less than 500 mg/L) for direct/indirect discharge or if clean water is needed for reuse. As with membrane processes, scaling is an issue with these technologies, and scale inhibitors may be needed for them to operate effectively (Igunnu and Chen, 2014).

Figure F-4. Picture of a mechanical vapor recompression unit near Decatur, Texas.

Source: Drewes et al. (2009). Permission provided.

CWTs such as the Judsonia Central Water Treatment Facility in Arkansas, and the Casella-Altela Regional Environmental Services and Clarion Altela Environmental Services, both in Pennsylvania, have NPDES permits and use MVR or thermal distillation for TDS removal. Figure F-5 shows a diagram of the treatment train at another facility, the Maggie Spain facility in Texas, which uses MVR in its treatment of Barnett Shale wastewater (Hayes and Severin, 2012a).

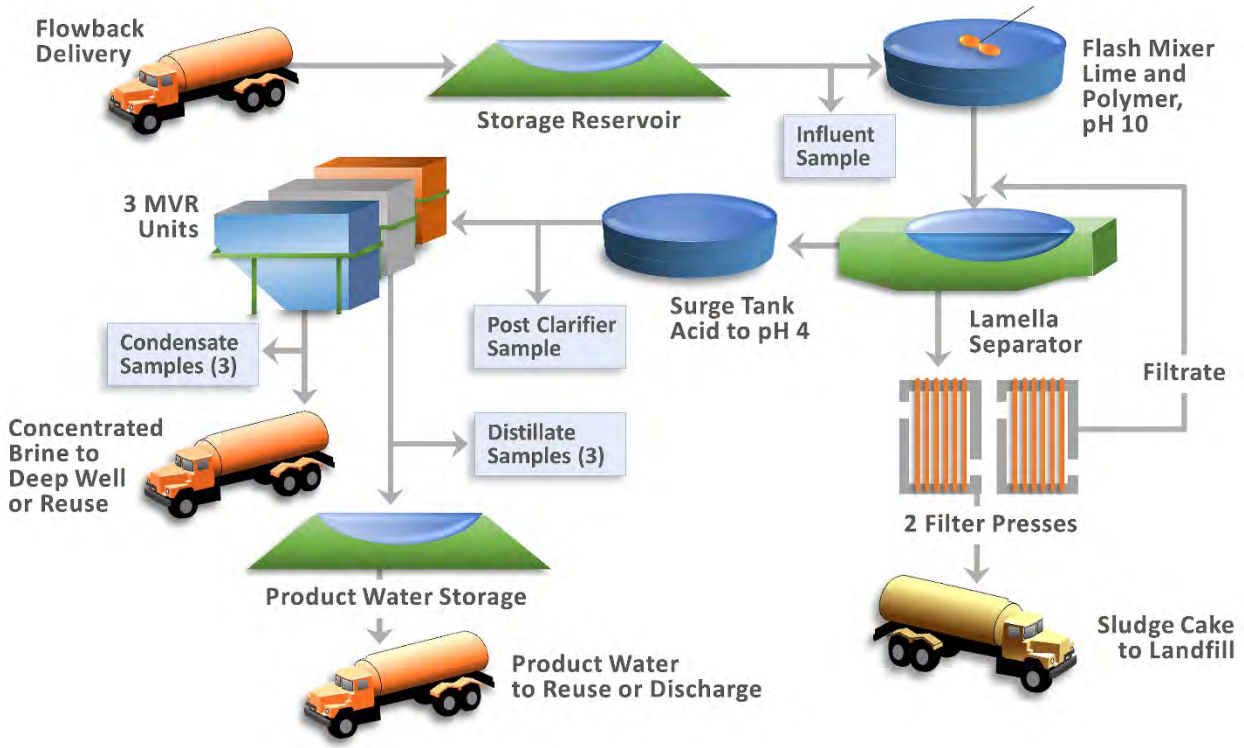

Figure F-5. Mechanical vapor recompression process design – Maggie Spain Facility.

Adapted from: Hayes and Severin (2012a).

Crystallizers can be employed at CWTs to treat high-TDS waters or to further concentrate the waste stream from a distillation process, reducing residual waste disposal volumes. The crystallized salt can be landfilled, deep-well injected, or used to produce pure salt products that may be salable (Ertel et al., 2013).

Another thermal method, freeze-thaw evaporation, involves spraying wastewater onto a freezing pad, allowing ice crystals to form, and the brine mixture that remains in solution to drain from the ice (Drewes et al., 2009). In warmer weather, the ice thaws and the purified water is collected. This technology cannot treat waters with high methanol concentrations and is only suitable for areas where the temperature is below freezing in the winter months (Igunnu and Chen, 2014). In addition, freeze-thaw evaporation can only reduce TDS concentrations to approximately 1,000 mg/L, which is higher than the 500 mg/L TDS surface water discharge limit required by most permits (Igunnu and Chen, 2014).

F.2.2.5. Ion Exchange and Adsorption

Ion exchange (Figure F-6) is the process of exchanging ions on a media referred to as resin for unwanted ions in the water. Ion exchange is used to treat for target ions that may be difficult to remove by other treatment technologies or that may interfere with the effectiveness of advanced treatment processes.

Figure F-6. Picture of a compressed bed ion exchange unit.

Source: Drewes et al. (2009). Permission provided.

Adsorption is the process of adsorbing contaminants onto a charged granular media surface. Adsorption technologies can effectively remove organics, heavy metals, and some anions (Igunnu and Chen, 2014). With ion exchange and adsorption processes, the type of resin or adsorptive media used (e.g., activated carbon, organoclay, zeolites) dictates the specific contaminants that will be removed from the water (Drewes et al., 2009; Fakhru'l-Razi et al., 2009).

Because they can be easily overloaded by contaminants, ion exchange and adsorption treatment processes are generally used as a polishing step following other treatment processes or as a unit process in a treatment train rather than as stand-alone treatment (Drewes et al., 2009). Stand-alone units require more frequent regeneration and/or replacement of the spent media making these technologies more costly to operate (Igunnu and Chen, 2014). Figure F-7 shows a schematic of the Pinedale Anticline Water Reclamation Facility located in Wyoming, which uses an ion exchange unit with boron-selective resin as a polishing step to treat hydraulic fracturing wastewater specifically for boron (Boschee, 2012).

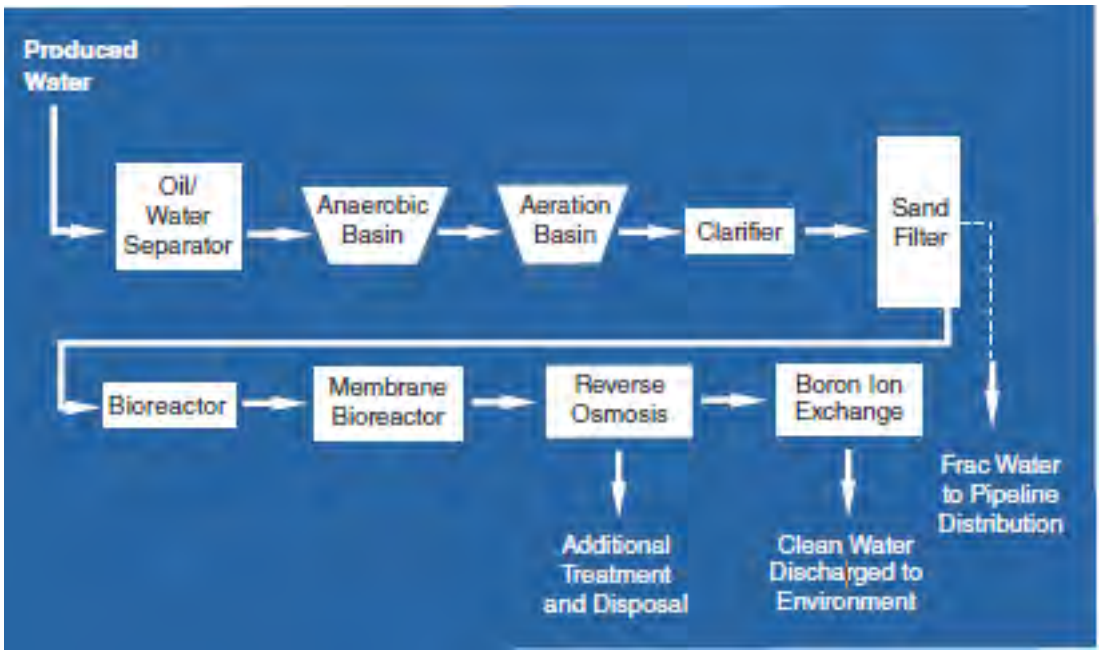

Figure F-7. Discharge water process used in the Pinedale Anticline field.

Source: Boschee (2012).

F.3. Treatment Technology Removal Capabilities

Table F-2 provides removal efficiencies for common hydraulic fracturing wastewater constituents by treatment technology. With the exception of TSS and TDS, the studies cited demonstrate removal for a subset of constituents in a category (e.g., Gomes et al., 2009) reported that electrodialysis was an effective treatment for oil and grease, not all organics). The removal efficiencies include ranges of 1 to 33% (denoted by +), 34% to 66% (denoted by ++), and greater than 66% removal (denoted by +++). Cells denoted with "--" indicate that the treatment technology is not suitable for removal of that constituent or group of constituents. If a particular treatment technology only lists removal efficiencies for TDS, it can be assumed that in some cases, cations and anions would also be removed by that technology; therefore, where specific results were not provided in literature, cells denoted with "Assumed" refer to cations and anions that comprise TDS.

Table F-2. Removal efficiency of different hydraulic fracturing wastewater constituents using various wastewater treatment technologies.[a]

Treatment Technology	Hydraulic Fracturing Wastewater Constituents					
	TSS	TDS	Anions	Metals	Radio-nuclides	Organics
Hydrocyclones	+++ (Duraisamy et al., 2013)	--	--	--	--	++ (Duraisamy et al., 2013)
Evaporation (freeze-thaw evaporation)	+++ (Igunnu and Chen, 2014; Drewes et al., 2009)	+++ (Igunnu and Chen, 2014; Drewes et al., 2009; Arthur et al., 2005)	Assumed	+++ (Igunnu and Chen, 2014; Drewes et al., 2009; Arthur et al., 2005)	--	+++ (Igunnu and Chen, 2014; Duraisamy et al., 2013; Drewes et al., 2009)
Filtration (granular media)	+++ (Barrett, 2010)	--	--	+++[b] (Duraisamy et al., 2013)	--	+++ (Shafer, 2011; Drewes et al., 2009)
Chemical precipitation	+++ (Fakhru'l-Razi et al., 2009)	--	--	+++ (Fakhru'l-Razi et al., 2009; AWWA, 1999)	+++[c] (Zhang et al., 2014)	+++ (Fakhru'l-Razi et al., 2009)
Sedimentation (clarifier)	++ (NMSU DACC WUTAP, 2007)	--	--	--	--	--
Dissolved air flotation	+++ (Shammas, 2010)	--	--	--	--	++/+++ (Duraisamy et al., 2013; Fakhru'l-Razi et al., 2009)
Electro-coagulation	+++ (Igunnu and Chen, 2014; Bukhari, 2008)	--	--	+ (Igunnu and Chen, 2014)	--	+++ (Igunnu and Chen, 2014; Duraisamy et al., 2013; Fakhru'l-Razi et al., 2009)
Advanced oxidation and precipitation	--	+ (Abrams, 2013)	--	+/+++ (Abrams, 2013)	--	+++[d] (Duraisamy et al., 2013) (Fakhru'l-Razi et al., 2009)

Treatment Technology	Hydraulic Fracturing Wastewater Constituents					
	TSS	TDS	Anions	Metals	Radio-nuclides	Organics
Reverse osmosis	--	++/+++[e] (Alzahrani et al., 2013; Drewes et al., 2009)	+++ (Alzahrani et al., 2013) (Arthur et al., 2005)	++/+++[f] (Alzahrani et al., 2013) (Drewes et al., 2009; AWWA, 1999)	+++ (Drewes et al., 2009)	+/++/+++[g] (Drewes et al., 2009; Munter, 2000)
Membrane filtration (UF/MF)	+++ (Arthur et al., 2005)	--	--	+++ (Fakhru'l-Razi et al., 2009)	--	++/+++ (Duraisamy et al., 2013; Fakhru'l-Razi et al., 2009; Hayes and Arthur, 2004; AWWA, 1999)[h]
Forward osmosis	--	+++ (Drewes et al., 2009)	Assumed	Assumed	--	--
Distillation, including thermal distillation (e.g., mechanical vapor recompression (MVR))		+++[i] (Hayes et al., 2014; Bruff and Jikich, 2011; Drewes et al., 2009)	+++ (Bruff and Jikich, 2011; Drewes et al., 2009)	+++ (Hayes et al., 2014; Bruff and Jikich, 2011; Drewes et al., 2009)	+++ (Bruff and Jikich, 2011; Drewes et al., 2009)	+/++/+++ (Hayes et al., 2014; Duraisamy et al., 2013; Drewes et al., 2009; Fakhru'l-Razi et al., 2009)
Ion exchange	--	--	+++ (Drewes et al., 2009)	+++ (Drewes et al., 2009; Arthur et al., 2005)	+++ (Drewes et al., 2009)	+/++/+++ (Fakhru'l-Razi et al., 2009; Munter, 2000)[j]
Crystallization	--	+++ (ER, 2014)	Assumed	Assumed	--	--
Electrodialysis	--	+++[k] (Drewes et al., 2009; Gomes et al., 2009; Arthur et al., 2005)	++/+++ (Banasiak and Schäfer, 2009)	+/++/+++ (Banasiak and Schäfer, 2009)	--	+++ (Gomes et al., 2009)
Capacitive deionization (emerging technology)	--	+++[l] (Drewes et al., 2009)	--	--	--	--

Treatment Technology	Hydraulic Fracturing Wastewater Constituents					
	TSS	TDS	Anions	Metals	Radio-nuclides	Organics
Adsorption[m]	--	--	+/++/+++[n] (Habuda-Stanic et al., 2014)	+++ (Igunnu and Chen, 2014; Drewes et al., 2009)	--	+/++/+++ (Arthur et al., 2005; Hayes and Arthur, 2004; Munter, 2000)
Biological treatment	+++ (Igunnu and Chen, 2014; Drewes et al., 2009)	--	--	--	--	+/++/+++ (Igunnu and Chen, 2014; Drewes et al., 2009; Fakhru'l-Razi et al., 2009)
Constructed wetland/reed beds	++/+++ (Manios et al., 2003)	+ (Arthur et al., 2005)	--	++/+++ (Fakhru'l-Razi et al., 2009)	--	+/ +++ (Fakhru'l-Razi et al., 2009; Arthur et al., 2005)

[a] To the extent possible, removal efficiencies are based on an individual treatment technology that does not assume extensive pretreatment or combined treatment processes. However, it should be noted that some processes cannot effectively operate without pretreatment (e.g., RO, media filtration, sedimentation).

[b] Pretreatment (pH adjustment, aeration, solids separation) required.

[c] Radium co-precipitation with barium sulfate.

[d] The Fenton process.

[e] Typically requires pretreatment. Not a viable technology if TDS influent >50,000 mg/L.

[f] Iron and manganese oxides will foul the membranes.

[g] Some organics will foul the membranes (e.g., organic acids).

[h] Ultrafiltration membrane was modified with nanoparticles.

[i] Can typically handle high TDS concentrations.

[j] Resin consisted of modified zeolites that targeted removal of BTEX.

[k] Influent TDS for this technology should be <8,000 mg/L.

[l] Specific technology was an electronic water purifier which is a hybrid of capacitive deionization. Influent TDS for this technology should be <3,000 mg/L.

[m] Typically polishing step, otherwise can overload bed quickly with organics.

[n] Removal efficiency is dependent on the type of adsorbent used and the water quality characteristics (e.g., pH).

Given the variety of properties among classes of organic constituents, different treatment processes may be required depending upon the types of organic compounds needing removal. Table F-3 lists treatment processes and the classes of organic compounds they can treat.

Table F-3. Treatment processes for hydraulic fracturing wastewater organic constituents.

Treatment processes	Organic compounds removed	References
Adsorption with activated carbon	Soluble organic compounds	Fakhru'l-Razi et al. (2009)
Adsorption with organoclay media	Insoluble organic compounds	Fakhru'l-Razi et al. (2009)
Aeration	Volatile organic compounds	Tchobanoglous et al. (2013)
Dissolved air flotation	Volatile organic compounds, dispersed oil	Drewes et al. (2009)
Freeze/thaw evaporation[a]	TPH, volatile organic compounds, semi-volatile organic compounds	Duraisamy et al. (2013); Drewes et al. (2009)
Ion exchange (with modified zeolites)	BTEX, chemical oxygen demand, biochemical oxygen demand	Hayes et al. (2014); Duraisamy et al. (2013); Drewes et al. (2009); Fakhru'l-Razi et al. (2009); Munter (2000)
Distillation	BTEX, polycyclic aromatic hydrocarbons (PAHs)	Hayes et al. (2014); Duraisamy et al. (2013); Drewes et al. (2009); Fakhru'l-Razi et al. (2009).
Chemical precipitation	Oil & grease	Drewes et al. (2009); Fakhru'l-Razi et al. (2009)
Chemical Oxidation	Oil & grease	Drewes et al. (2009); Fakhru'l-Razi et al. (2009)
Media filtration (walnut shell media or sand)	Oil & grease	Drewes et al. (2009); Fakhru'l-Razi et al. (2009)
Microfiltration	Oil & grease	Drewes et al. (2009); Fakhru'l-Razi et al. (2009)
Ultrafiltration	Oil & grease, BTEX	Drewes et al. (2009); Fakhru'l-Razi et al. (2009)
Reverse osmosis[b]	Dissolved organics	Drewes et al. (2009); U.S. EPA (2005)
Electrocoagulation	Chemical oxygen demand, Biochemical oxygen demand	Fakhru'l-Razi et al. (2009)
Biologically aerated filters	Oil & grease, TPH, BTEX	Fakhru'l-Razi et al. (2009)
Reed bed technologies	Oil & grease, TPH, BTEX	Fakhru'l-Razi et al. (2009)
Hydrocyclone separators	Dispersed oil	Drewes et al. (2009)

[a] Technology cannot be used if the methanol concentration in the hydraulic fracturing wastewater exceeds 5%.

[b] RO will remove specific classes of organic compounds with removal efficiencies dependent on the compound's structure and the physical and chemical properties of the hydraulically fractured wastewater. Organoacids will foul membranes.

Table F-4 presents estimated effluent concentrations that could be produced by a variety of unit treatment processes for several example constituents and for various influent concentrations. This

analysis uses treatment process removal efficiencies from literature used to develop Table F-2 and average wastewater concentrations of several constituents presented in Chapter 7 and Appendix E. These estimates were done to illustrate the combined effects of influent wastewater composition and treatment process choice on achievable effluent concentrations. The removal efficiencies represent a variety of studies, primarily at bench and pilot scale, and done with either conventional or hydraulic fracturing wastewater. Removal efficiency for a given treatment process can vary due to a number of factors, and constituent removal may be different in a full-scale facility that uses several processes. Thus, the calculations shown in Table F-4 are intended to be rough approximations for illustrative purposes.

Table F-4. Estimated effluent concentrations for example constituents based on treatment process removal efficiencies.

Shale/ Sandstone Play	Contaminant	MCL	Avg. Influent Conc.	Units	Freeze-Thaw Evaporation	Media Filtration	Chemical Precipitation			Flotation (DAF)	Electro-coagulation	Advanced Oxidation and precipitation	Reverse osmosis	Membrane Filtration (UF/MF)	Distillation			Ion exchange			Electrodialysis	Adsorption			Biological Treatment (biodisks, BAFs)			Constructed Wetland
Bakken	Barium	**2**	10	mg/L		1						0.44	0.8		0.1	-	0.3	ND	-	0.7								2.2
Barnett	Barium	**2**	3.6	mg/L		0.4						0.16	0.29		0.036	-	0.11	ND	-	0.3								0.8
Fayetteville	Barium	**2**	4	mg/L		0.4						0.18	0.32		0.04	-	0.12	ND	-	0.3								0.9
Marcellus	Barium	**2**	2200	mg/L		220						98	180		22	-	67	ND	-	160								490
Cotton Valley	Barium	**2**	160	mg/L		16						7	13		1.6	-	4.8	ND	-	11								35
Mesaverde	Barium	**2**	140	mg/L		14						6.1	11		1.4	-	4.2	ND	-	9.7								31
Marcellus	Cadmium	**5**	25	µg/L	2.5	2.5							13										5					15
Bakken	Strontium	--	760	mg/L		76									7.6	-	23	53										
Barnett	Strontium	--	530	mg/L		53									5.3	-	16	37										
Fayetteville	Strontium	--	27	mg/L		2.7									0.27	-	0.81	1.9										
Marcellus	Strontium	--	1700	mg/L		170									17	-	51	120										
Cotton Valley	Strontium	--	2300	mg/L		230									23	-	69	160										
Devonian Sandstone	Strontium	--	3900	mg/L		390									39	-	120	270										
Marcellus	Radium 226	--	620	pCi/L			32	-	440				6.2		6.2	-	19	44										

Shale/ Sandstone Play	Contaminant	MCL	Avg. Influent Conc.	Units	Freeze-Thaw Evaporation	Media Filtration	Chemical Precipitation			Flotation (DAF)	Electro-coagulation	Advanced Oxidation and precipitation	Reverse osmosis	Membrane Filtration (UF/MF)	Distillation			Ion exchange			Electrodialysis	Adsorption			Biological Treatment (biodisks, BAFs)			Constructed Wetland
Devonian Sandstone	Radium 226	--	2400	pCi/L			120	-	1700				24		24	-	71	170										
Marcellus	Radium 228	--	120	pCi/L			6.2	-	85				1.2		1.2	-	3.6	8.4										
Marcellus	Total Radium	**5**	2500	pCi/L			130	-	1800				25		25	-	76	180										
Barnett	TOC	--	9.8	mg/L										0.2								0.98	-	2.9	2.1	-	4	1
Marcellus	TOC	--	160	mg/L										3.2								16	-	48	35	-	58	16
Cotton Valley	TOC	--	200	mg/L										4								20	-	59	44	-	71	20
Barnett	BOD	--	580	mg/L							58							290	-	440					29	-	87	47
Marcellus	BOD	--	40	mg/L							4							20	-	30					2	-	6	3.2
Barnett	O&G	--	160	mg/L		16								16							8	1.6			43			9.8
Marcellus	O&G	--	74	mg/L		7.4								7.4							3.7	0.74			19			4.4
Barnett	Benzene	**5**	680	µg/L	68									310		6.8						110						ND
Marcellus	Benzene	**5**	360	µg/L	36									170		3.6						58						ND
Barnett	Toluene	**1,000**	760	µg/L	76									350								84						ND
Marcellus	Toluene	**1,000**	1100	µg/L	110									510								120						ND
Barnett	Ethylbenzene	**700**	29	µg/L	2.9					17												3.2						ND
Marcellus	Ethylbenzene	**700**	150	µg/L	15					90												17						ND
Barnett	Xylenes	**10,000**	360	µg/L	36									170								14						ND
Marcellus	Xylenes	**10,000**	1300	µg/L	130									600								52						ND
Barnett	BTEX	--	1800	µg/L	180							7.3				91		270	-	550		3.7	-	91				

Shale/ Sandstone Play	Contaminant	MCL	Avg. Influent Conc.	Units	Freeze-Thaw Evaporation	Media Filtration	Chemical Precipitation			Flotation (DAF)	Electro-coagulation	Advanced Oxidation and precipitation	Reverse osmosis	Membrane Filtration (UF/MF)	Distillation			Ion exchange			Electrodialysis	Adsorption			Biological Treatment (biodisks, BAFs)			Constructed Wetland
Marcellus	BTEX	--	2900	µg/L	290							12				150		440	-	870		5.8	-	150				
Barnett	Naphthalene	--	240	µg/L								0.95																
Marcellus	Naphthalene	--	360	µg/L								1.4																
Barnett	1,2,4-Trimethyl-benzene	--	170	µg/L								0.69																
Marcellus	1,2,4-Trimethyl-benzene	--	430	µg/L								1.7																
Barnett	1,2,4-Trimethyl-benzene	--	59	µg/L								0.24																
Marcellus	1,2,4-Trimethyl-benzene	--	310	µg/L								1.2																

ND = Non-detect

F.4. Centralized Waste Treatment Facilities and Waste Management Options

CWTs are designed to treat for site-specific wastewater constituents so that the effluent meets the requirements of the designated disposal option(s) (i.e., reuse, direct/indirect discharge). The most basic treatment processes that a CWT might use include (Easton, 2014; Duhon, 2012):

- Physical treatment technologies such as dissolved air or gas flotation technologies, media filtration, hydrocyclones, and clarification;
- Chemical treatment technologies such as chemical precipitation and chemical oxidation; and
- Biological treatment technologies such as biological aerated filter systems and reed beds.

While these technologies are effective at removing oil and grease, suspended solids, scale-forming compounds, and some heavy metals, if TDS should be reduced as required by the intended disposal option, advanced processes such as RO, thermal distillation, or evaporation are necessary.

F.4.1. Discharge Options for CWTs

Direct discharge CWTs are allowed to discharge treated wastewater directly to surface waters under the NPDES permit program. Discharge limitations may be based on water quality standards in the NPDES and technology-based effluent limitation guidelines under 40 CFR Part 437. In addition, permitting authorities have permitted facilities for discharge under 40 CFR 435, Subpart E. Judsonia Central Water Treatment Facility in Sunnydale, Arkansas is permitted to directly discharge treated effluent from produced and flowback waters from the Fayetteville Shale play to Byrd pond located on the property. Pinedale Anticline Field Wastewater Treatment Facility in Wyoming, WY, originally designed to treat produced water from tight gas plays in the Pinedale Anticline Field to levels suitable for reuse, was upgraded to include RO treatment for discharge to a local river. CWTs with NPDES discharge permits may also opt to treat oil and gas wastewater for reuse. Some facilities have the ability to treat wastewater to different qualities (e.g., with or without TDS removal), which they might do to target various reuse water quality criteria. Both the Judsonia facility and Pinedale facility discussed above have the ability to employ either TDS- or non-TDS-removal treatment depending on the customers' needs.

Indirect discharge CWTs may treat hydraulic fracturing wastewater and then discharge the treated wastewater effluent to a POTW. Discharge to the POTW is controlled by an Industrial User mechanism, which incorporates pretreatment standards established in 40 CFR Part 437. Two facilities located in Pennsylvania (Eureka Resources) and Ohio (Patriot Water Treatment) include indirect discharge as an option in wastewater treatment. The Eureka-Williamsport facility accepts wastewater (primarily from the Marcellus Shale play) and either treats it for reuse or discharges it to the local POTW. The Patriot facility offers services to hydraulic fracturing operators in the Marcellus and Utica Shale plays for removal of solids and metals using chemical treatment. As of March 2015, however, the Patriot facility is limited by the Ohio Environmental Protection Agency in accepting only "low salinity" (<50,000 mg/L TDS) produced water and may only discharge 100,000 gallons (380,000 L) per day to the Warren Ohio POTW.

Zero-discharge CWTs do not discharge treated wastewater; instead, the wastewater is treated and reused in subsequent hydraulic fracturing operations. WVWRI (2012) state that this practice reduces potential effects on surface drinking water sources by reducing both direct and indirect discharges. Zero-discharge facilities may offer different levels of treatment including minimal treatment (for example, filtration), low-level treatment (chemical precipitation), and/or advanced treatment (evaporation, crystallization). Reserved Environmental Services (RES) Mt. Pleasant, Pennsylvania, is a zero liquid discharge facility permitted by PA DEP to treat wastewater from the Marcellus Shale play for reuse. Residual solids are dewatered and sent to a landfill. Treated wastewater effluent is stored, monitored, and chlorinated for reuse (ONG Services, 2015).

F.5. Water Quality for Reuse

As of 2015, there is no consensus on the water quality requirements for reuse of wastewater for hydraulic fracturing, and operator opinions vary on the minimum standards for the water quality needed for fracturing fluids (Vidic et al., 2013; Acharya et al., 2011). Table F-5 provides a list of constituents and the recommended or observed target concentrations for reuse applications. The wide concentration ranges for many constituents (e.g., TDS ranges from 500 to 70,000 mg/L), suggest that water quality requirements for reuse are dictated by operation-specific requirements, including operator preference and selection of fracturing fluid chemistry.

Table F-5. Water quality requirements for reuse.

Source: U.S. EPA (2015g).

Constituent	Reasons for Limiting Concentrations	Recommended or observed base fluid target concentrations (mg/L, after blending)[b]
TDS	Fluid stability	500 – 70,000
Chloride	Fluid stability	2,000 – 90,000
Sodium	Fluid stability	2,000 – 5,000
Metals		
Iron	Scaling	1 – 15
Strontium	Scaling	1
Barium	Scaling	2 – 38
Silica	Scaling	20
Calcium	Scaling	50 – 4,200
Magnesium	Scaling	10 – 1,000
Sulfate	Scaling	124 – 1,000
Potassium	Scaling	100 – 500
Scale formers[a]	Scaling	2,500

Constituent	Reasons for Limiting Concentrations	Recommended or observed base fluid target concentrations (mg/L, after blending)[b]
Other		
Phosphate	Not Reported	10
TSS	Plugging	50 – 1,500
Oil	Fluid stability	5 – 25
Boron	Fluid stability	0 – 10
pH (S.U.)	Fluid stability	6.5 – 8.1
Bacteria (counts/mL)	Bacterial growth	0 – 10,000

[a] Includes total of barium, calcium, manganese, and strontium.

[b] Unless otherwise noted.

Wastewater quality can be managed for reuse by either blending it with freshwater and allowing dilution to bring the concentrations of problematic constituents to an acceptable range or through treatment (Veil, 2010). Treatment, if needed, can be conducted at facilities that are mobile, semi-permanent modular systems, or fully permanent CWTs (Nicot et al., 2012). At a minimum, hydraulic fracturing service providers generally prefer that the wastewater be treated to remove TSS, microorganisms, and constituents that form scale or inhibit crosslinking in gelled fluid systems (Boschee, 2014). Figure F-8 shows a schematic of a treatment system to treat wastewater for reuse that can remove suspended solids, hardness, and organic constituents.

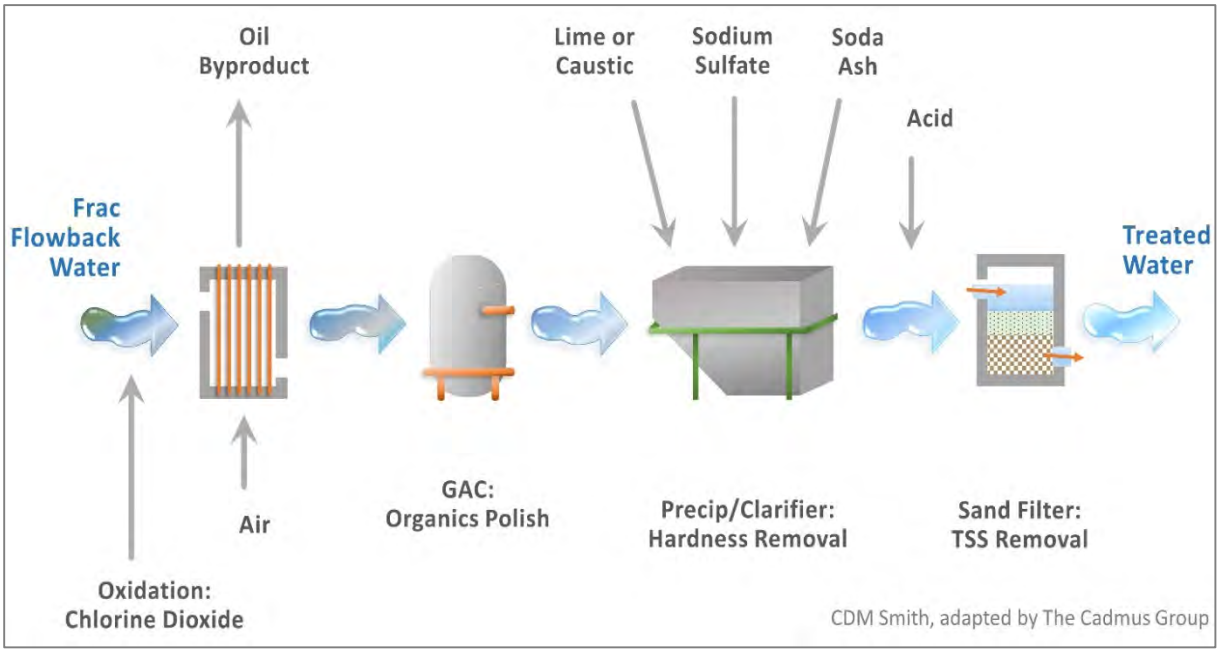

Figure F-8. Diagram of treatment for reuse of flowback and produced water.

Source: Kimball (2010).

In the Marcellus, the wastewater to be reused is first generally treated with oil/gas-water separation, filtration, and dilution (Ma et al., 2014). Although many Marcellus treatment facilities only supply basic reuse treatment that removes oil and solids, advanced treatment facilities that use techniques such as RO or distillation methods are also in operation (Veil, 2010).

Reuse concerns can vary with the type of hydraulic fracturing fluid used (e.g., slickwater, linear gel, crosslinked gel, foam) (Wasylishen and Fulton, 2012) and the anticipated changes in water chemistry over time (transition from flowback to produced water) (Hammer and VanBriesen, 2012). Elevated TDS is a concern, but residual constituents from previous fluid mixtures (e.g., breakers) may also cause difficulties when reusing water for subsequent fracturing operations (Montgomery, 2013; Walsh, 2013).

On-Site Treatment for Reuse

On-site systems that treat produced water for reuse can reduce potential impacts to drinking water resources associated with transportation and disposal and facilitate the logistics of reuse by preparing the water close to well sites. These systems sometimes consist of mobile units containing one or more treatment processes that can be moved from site to site to treat waters in newly developed sites that are not yet producing at full-scale. Semi-permanent facilities that serve a specific area also exist (Halldorson, 2013; Boschee, 2012).

Treatment systems are typically tailored for site-specific produced water chemical concentrations and desired water quality treatment goals, including whether significant TDS removal is needed. If

low TDS water is needed, more advanced treatment will be required (see Section 8.5 of Chapter 8), which can increase the treatment costs to three to four times higher than for treatment systems that do not remove TDS (Halldorson, 2013). On-site facilities may be warranted where truck hauling or seasonal accessibility to and from a central facility is an issue (Boschee, 2014; Tiemann et al., 2014). Operators may also consider on-site facilities if they have not fully committed to an area and the well counts are initially low. In those instances, they can later decide to add or remove units based on changing production volumes (Boschee, 2014).

F.6. Hydraulic Fracturing Impacts on POTWs

F.6.1. Potential Impacts on Treatment Processes

Wastewater treatment processes used by POTWs are generally not designed or operated for wastewater containing high salt concentrations (>0.1-5% salt). Four basic problems for biological treatment of saline water have been described (Woolard and Irvine, 1995): 1) microbes in conventional treatment systems tend to be sensitive to changes in ionic strength, 2) microbial metabolic functions are disrupted leading to decreased degradation of carbon compounds, 3) effluent suspended solids are increased due to cell lysis and/or a reduction in organisms that promote flocculation, and 4) the extent of salt acclimation is limited in conventional systems.

Biological pre-treatment may be beneficial as an added process in pre-treatment (e.g. prior to indirect discharge from a CWT to a POTW) for removal of organic contaminants. Specialized treatment systems using salt-tolerant bacteria may be beneficial as an additional level of treatment for pre-treating (or polishing) wastewaters in centralized treatment systems. (These processes differ from conventional biological processes in standard wastewater treatment, which are not suitable for large volumes of UOG wastewater.) In particular, membrane bioreactors (MBRs) have been examined for the treatment of oil and gas wastewater (Dao et al., 2013; Kose et al., 2012; Miller, 2011). MBRs provide advantages over conventional aeration basin processes as they can be implemented into existing treatment trains more easily and have a much smaller footprint than aeration basins.

Because sudden increases in chloride concentration, above 5-8 g/L, may cause problems for wastewater treatment (Ludzack and Noran, 1965). POTWs planning to accept indirect discharge in the future may find it valuable to restrict influent salt concentrations to a level that will not disturb existing biological treatment processes.

F.7. Hydraulic Fracturing and DBPs

F.7.1.1. Disinfection By-Products

This section provides background information on disinfection by-products (DBPs) and their formation to support the discussion in Section 8.6.1 of Chapter 8 regarding impacts on surface waters and downstream drinking water utilities due to elevated bromide and iodide in hydraulic fracturing wastewaters.

Regulated DBPs are a small subset of the full spectrum of DBPs that include other chlorinated and brominated DBPs as well as nitrogenous and iodated DBPs. Some of the emerging unregulated DBPs may be more toxic than their regulated counterparts (Harkness et al., 2015; McGuire et al., 2014; Parker et al., 2014). Of the many types of DBPs that can form when drinking water is disinfected, SDWA's Stage 1 and Stage 2 DBP Rules regulate four total trihalomethanes (TTHMs), five haloacetic acids (HAA5s), bromate, and chlorite (U.S. EPA, 2006).

Most brominated DBPs form when water containing organic material and bromide reacts with a disinfectant such as chlorine during drinking water treatment. Parameters that affect DBP formation include concentration and type of organic material, disinfectant concentration, pH, water temperature, and disinfectant contact time. In addition, many studies have found that elevated bromide levels correlate with increased DBP formation (Singer, 2010; Obolensky and Singer, 2008; Matamoros et al., 2007; Hua et al., 2006; Yang and Shang, 2004). Some studies found similar results for iodide as well (McGuire et al., 2014; Parker et al., 2014). Pope et al. (2007) reported that increased bromide levels are the second best indicator of DBP formation, with pH being the first.

In addition, research finds that higher levels of bromide and iodide contribute to increased concentrations of the brominated and iodated forms of DBPs (both regulated and unregulated), which tend to be more cytotoxic, genotoxic, and carcinogenic than chlorinated species (McGuire et al., 2014; Parker et al., 2014; States et al., 2013; Krasner, 2009; Richardson et al., 2007). Studies generally report that the ratios of halogen incorporation into DBPs reflect the ratio of halogen concentrations in the source water (Criquet et al., 2012; Jones et al., 2012; Obolensky and Singer, 2008).

From a regulatory perspective, elevated bromide levels create difficulties in meeting drinking water MCLs. When the TTHMs are predominately in the form of brominated DBPs, the higher molecular weight of bromide (79.9 g/mol) relative to chloride (35.5 g/mol) causes the overall mass of the TTHM sum to increase. This can lead to elevated concentrations of TTHM, in turn potentially leading to violations of the TTHM MCL for the drinking water utility (Francis et al., 2009).

High bromide levels are also cited as causing formation of nitrogenous DBP N-nitrosodimethylamine (NDMA) in water disinfected with chloramines (Luh and Mariñas, 2012). Although NDMA is not regulated by the EPA as of early 2015, it is listed as a priority toxic pollutant, and the EPA is planning to evaluate NDMA and other nitrosamines as candidates for regulation during the six-year review of the Microbial and Disinfection Byproducts (MDBP) rules (U.S. EPA, 2014a).

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Appendix G

Identification and Hazard Evaluation of Chemicals across the Hydraulic Fracturing Water Cycle Supplemental Tables and Information

Appendix G. Identification and Hazard Evaluation of Chemicals across the Hydraulic Fracturing Water Cycle Supplemental Tables and Information

Appendix G provides detail and supporting information on the oral reference values (RfVs) and oral slope factors (OSFs) that were identified in Chapter 9 of this assessment.[1] Section G.1 provides detail on the criteria used to select sources of RfVs and OSFs for chemicals used or detected in hydraulic fracturing processes, and lists all sources of RfVs and OSFs that were considered for this study. Section G.2 provides a glossary of the toxicity value terminology that is used by these various sources. Lastly, all of the RfVs and OSFs collected from these sources are provided in Table G-1 and Table G-2. Tables G-1a through G-1d show the available RfVs and OSFs for chemicals used in hydraulic fracturing fluids, and Tables G-2a through G-2d show the available RfVs and OSFs for chemicals detected in hydraulic fracturing flowback and wastewater. These tables provide cancer weight-of-evidence (WOE) characterizations for these chemicals where available, and indicate whether each chemical has available data on physicochemical properties or occurrence.

G.1. Criteria for Selection and Inclusion of Reference Value (RfV) and Oral Slope Factor (OSF) Data Sources

The criteria listed below were used to evaluate the quality of RfVs and OSFs considered for use in the hazard analyses conducted in Chapter 9. These criteria were originally outlined in the hydraulic fracturing research plan (U.S. EPA, 2011a) and interim progress report (U.S. EPA, 2012c). Only data sources that met these criteria were considered of sufficient quality to be included in the analyses.

The following criteria had to be met for a source to be deemed of sufficient quality:

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.
    a. Governmental bodies include sovereign states, and federated states/units.
    b. Intergovernmental bodies are those whose members are sovereign states, and the subdivisions or agencies of such intergovernmental bodies. The United Nations is an example of an intergovernmental body. The International Agency for Research on Cancer (IARC) is an agency of the World Health Organization (WHO), which is itself an agency of the United Nations. Thus, IARC is considered a subdivision of the United Nations.

[1] As defined in Chapter 9, the term RfV refers to reference values for noncancer effects occurring via the oral route of exposure and for chronic durations, except where noted.

2) The data source must include peer-reviewed RfVs, peer-reviewed OSFs, or peer reviewed qualitative assessments.
    a. A committee that is established to derive the RfVs, OSFs, or qualitative assessments can have members of that same committee provide the peer review, so long as either the entire committee, or members of the committee who did not participate in the derivation of a specific section of a work product, conduct the review.
    b. Peer reviewers who work for grantees of the organization deriving the RfVs, OSFs, or qualitative assessments are generally allowed, and this will not be considered to constitute a conflict/duality of interest.
    c. Peer reviewers may work in the same or different office, so long as they did not participate in any way in the development of the product, and these individuals must be free of conflicts/duality of interest with respect to the chemical(s) assigned.
        i. For instance, peer reviewers for Program X, conducted by Office A, may also be employed by Office A so long as they did not participate in the creation of the Program X product they are reviewing.

3) The RfVs, OSFs, or qualitative assessments must be based on peer-reviewed scientific data.
    a. There are cases where industry reports that were not published in a peer-reviewed, scholarly journal may be used, if the industry report has been adequately peer-reviewed by an external body (external to the group generating the report, and external to the group generating the peer-reviewed RfVs, peer-reviewed OSFs, or peer-reviewed qualitative assessment) that is free of conflicts/dualities of interest.

4) The RfVs, OSFs, or qualitative assessments must be focused on protection of the general public.
    a. Sources that are focused on workers are not appropriate as workers are assumed to accommodate additional risk than the general public due to their status as workers.

5) The body generating the values or qualitative assessments must be free of conflicts of interest with respect to the chemicals for which it derives RfVs, OSFs, or qualitative assessments.
    a. If a body generating the RfVs, OSFs, or qualitative assessments accepts funding from an interested party (i.e., a company or organization that may be impacted by past, present, or future values or qualitative assessments), then the body has a conflict of interest.
    b. For instance, if a non-profit organization is funded by an industry trade group, and the non-profit generates RfVs, OSFs, or qualitative assessments for chemicals that trade group is interested in, then the non-profit is considered to have a conflict of interest with respect to those chemicals.

It is important to note that having a conflict/duality of interest for one chemical is sufficient to disqualify the entire database, as it is assumed that conflicts/dualities of interest may exist for other chemicals as well.

G.1.1. Included Sources

We applied our criteria to 16 different sources of RfVs and/or OSFs. After application of our criteria, we were left with eight sources. For those sources which did not meet our criteria, we provide an explanation of why they were excluded.

The following sources were evaluated, met our criteria, and were selected as sources of reference doses or cancer slope factors for this analysis:

- **U.S. EPA Integrated Risk Information System (IRIS)**
- **U.S. EPA Human Health Benchmarks for Pesticides (HHBP)**
- **U.S. EPA Provisional Peer-Reviewed Toxicity Values (PPRTVs)**
- **U.S. Agency for Toxic Substances and Disease Registry (ATSDR) Minimum Risk Levels (MRLs)**
- **California EPA Toxicity Criteria Database**
- **International Programme On Chemical Safety (IPCS) Concise International Chemical Assessment Documents (CICAD)**

The following sources were evaluated, met our criteria, and were selected as sources of qualitative cancer classifications:

- **International Agency for Research on Cancer (IARC)**
- **US National Toxicology Program Report on Carcinogens (RoC)**

RfVs and/or OSFs from these data sources are listed in Tables G-1a through G-1d for chemicals used in hydraulic fracturing fluid formulation, and Tables G-2a through G-2d for chemicals reported in hydraulic fracturing flowback and produced water.

In addition, Table G-1 and Table G-2 also list the EPA's drinking water maximum contaminant levels (MCLs) and maximum contaminant goal levels (MCLG) when available. These values are generally based on IRIS values, and are treatment-based. MCL and MCLG values are listed for reference only, and were not considered in the hazard analysis presented in Chapter 9.

G.1.2. Excluded Sources

- **American Conference of Governmental Industrial Hygienists:** The assessments derived by this body are specific to workers and are not generalizable to the general public. In addition, this body is not a governmental or intergovernmental body. Thus, these values were excluded based on criteria 1 and 4.
- **European Chemicals Bureau, Classification and Labeling Annex I of Directive 67/548/EEC:** These assessments are not based on peer-reviewed values, but are based on data supplied by manufacturers. Further, the enabling legislation states that "Manufacturers, importers, and downstream users shall examine the information…to ascertain whether it is adequate, reliable and scientifically valid for the purpose of the

evaluation…" This clearly demonstrates that the data and the evaluation are not required to be peer-reviewed. Thus, these values were excluded based on criterion 2.

- **Toxicology Excellence for Risk Assessment's (TERA's) International Toxicity Estimates for Risk Assessment (ITER):** The ITER database is developed by TERA a 501(c)(3) non-profit. TERA accepts funding from various sources, including interested parties that may be impacted by their assessment work. Thus, ITER is excluded based on criteria 1 and 5.
- **Other U.S. states:** The EPA evaluated values from all states that had values reported on their websites. If a state's values were determined to be largely duplicative of the EPA's values (e.g., the state adopts EPA values, such as the regional screening levels, and does not typically generate its own peer-reviewed values), that state's values were no longer considered. The EPA contacted those states whose values were determined to not be duplicative of EPA's values, and confirmed whether or not a peer review process was used to develop the state's values. The EPA determined that of the states with values not duplicative of the EPA's values, only California's values met all of the EPA's criteria for this report. Other states with publicly accessible RfVs and/or OSFs include: Alabama, Florida, Hawaii, and Texas.
- **WHO Guidelines for Drinking-Water Quality:** The WHO Guidelines' values are not RfVs, but rather drinking water values.

G.2. Glossary of Toxicity Value Terminology

This section defines the toxicity values and qualitative cancer classifications that are frequently found in the sources identified above.

Lowest-observed-adverse-effect level (LOAEL): 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. Source: U.S. EPA (2011c).

Maximum allowable daily level (MADL): 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. Source: OEHHA (2012).

Maximum contaminant level (MCL): The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCLGs as feasible using the best available treatment technology and taking cost into consideration. MCLs are enforceable standards. Source: U.S. EPA (2014b).

Maximum contaminant level goal (MCLG): The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are nonenforceable public health goals. Source: U.S. EPA (2014b).

Minimum risk level (MRL): An ATSDR 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),

noncancerous 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.

- **Chronic MRL:** Duration of exposure is 365 days or longer.
- **Intermediate MRL:** Duration of exposure is >14 to 364 days.
- **Acute MRL**: Duration of exposure is 1 to 14 days.

Source: ATSDR (2009).

No-observed-adverse-effect level (NOAEL): 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 (2011c).

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. Source: U.S. EPA (2011c).

Reference dose (RfD) (U.S. EPA IRIS and PPRTV definition): 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. The RfD is generally used in the EPA's noncancer health assessments.

- **Chronic RfD:** Duration of exposure is up to a lifetime.
- **Subchronic RfD (sRFD)**: Duration of exposure is up to 10% of an average lifespan.

Source: U.S. EPA (2011c).

Reference dose (RfD) (U.S. EPA HHBP definition): The particular concentration of a chemical that is known not to cause health problems. A standard that also may be referred to as the acceptable daily intake. Derived using the same EPA guidance for IRIS and PPRTV RfD determination. Source: U.S. EPA (2015e).

Tolerable daily intake (TDI): 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. Source: WHO (2015).

Weight-of-evidence (WOE) characterization for carcinogenicity: A system used for characterizing the extent to which the available data support the hypothesis that an agent causes cancer in humans.

- **EPA 1986 guidelines:** Under the EPA's 1986 risk assessment guidelines, the WOE was described by categories "A through E," with Group A for known human carcinogens through Group E for agents with evidence of noncarcinogenicity. Five standard WOE descriptors were used:
    - A: Human carcinogen
    - B1: Probable human carcinogen—based on limited evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in animals
    - B2: Probable human carcinogen—based on sufficient evidence of carcinogenicity in animals
    - C: Possible human carcinogen
    - D: Not classifiable as to human carcinogenicity
    - E: Evidence of noncarcinogenicity for humans

  Source: U.S. EPA (2011c).

- **EPA 1996 proposed guidelines:** The EPA's 1996 proposed guidelines outlined a major change in the way hazard evidence was weighted in reaching conclusions about the human carcinogenic potential of agents. These guidelines replaced the WOE letter categories with the use of standard descriptors of conclusions incorporated into a brief narrative. Three categories of descriptors with the narrative were used:
    - Known/likely
    - Cannot be determined
    - Not likely

  Source: U.S. EPA (1996).

- **EPA 1999 guidelines:** The 1999 guidelines adopted a framework incorporating hazard identification, dose-response assessment, exposure assessment, and risk characterization with an emphasis on characterization of evidence and conclusions in each part of the assessment. Five descriptors summarizing the WOE in the narrative were used:
    - Carcinogenic to humans
    - Likely to be carcinogenic to humans
    - Suggestive evidence of carcinogenicity, but not sufficient to assess human carcinogenic potential
    - Data are inadequate for an assessment of human carcinogenic potential
    - Not likely to be carcinogenic to humans

  Source: U.S. EPA (1999).

- **EPA 2005 guidelines:** The approach outlined in the EPA's 2005 guidelines for carcinogen risk assessment considers all scientific information in determining whether and under what conditions an agent may cause cancer in humans and provides a narrative approach to

characterize carcinogenicity rather than categories. Five standard WOE descriptors are used as part of the narrative:

- Carcinogenic to humans
- Likely to be carcinogenic to humans
- Suggestive evidence of carcinogenic potential
- Inadequate information to assess carcinogenic potential
- Not likely to be carcinogenic to humans

Source: U.S. EPA (2011c).

- **IARC Monographs on the evaluation of carcinogenic risks to humans**: The IARC classifies carcinogen risk as a matter of scientific judgement that reflects the strength of the evidence derived from studies in humans, in experimental animals, from mechanistic data, and from other relevant data. Five WOE classifications are used:
  - 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

  Source: IARC (2015).
- **NTP:** The NTP describes the results of individual experiments on a chemical agent and notes the strength of the evidence for conclusions regarding each study. Negative results, in which the study animals do not have a greater incidence of neoplasia than control animals, do not necessarily mean that a chemical is not a carcinogen, inasmuch as the experiments are conducted under a limited set of conditions. Positive results demonstrate that a chemical is carcinogenic for laboratory animals under the conditions of the study and indicate that exposure to the chemical has the potential for hazard to humans. For each separate experiment, one of the following five categories is selected to describe the findings. These categories refer to the strength of the experimental evidence and not to potency or mechanism.
  - Clear evidence of carcinogenic activity
  - Some evidence of carcinogenic activity
  - Equivocal evidence of carcinogenic activity
  - No evidence of carcinogenic activity
  - Inadequate study of carcinogenic activity

  Source: NTP (2014a).
- **The RoC** is a congressionally mandated, science-based, public health report that identifies agents, substances, mixtures, or exposures (collectively called "substances") in our

environment that may potentially put people in the United States at increased risk for cancer. NTP prepares the RoC on behalf of the Secretary of the Health and Human Services. The listing criteria in the RoC Document are:

- Known to be a human carcinogen
- Reasonably anticipated to be a human carcinogen

Source: NTP (2014b).

G.3. Tables

Table G-1a. Chemicals reported to be used in hydraulic fracturing fluids, with available federal chronic RfVs and OSFs.

Chemicals from the FracFocus database are listed first, ranked by IRIS reference dose (RfD). The "--" symbol indicates that no value was available from the sources consulted. Additionally, an "x" indicates the availability of usage data from FracFocus (U.S. EPA, 2015a) and physicochemical properties data from EPI Suite™ (see Appendix C). Italicized chemicals are found in both fracturing fluids and flowback/produced water.

				IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
Chemical Name	**CASRN**	**Frac-Focus data available**	**Physico-chemical data available**	**Chronic RfD[a] (mg/kg-day)**	**OSF[b] (per mg/kg-day)**	**Cancer WOE character-ization[c]**	**Chronic RfD[a] (mg/kg-day)**	**OSF[b] (per mg/kg-day)**	**Cancer WOE character-ization[c]**	**Chronic oral MRL[d] (mg/kg-day)**	**Chronic RfD[e] (mg/kg-day)**	**Public health goal[f] (MCLG) (mg/L)**	**MCL[g] (mg/L)**
Acrylamide	79-06-1	x	x	0.002	0.5	"Likely to be carcinogenic to humans"	--	--	--	0.001	--	0	--
Propargyl alcohol	107-19-7	x	x	0.002	--	--	--	--	--	--	--	--	--
Furfural	98-01-1	x	x	0.003	--	--	--	--	--	--	0.01	--	--
Benzene	*71-43-2*	*x*	*x*	*0.004*	*0.015-0.055*	*A*	--	--	--	*0.0005*	--	*0*	*0.005*
Dichloromethane	*75-09-2*	*x*	*x*	*0.006*	*0.002*	*"Likely to be carcinogenic in humans"*	--	--	--	*0.06*	--	*0*	*0.005*
Naphthalene	*91-20-3*	*x*	*x*	*0.02*	--	"Data are inadequate to assess human carcinogenic potential"	--	--	--	--	--	--	--

Chemical Name	CASRN	Frac-Focus data available	Physico-chemical data available	IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
				Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic oral MRL[d] (mg/kg-day)	Chronic RfD[e] (mg/kg-day)	Public health goal[f] (MCLG) (mg/L)	MCL[g] (mg/L)
1,4-Dioxane	*123-91-1*	*x*	*x*	*0.03*	*0.1*	*"Likely to be carcinogenic to humans"*	--	--	--	*0.1*	--	--	--
Sodium chlorite	7758-19-2	x		0.03	--	*"Data are inadequate to assess human carcinogen-icity"*	--	--	--	--	--	1	0.8
Chlorine dioxide	10049-04-4	x		0.03	--	"Data are inadequate to assess human carcinogen-icity"	--	--	--	--	--	--	--
1,3-Dichloropropene	542-75-6	x	x	0.03	0.05	"Likely to be a human carcinogen"	--	--	--	0.03	--	--	--
Bisphenol A	80-05-7	x	x	0.05	--	--	--	--	--	--	--	--	--
Toluene	*108-88-3*	*x*	*x*	*0.08*	--	*"Inadequate information to assess the carcinogenic potential"*	--	--	--	--	--	*1*	*1*
Ethylbenzene	*100-41-4*	*x*	*x*	*0.1*	--	*D*	--	--	--	--	--	*0.7*	*0.7*

Chemical Name	CASRN	Frac-Focus data available	Physico-chemical data available	IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
				Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic oral MRL[d] (mg/kg-day)	Chronic RfD[e] (mg/kg-day)	Public health goal[f] (MCLG) (mg/L)	MCL[g] (mg/L)
1-Butanol	71-36-3	x	x	0.1	--	D	--	--	--	--	--	--	--
Cumene	*98-82-8*	*x*	*x*	*0.1*	--	*D*	--	--	--	--	--	--	--
Acetophenone	*98-86-2*	*x*	*x*	*0.1*	--	*D*	--	--	--	--	--	--	--
2-Butoxyethanol	111-76-2	x	x	0.1	--	"Not likely to be carcino-genic to humans"	--	--	--	--	--	--	--
Xylenes	*1330-20-7*	*x*	*x*	*0.2*	--	*"Data are inadequate to assess the carcinogenic potential"*	--	--	--	*0.2*	--	*10*	*10*
Formaldehyde	50-00-0	x	x	0.2	--	B1	--	--	--	0.2	--	--	--
Phenol	*108-95-2*	*x*	*x*	*0.3*	--	*"Data are inadequate for an assessment of human carcinogenic potential"*	--	--	--	--	--	--	--
2-Methyl-1-propanol	78-83-1	x	x	0.3	--	--	--	--	--	--	--	--	--

Chemical Name	CASRN	Frac-Focus data available	Physico-chemical data available	IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
				Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic oral MRL[d] (mg/kg-day)	Chronic RfD[e] (mg/kg-day)	Public health goal[f] (MCLG) (mg/L)	MCL[g] (mg/L)
Acetone	*67-64-1*	*x*	*x*	*0.9*	--	*"Data are inadequate for an assessment of human carcinogenic potential"*	--	--	--	--	--	--	--
Ethyl acetate	141-78-6	x	x	0.9	--	--	--	--	IN	--	--	--	--
Ethylene glycol	*107-21-1*	*x*	*x*	*2*	--	--	--	--	--	--	--	--	--
Methanol	*67-56-1*	*x*	*x*	*2*	--	--	--	--	--	--	--	--	--
Benzoic acid	65-85-0	x	x	4	--	D	--	--	--	--	--	--	--
Aniline	62-53-3	x	x	--	0.0057	B2	0.007	--	--	--	--	--	--
Benzyl chloride	100-44-7	x	x	--	0.17	B2	0.002	--	--	--	--	--	--
(E)-Crotonaldehyde	123-73-9	x	x	--	--	C	0.001	--	--	--	--	--	--
N,N-Dimethylform amide	68-12-2	x	x	--	--	--	0.1	--	IN	--	--	--	--
Epichlorohydrin	106-89-8	x	x	--	0.0099	B2	0.006	--	--	--	--	0	--
1,2-Propylene glycol	*57-55-6*	*x*	*x*	--	--	--	*20*	--	*NL*	--	--	--	--

Chemical Name	CASRN	Frac-Focus data available	Physico-chemical data available	IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
				Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic oral MRL[d] (mg/kg-day)	Chronic RfD[e] (mg/kg-day)	Public health goal[f] (MCLG) (mg/L)	MCL[g] (mg/L)
2-(2-Butoxyethoxy) ethanol	112-34-5	x	x	--	--	--	0.03	--	IN	--	--	--	--
Hexanedioic acid	124-04-9	x	x	--	--	--	2	--	--	--	--	--	--
Quinoline	91-22-5	x	x	--	3	”Likely to be carcinogenic in humans”	--	--	--	--	--	--	--
Ethylenediamine	107-15-3	x	x	--	--	D	0.09	--	IN	--	--	--	--
Formic acid	*64-18-6*	*x*	*x*	--	--	--	*0.9*	--	*IN*	--	--	--	--
Sodium chlorate	7775-09-9	x		--	--	--	--	--	--	--	0.03	--	--
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides	68424-85-1	x		--	--	--	--	--	--	--	0.44	--	--
Benzenesulfonic acid, C10-16-alkyl derivs.	68584-22-5	x		--	--	--	--	--	--	--	0.5	--	--
Ammonium phosphate	7722-76-1	x		--	--	--	49	--	IN	--	--	--	--
Didecyldimethylam monium chloride	7173-51-5	x	x	--	--	--	--	--	--	--	0.1	--	--
2-(Thiocyano methylthio)benzot hiazole	21564-17-0	x	x	--	--	--	--	--	--	--	0.01	--	--

Chemical Name	CASRN	Frac-Focus data available	Physico-chemical data available	IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
				Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic oral MRL[d] (mg/kg-day)	Chronic RfD[e] (mg/kg-day)	Public health goal[f] (MCLG) (mg/L)	MCL[g] (mg/L)
Mineral oil - includes paraffin oil	8012-95-1	x		--	--	--	3	--	IN	--	--	--	--
Trisodium phosphate	7601-54-9	x		--	--	--	49	--	IN	--	--	--	--
Triphosphoric acid, pentasodium salt	7758-29-4	x		--	--	--	49	--	IN	--	--	--	--
Aluminum	*7429-90-5*	*x*		--	--	--	*1*	--	*IN*	*1*	--	--	--
Phosphoric acid	7664-38-2	x		--	--	--	48.6	--	IN	--	--	--	--
Iron	*7439-89-6*	*x*		--	--	--	*0.7*	--	*IN*	--	--	--	--
Tricalcium phosphate	7758-87-4	x		--	--	--	49	--	IN	--	--	--	--
Bis(2-chloroethyl) ether	*111-44-4*	*x*	*x*	--	*1.1*	*B2*	--	--	--	--	--	--	--
Dodecylbenzenesulfonic acid	27176-87-0	x	x	--	--	--	--	--	--	--	0.5	--	--
Hydrazine	302-01-2	x		--	3	B2	--	--	--	--	--	--	--
Tetrasodium pyrophosphate	7722-88-5	x		--	--	--	49	--	IN	--	--	--	--

Chemical Name	CASRN	Frac-Focus data available	Physico-chemical data available	IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
				Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic oral MRL[d] (mg/kg-day)	Chronic RfD[e] (mg/kg-day)	Public health goal[f] (MCLG) (mg/L)	MCL[g] (mg/L)
Potassium phosphate, tribasic	7778-53-2	x		--	--	--	49	--	IN	--	--	--	--
Sodium trimetaphosphate	7785-84-4	x		--	--	--	49	--	IN	--	--	--	--
Arsenic	*7440-38-2*			*0.0003*	*1.5*	*A*	--	--	--	*0.0003*	--	*0*	*0.010*
Phosphine	7803-51-2			0.0003	--	D	--	--	--	--	--	--	--
Acrolein	*107-02-8*		*x*	*0.0005*	--	*"Data are inadequate for an assessment of human carcinogenic potential"*	--	--	--	--	--	--	--
Chromium (VI)	*18540-29-9*			*0.003*	--	*A (inhaled); D(oral)*	--	--	--	*0.0009*	--	--	--
Di(2-ethylhexyl) phthalate	*117-81-7*		*x*	*0.02*	*0.014*	*B2*	--	--	--	*0.06*	--	*0*	*0.006*
Chlorine	*7782-50-5*			*0.1*	--	--	--	--	--	--	--	--	--
Styrene	100-42-5		x	0.2	--	--	--	--	--	--	--	0.1	0.1

Chemical Name	CASRN	Frac-Focus data available	Physico-chemical data available	IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
				Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic oral MRL[d] (mg/kg-day)	Chronic RfD[e] (mg/kg-day)	Public health goal[f] (MCLG) (mg/L)	MCL[g] (mg/L)
Zinc	*7440-66-6*			*0.3*	--	*"Inadequate information to assess carcinogenic potential"*	--	--	--	*0.3*	--	--	--
Acrylic acid	79-10-7		x	0.5	--	--	--	--	IN	--	--	--	--
Chromium (III)	*16065-83-1*			*1.5*	--	*"Data are inadequate for an assessment of human carcinogenic potential"*	--	--	--	--	--	--	--
Phthalic anhydride	85-44-9		x	2	--	--	--	--	--	--	--	--	--
Cyclohexanone	108-94-1		x	5	--	--	--	--	IN	--	--	--	--
1,2-Propylene oxide	75-56-9		x	--	0.24	B2	--	--	--	--	0.001	--	--
2-(2-Ethoxyethoxy) ethanol	111-90-0		x	--	--	--	0.06	--	IN	--	--	--	--
Tributyl phosphate	126-73-8		x	--	--	--	0.01	0.009	LI	0.08	--	--	--
2-Methoxyethanol	109-86-4		x	--	--	--	0.005	--	IN	--	--	--	--
Polyphosphoric acids, sodium salts	68915-31-1			--	--	--	49	--	IN	--	--	--	--
Phosphoric acid, diammonium salt	7783-28-0			--	--	--	49	--	IN	--	--	--	--

Chemical Name	CASRN	Frac-Focus data available	Physico-chemical data available	IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
				Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic oral MRL[d] (mg/kg-day)	Chronic RfD[e] (mg/kg-day)	Public health goal[f] (MCLG) (mg/L)	MCL[g] (mg/L)
Sodium pyrophosphate	7758-16-9			--	--	--	49	--	IN	--	--	--	--
Phosphoric acid, aluminium sodium salt	7785-88-8			--	--	--	49	--	IN	--	--	--	--

ATSDR = Agency for Toxic Substances and Disease Registry; CASRN = Chemical Abstract Service Registry Number; IRIS = Integrated Risk Information System; PPRTV = Provisional Peer Reviewed Toxicity Values; HHBP = Human Health Benchmarks for Pesticides

[a] Reference dose (RfD) (IRIS and PPRTV definition): 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 no observed-adverse-effect level (NOAEL), lowest observed-adverse-effect level (LOAEL), or benchmark dose (BMD), with uncertainty factors generally applied to reflect limitations of the data used. The RfD is generally used in the EPA's noncancer health assessments. Chronic RfD: Duration of exposure is up to a lifetime.

[b] 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.

[c] Weight of evidence (WOE) characterization for carcinogenicity: A system used for characterizing the extent to which the available data support the hypothesis that an agent causes cancer in humans. See glossary for details.

[d] Minimum risk level (MRL): An ATSDR 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), noncancerous 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. Chronic MRL: Duration of exposure is 365 days or longer.

[e] Reference dose (RfD) (HHBP definition): The particular concentration of a chemical that is known not to cause health problems. A standard that also may be referred to as the acceptable daily intake. Derived using the same EPA guidance for RfD determination.

[f] Maximum contaminant level goal (MCLG): The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are nonenforceable public health goals.

[g] Maximum contaminant level (MCL): The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCLGs as feasible using the best available treatment technology and taking cost into consideration. MCLs are enforceable standards.

Table G-1b. Chemicals reported to be used in hydraulic fracturing fluids, with available state chronic RfVs and OSFs.

Chemicals from the FracFocus database are listed first, ranked by California EPA maximum allowable daily level (MADL). The "--" symbol indicates that no value was available from the sources consulted. Additionally, an "x" indicates the availability of usage data from FracFocus (U.S. EPA, 2015a) and physicochemical properties data from EPI Suite™ (see Appendix C). Italicized chemicals are found in both fracturing fluids and flowback/produced water.

Chemical name	CASRN	FracFocus data available	Physico-chemical data available	California	
				Oral MADL[a] (µg/day)	OSF[b] (per mg/kg-day)
Ethylene oxide	75-21-8	x	x	20	0.31
Benzene	*71-43-2*	*x*	*x*	*24*	*0.1*
N-Methyl-2-pyrrolidone	872-50-4	x	x	17000	--
Acrylamide	79-06-1	x	x	140	4.5
Aniline	62-53-3	x	x	--	0.0057
Benzyl chloride	100-44-7	x	x	--	0.17
1,4-Dioxane	*123-91-1*	*x*	*x*	--	*0.027*
Epichlorohydrin	106-89-8	x	x	--	0.08
Ethylbenzene	*100-41-4*	*x*	*x*	--	*0.011*
Nitrilotriacetic acid	139-13-9	x	x	--	0.0053
Nitrilotriacetic acid trisodium monohydrate	18662-53-8	x	x	--	0.01
Thiourea	62-56-6	x	x	--	0.072
Bis(2-chloroethyl) ether	*111-44-4*	*x*	*x*	--	*2.5*
1,3-Butadiene	106-99-0	x	x	--	0.6
Hydrazine	302-01-2	x		--	3
1,3-Dichloropropene	542-75-6	x	x	--	0.091
Dichloromethane	*75-09-2*	*x*	*x*	--	*0.014*
Lead	*7439-92-1*			*0.5*	*0.0085*
Chromium (VI)	*18540-29-9*			*8.2*	*0.5*
2-Methoxyethanol	109-86-4		x	63	--
2-Ethoxyethanol	110-80-5		x	750	--

Chemical name	CASRN	FracFocus data available	Physico-chemical data available	California	
				Oral MADL[a] (µg/day)	OSF[b] (per mg/kg-day)
Di(2-ethylhexyl) phthalate	*117-81-7*		*x*	*20 (neonate male)* *58 (infant male)* *410 (adult)*	*0.003*
1,2-Propylene oxide	75-56-9		x	--	0.24
Arsenic	*7440-38-2*			--	*9.5*

[a] Maximum allowable daily level (MADL): 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.

[b] 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.

Table G-1c. Chemicals reported to be used in hydraulic fracturing fluids, with available international chronic RfVs and OSFs.

Chemicals from the FracFocus database are listed first, ranked by CICAD reference dose (TDI, or tolerable daily intake). An "x" indicates the availability of usage data from FracFocus (U.S. EPA, 2015a) and physicochemical properties data from EPI Suite™ (see Appendix C). Italicized chemicals are found in both fracturing fluids and flowback/produced water.

Chemical name	CASRN	FracFocus data available	Physicochemical data available	IPCS Chronic TDI[a] (mg/kg-day)
D-Limonene	5989-27-5	x	x	0.1
Potassium iodide	7681-11-0	x		0.01
Sodium iodide	7681-82-5	x		0.01
Copper(I) iodide	7681-65-4	x		0.01
Glyoxal	107-22-2	x	x	0.2
Ethylene glycol	*107-21-1*	*x*	*x*	*0.05*
N-Methyl-2-pyrrolidone	872-50-4	x	x	0.6
Strontium chloride	10476-85-4			0.13
Chromium (VI)	*18540-29-9*			*0.0009*

IPCS = International Programme on Chemical Safety; CICAD = Concise International Chemical Assessment Documents

[a] Tolerable daily intake (TDI): 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.

Table G-1d. Chemicals reported to be used in hydraulic fracturing fluids, with available less-than-chronic RfVs and OSFs.

Chemicals from the FracFocus database are listed first, ranked by PPRTV subchronic reference dose (sRfD). The "--" symbol indicates that no value was available from the sources consulted. Additionally, an "x" indicates the availability of usage data from FracFocus (U.S. EPA, 2015a) and physicochemical properties data from EPI Suite™ (see Appendix C). Italicized chemicals are found in both fracturing fluids and flowback/produced water.

Chemical name	CASRN	FracFocus data available	Physico-chemical data available	PPRTV	ATSDR	
				sRfD[a] (mg/kg-day)	Acute oral MRL[b] (mg/kg-day)	Intermediate oral MRL[c] (mg/kg-day)
Benzyl chloride	100-44-7	x	x	0.002	--	--
Epichlorohydrin	106-89-8	x	x	0.006	--	--
(E)-Crotonaldehyde	123-73-9	x	x	0.01	--	--
Benzene	*71-43-2*	*x*	*x*	*0.01*	--	--
Ethylbenzene	*100-41-4*	*x*	*x*	*0.05*	--	*0.4*
Ethylenediamine	107-15-3	x	x	0.2	--	--
N,N-Dimethylformamide	68-12-2	x	x	0.3	--	--
2-(2-Butoxyethoxy)ethanol	112-34-5	x	x	0.3	--	--
Hexane	110-54-3	x	x	0.3	--	--
Xylenes	*1330-20-7*	*x*	*x*	*0.4*	*1*	*0.4*
Antimony trioxide	1309-64-4	x		0.5	--	--
Iron	*7439-89-6*	*x*		*0.7*	--	--
Toluene	*108-88-3*	*x*	*x*	*0.8*	*0.8*	*0.02*
Formic acid	*64-18-6*	*x*	*x*	*0.9*	--	--
Hexanedioic acid	124-04-9	x	x	2	--	--
Benzoic acid	65-85-0	x	x	4	--	--
1,2-Propylene glycol	*57-55-6*	*x*	*x*	*20*	--	--
Mineral oil - includes paraffin oil	8012-95-1	x		30	--	--
Phosphoric acid	7664-38-2	x		48.6	--	--
Ammonium phosphate	7722-76-1	x		49	--	--
Trisodium phosphate	7601-54-9	x		49	--	--
Triphosphoric acid, pentasodium salt	7758-29-4	x		49	--	--

Chemical name	CASRN	FracFocus data available	Physico-chemical data available	PPRTV	ATSDR	
				sRfD[a] (mg/kg-day)	Acute oral MRL[b] (mg/kg-day)	Intermediate oral MRL[c] (mg/kg-day)
Tricalcium phosphate	7758-87-4	x		49	--	--
Tetrasodium pyrophosphate	7722-88-5	x		49	--	--
Potassium phosphate, tribasic	7778-53-2	x		49	--	--
Sodium trimetaphosphate	7785-84-4	x		49	--	--
Acrylamide	79-06-1	x	x	--	0.01	0.001
1,4-Dioxane	*123-91-1*	*x*	*x*	--	*5*	*0.5*
Ethylene glycol	*107-21-1*	*x*	*x*	--	*0.8*	*0.8*
Naphthalene	*91-20-3*	*x*	*x*	--	*0.6*	*0.6*
Phenol	*108-95-2*	*x*	*x*	--	*1*	--
Sodium chlorite	7758-19-2	x		--	--	0.1
Acetone	*67-64-1*	*x*	*x*	--	--	*2*
2-Butoxyethanol	111-76-2	x	x	--	0.4	0.07
Aluminum	*7429-90-5*	*x*		--	--	*1*
Formaldehyde	50-00-0	x	x	--	--	0.3
1,3-Dichloropropene	542-75-6	x	x	--	--	0.04
Dichloromethane	*75-09-2*	*x*	*x*	--	*0.2*	--
Antimony trichloride	10025-91-9			0.0004	--	--
2-Methoxyethanol	109-86-4		x	0.02	--	--
Tributyl phosphate	126-73-8		x	0.03	1.1	0.08
Acrylic acid	79-10-7		x	0.2	--	--
2-(2-Ethoxyethoxy) ethanol	111-90-0		x	0.6	--	--
Cyclohexanone	108-94-1		x	2	--	--
Polyphosphoric acids, sodium salts	68915-31-1			49	--	--
Phosphoric acid, diammonium salt	7783-28-0			49	--	--
Sodium pyrophosphate	7758-16-9			49	--	--

Chemical name	CASRN	FracFocus data available	Physico-chemical data available	PPRTV	ATSDR	
				sRfD[a] (mg/kg-day)	Acute oral MRL[b] (mg/kg-day)	Intermediate oral MRL[c] (mg/kg-day)
Phosphoric acid, aluminium sodium salt	7785-88-8			49	--	--
Acrolein	*107-02-8*		*x*	--	--	*0.004*
Di(2-ethylhexyl) phthalate	*117-81-7*		*x*	--	--	*0.1*
Styrene	100-42-5		x	--	0.1	--
Arsenic	*7440-38-2*			--	*0.005*	--
Chromium (VI)	*18540-29-9*			--	--	*0.005*
Copper	*7440-50-8*			--	*0.01*	*0.01*
Zinc	*7440-66-6*			--	--	*0.3*

[a] Reference dose (RfD): 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 no observed-adverse-effect level (NOAEL), lowest observed-adverse-effect level (LOAEL), or benchmark dose (BMD), with uncertainty factors generally applied to reflect limitations of the data used. The RfD is generally used in the EPA's noncancer health assessments. Subchronic RfD (sRFD): Duration of exposure is up to 10% of an average lifespan.

[b] Minimum risk level (MRL): An ATSDR 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), noncancerous 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. Acute MRL: Duration of exposure is 1 to 14 days.

[c] Minimum risk level (MRL): An ATSDR 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), noncancerous 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. Intermediate MRL: Duration of exposure is >14 to 364 days.

Table G-2a. Chemicals reported to be detected in flowback or produced water, with available federal chronic RfVs and OSFs.

Chemicals are ranked by IRIS reference dose (RfD). The "--" symbol indicates that no value was available from the sources consulted. Additionally, an "x" indicates the availability of measured concentration data in flowback or produced water (see Appendix E) and physicochemical properties data from EPI Suite™ (see Appendix C). Italicized chemicals are found in both fracturing fluids and flowback/produced water.

				IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
Chemical Name	**CASRN**	**Concen-tration data available**	**Physico-chemical data available**	**Chronic RfD[a] (mg/kg-day)**	**OSF[b] (per mg/kg-day)**	**Cancer WOE character-ization[c]**	**Chronic RfD[a] (mg/kg-day)**	**OSF[b] (per mg/kg-day)**	**Cancer WOE character-ization[c]**	**Chronic oral MRL[d] (mg/kg-day)**	**Chronic RfD[e] (mg/kg-day)**	**Public health goal[f] (MCLG) (mg/L)**	**MCL[g] (mg/L)**
Heptachlor epoxide	1024-57-3		x	0.000013	9.1	B2	--	--	--	--	--	0	0.0002
Phosphorus	7723-14-0	x		0.00002	--	D	--	--	--	--	--	--	--
Aldrin	309-00-2		x	0.00003	17	B2	--	--	--	0.00003	--	--	--
Dieldrin	60-57-1		x	0.00005	16	B2	--	--	--	0.00005	--	--	--
Arsenic	*7440-38-2*	x		*0.0003*	*1.5*	*A*	--	--	--	*0.0003*	--	*0*	*0.010*
Lindane	58-89-9		x	0.0003	--	--	--	--	--	--	--	0.0002	0.0002
Antimony	7440-36-0	x		0.0004	--	--	--	--	IN	--	--	0.006	0.006
Acrolein	*107-02-8*		*x*	*0.0005*	--	*"Data are inadequate for an assessment of human carcinogenic potential"*	--	--	--	--	--	--	--
Cadmium	7440-43-9	x		0.0005 (water)	--	B1	--	--	--	0.0001	--	0.005	0.005
Heptachlor	76-44-8		x	0.0005	4.5	B2	--	--	--	--	--	0	0.0004

Chemical Name	CASRN	Concen-tration data available	Physico-chemical data available	IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
				Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic oral MRL[d] (mg/kg-day)	Chronic RfD[e] (mg/kg-day)	Public health goal[f] (MCLG) (mg/L)	MCL[g] (mg/L)
Cyanide	57-12-5		x	0.0006	--	"Inadequate information to assess the carcinogenic potential"	--	--	--	--	--	0.2	0.2
Pyridine	110-86-1	x	x	0.001	--	--	--	--	--	--	--	--	--
Methyl bromide	74-83-9		x	0.0014	--	D	--	--	--	--	0.02	--	--
Beryllium	7440-41-7	x		0.002	--	B1	--	--	--	0.002	--	0.004	0.004
Chromium (VI)	*18540-29-9*			*0.003*	--	*A (inhaled); D(oral)*	--	--	--	*0.0009*	--	--	--
Benzene	*71-43-2*	*x*	*x*	*0.004*	*0.015-0.055*	*A*	--	--	--	*0.0005*	--	*0*	*0.005*
2-Methylnaphthalene	91-57-6	x	x	0.004	--	"Data are inadequate to assess human carcinogenic potential"	--	--	--	0.04	--	--	--
Molybdenum	7439-98-7	x		0.005	--	--	--	--	--	--	--	--	--
Silver	7440-22-4	x		0.005	--	D	--	--	--	--	--	--	--
Selenium	7782-49-2	x		0.005	--	D	--	--	--	0.005	--	0.05	0.05
Dichloromethane	*75-09-2*		*x*	*0.006*	*0.002*	*"Likely to be carcinogenic in humans"*	--	--	--	*0.06*	--	*0*	*0.005*

Chemical Name	CASRN	Concen-tration data available	Physico-chemical data available	IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
				Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic oral MRL[d] (mg/kg-day)	Chronic RfD[e] (mg/kg-day)	Public health goal[f] (MCLG) (mg/L)	MCL[g] (mg/L)
1,2,4-Trichlorobenzene	120-82-1		x	0.01	--	D	--	0.029	LI	0.1	--	0.07	0.07
Tetrachloroethylene	127-18-4		x	0.006	0.0021	"Likely to be carcinogenic in humans"	--	--	--	0.008	--	0	0.005
Chloroform	67-66-3	x	x	0.01	--	B2	--	--	--	0.01	--	--	--
Di(2-ethylhexyl) phthalate	*117-81-7*	*x*	*x*	*0.02*	*0.014*	*B2*	--	--	--	*0.06*	--	*0*	*0.006*
Naphthalene	*91-20-3*	*x*	*x*	*0.02*	--	*"Data are inadequate to assess human carcinogenic potential"*	--	--	--	--	--	--	--
2,4-Dimethylphenol	105-67-9	x	x	0.02	--	--	--	--	IN	--	--	--	--
Chlorodibromomethane	124-48-1		x	0.02	0.084	C	--	--	--	0.09	--	--	--
Bromoform	75-25-2		x	0.02	0.0079	B2	--	--	--	0.02	--	--	--
Bromodichloromethane	75-27-4		x	0.02	0.062	B2	--	--	--	0.02	--	--	--
Diphenylamine	122-39-4	x	x	0.025	--	--	--	--	IN	--	0.1	--	--
1,4-Dioxane	*123-91-1*	*x*	*x*	*0.03*	*0.1*	*"Likely to be carcinogenic to humans"*	--	--	--	*0.1*	--	--	--

Chemical Name	CASRN	Concen-tration data available	Physico-chemical data available	IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
				Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic oral MRL[d] (mg/kg-day)	Chronic RfD[e] (mg/kg-day)	Public health goal[f] (MCLG) (mg/L)	MCL[g] (mg/L)
Pyrene	129-00-0	x	x	0.03	--	D	--	--	--	--	--	--	--
Fluoranthene	206-44-0	x	x	0.04	--	D	--	--	IN	--	--	--	--
Fluorene	86-73-7	x	x	0.04	--	D	--	--	--	--	--	--	--
m-Cresol	108-39-4	x	x	0.05	--	C	--	--	--	--	--	--	--
o-Cresol	95-48-7	x	x	0.05	--	C	--	--	IN	--	--	--	--
Toluene	*108-88-3*	*x*	*x*	*0.08*	--	*"Inadequate information to assess the carcinogenic potential"*	--	--	--	--	--	*1*	*1*
Chlorine	*7782-50-5*			*0.1*	--	--	--	--	--	--	--	--	--
Ethylbenzene	*100-41-4*	*x*	*x*	*0.1*	--	*D*	--	--	--	--	--	*0.7*	*0.7*
Cumene	*98-82-8*	*x*	*x*	*0.1*	--	*D*	--	--	--	--	--	--	--
Acetophenone	*98-86-2*	*x*	*x*	*0.1*	--	*D*	--	--	--	--	--	--	--
Carbon disulfide	75-15-0	x	x	0.1	--	--	--	--	--	--	--	--	--
Dibutyl phthalate	84-74-2	x	x	0.1	--	D	--	--	--	--	--	--	--

Chemical Name	CASRN	Concen-tration data available	Physico-chemical data available	IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
				Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic oral MRL[d] (mg/kg-day)	Chronic RfD[e] (mg/kg-day)	Public health goal[f] (MCLG) (mg/L)	MCL[g] (mg/L)
Nitrite	14797-65-0	x		0.1	--	--	--	--	--	--	--	1	1
Manganese	7439-96-5	x		0.14	--	D	--	--	--	--	--	--	--
Xylenes	*1330-20-7*	*x*	*x*	*0.2*	--	*"Data are inadequate to assess the carcinogenic potential"*	--	--	--	*0.2*	--	*10*	*10*
Barium	7440-39-3	x		0.2	--	"Not likely to be carcinogenic to humans"	--	--	--	0.2	--	2	2
Boron	7440-42-8	x		0.2	--	"Data are inadequate to assess the carcinogenic potential"	--	--	--	--	--	--	--
Zinc	*7440-66-6*	x		*0.3*	--	*"Inadequate information to assess carcinogenic potential"*	--	--	--	*0.3*	--	--	--
Phenol	*108-95-2*	*x*	*x*	*0.3*	--	*"Data are inadequate to assess human carcinogenicity"*	--	--	--	--	--	--	--

Chemical Name	CASRN	Concen-tration data available	Physico-chemical data available	IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
				Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic oral MRL[d] (mg/kg-day)	Chronic RfD[e] (mg/kg-day)	Public health goal[f] (MCLG) (mg/L)	MCL[g] (mg/L)
Strontium	7440-24-6	x		0.6	--	--	--	--	--	--	--	--	--
Methyl ethyl ketone	78-93-3		x	0.6	--	"Data are inadequate to assess carcinogenic potential"	--	--	--	--	--	--	--
Diethyl phthalate	84-66-2		x	0.8	--	D	--	--	--	--	--	--	--
Acetone	*67-64-1*	*x*	*x*	*0.9*	--	*"Data are inadequate to assess human carcinogenicity"*	--	--	--	--	--	--	--
Chromium (III)	*16065-83-1*			*1.5*	--	*"Data are inadequate to assess human carcinogenicity"*	--	--	--	--	--	--	--
Nitrate	14797-55-8	x		1.6	--	--	--	--	--	--	--	10	10
Ethylene glycol	*107-21-1*		*x*	*2*	--	--	--	--	--	--	--	--	--
Methanol	*67-56-1*		*x*	*2*	--	--	--	--	--	--	--	--	--
1,2-Propylene glycol	*57-55-6*		*x*	--	--	--	*20*	--	*NL*	--	--	--	--
Formic acid	*64-18-6*		*x*	--	--	--	*0.9*	--	*IN*	--	--	--	--
Aluminum	*7429-90-5*	*x*		--	--	--	*1*	--	*IN*	*1*	--	--	--

Chemical Name	CASRN	Concen-tration data available	Physico-chemical data available	IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
				Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic oral MRL[d] (mg/kg-day)	Chronic RfD[e] (mg/kg-day)	Public health goal[f] (MCLG) (mg/L)	MCL[g] (mg/L)
Iron	*7439-89-6*	x		--	--	--	*0.7*	--	*IN*	--	--	--	--
Bis(2-chloroethyl) ether	*111-44-4*		*x*	--	*1.1*	*B2*	--	--	--	--	--	--	--
Benzyl alcohol	100-51-6	x	x	--	--	--	0.1	--	IN	--	--	--	--
Butylbenzene	104-51-8		x	--	--	--	0.05	--	IN	--	--	--	--
Acrylonitrile	107-13-1		x	--	0.54	B1	--	--	--	0.04	--	--	--
Phorate	298-02-2		x	--	--	--	--	--	--	--	0.0005	--	--
beta-Hexachloro cyclohexane	319-85-7		x	--	1.8	C	--	--	--	--	--	--	--
Benzo(a)pyrene	50-32-8	x	x	--	7.3	B2	--	--	--	--	--	0	0.0002
p,p'-DDE	72-55-9		x	--	0.34	B2	--	--	--	--	--	--	--
Lithium	7439-93-2	x		--	--	--	0.002	--	IN	--	--	--	--

Chemical Name	CASRN	Concen-tration data available	Physico-chemical data available	IRIS			PPRTV			ATSDR	HHBP	National Primary Drinking Water Regulations	
				Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic RfD[a] (mg/kg-day)	OSF[b] (per mg/kg-day)	Cancer WOE character-ization[c]	Chronic oral MRL[d] (mg/kg-day)	Chronic RfD[e] (mg/kg-day)	Public health goal[f] (MCLG) (mg/L)	MCL[g] (mg/L)
Cobalt	7440-48-4	x		--	--	--	0.0003	--	LI	--	--	--	--
Vanadium	7440-62-2	x		--	--	--	0.00007	--	IN	--	--	--	--
N-Nitrosodiphenylamine	86-30-6	x	x	--	0.0049	B2	--	--	--	--	--	--	--

ATSDR = Agency for Toxic Substances and Disease Registry; CASRN = Chemical Abstract Service Registry Number; IRIS = Integrated Risk Information System; PPRTV = Provisional Peer Reviewed Toxicity Values; HHBP = Human Health Benchmarks for Pesticides

[a] Reference dose (RfD) (IRIS and PPRTV definition): 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 no observed-adverse-effect level (NOAEL), lowest observed-adverse-effect level (LOAEL), or benchmark dose (BMD), with uncertainty factors generally applied to reflect limitations of the data used. The RfD is generally used in the EPA's noncancer health assessments. Chronic RfD: Duration of exposure is up to a lifetime.

[b] 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.

[c] Weight of evidence (WOE) characterization for carcinogenicity: A system used for characterizing the extent to which the available data support the hypothesis that an agent causes cancer in humans. See glossary for details.

[d] Minimum risk level (MRL): An ATSDR 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), noncancerous 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. Chronic MRL: Duration of exposure is 365 days or longer.

[e] Reference dose (RfD) (HHBP definition): The particular concentration of a chemical that is known not to cause health problems. A standard that also may be referred to as the acceptable daily intake. Derived using the same EPA guidance for RfD determination.

[f] Maximum contaminant level goal (MCLG): The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are nonenforceable public health goals.

[g] Maximum contaminant level (MCL): The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCLGs as feasible using the best available treatment technology and taking cost into consideration. MCLs are enforceable standards.

Table G-2b. Chemicals reported to be detected in flowback or produced water, with available state chronic RfVs and OSFs.

Chemicals are ranked by California EPA maximum allowable daily level (MADL). The "--" symbol indicates that no value was available from the sources consulted. Additionally, an "x" indicates the availability of measured concentration data in flowback or produced water (see Appendix E) and physicochemical properties data from EPI Suite™ (see Appendix C). Italicized chemicals are found in both fracturing fluids and flowback/produced water.

Chemical name	CASRN	Concen-tration data available	Physico-chemical data available	California	
				Oral MADL[a] (µg/day)	OSF[b] (per mg/kg-day)
Lead	*7439-92-1*	*x*		*0.5*	*0.0085*
Cadmium	7440-43-9	x		4.1	15
Chromium (VI)	*18540-29-9*			*8.2*	*0.5*
Dibutyl phthalate	84-74-2	x	x	8.7	--
Benzene	*71-43-2*	*x*	*x*	*24*	*0.1*
Acrylonitrile	107-13-1		x	--	1
1,4-Dioxane	*123-91-1*	*x*	*x*	*--*	*0.027*
Ethylbenzene	*100-41-4*	*x*	*x*	*--*	*0.011*
Di(2-ethylhexyl) phthalate	*117-81-7*	*x*	*x*	*20 (neonate male) 58 (infant male) 410 (adult)*	*0.003*
Arsenic	*7440-38-2*	*x*		*--*	*9.5*
Bis(2-chloroethyl) ether	*111-44-4*		*x*	*--*	*2.5*
Heptachlor epoxide	1024-57-3		x	--	5.5
1,2,4-Trichlorobenzene	120-82-1		x	--	0.0036
Tetrachloroethylene	127-18-4		x	--	0.051
Indeno(1,2,3-cd)pyrene	193-39-5	x	x	--	1.2
Benzo(b)fluoranthene	205-99-2	x	x	--	1.2
Benzo(k)fluoranthene	207-08-9	x	x	--	1.2
Aldrin	309-00-2		x	--	17
beta-Hexachlorocyclohexane	319-85-7		x	--	1.5
Benzo(a)pyrene	50-32-8	x	x	--	2.9
Dibenz(a,h)anthracene	53-70-3	x	x	--	4.1
7,12-Dimethylbenz(a)anthracene	57-97-6		x	--	250
Lindane	58-89-9		x	--	1.1
Dieldrin	60-57-1		x	--	16
Chloroform	67-66-3	x	x	--	0.019

Chemical name	CASRN	Concen-tration data available	Physico-chemical data available	California	
				Oral MADL[a] (µg/day)	OSF[b] (per mg/kg-day)
p,p'-DDE	72-55-9		x	--	0.34
Bromoform	75-25-2		x	--	0.011
Bromodichloromethane	75-27-4		x	--	0.13
Heptachlor	76-44-8		x	--	4.1
N-Nitrosodiphenylamine	86-30-6	x	x	--	0.009
Safrole	94-59-7		x	--	0.22
Dichloromethane	*75-09-2*		*x*	--	*0.014*

[a] Maximum allowable daily level (MADL): 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.

[b] 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.

Table G-2c. Chemicals reported to be detected in flowback or produced water, with available international chronic RfVs and OSFs.

Chemicals are ranked by CICAD reference dose (TDI – Tolerable Daily Intake). An "x" indicates the availability of measured concentration data in flowback or produced water (see Appendix E) and physicochemical properties data from EPI Suite™ (see Appendix C). Italicized chemicals are found in both fracturing fluids and flowback/produced water.

Chemical name	CASRN	Concentration data available	Physicochemical data available	IPCS Chronic TDI[a] (mg/kg-day)
Heptachlor	76-44-8		x	0.0001
Strontium	7440-24-6	x		0.13
Chloroform	67-66-3	x	x	0.015
Mercury	7439-97-6	x		0.002
Barium	7440-39-3	x		0.02
Beryllium	7440-41-7	x		0.002
Ethylene glycol	*107-21-1*		*x*	*0.05*
Tetrachloroethene	127-18-4		x	0.05
Chromium (VI)	*18540-29-9*			*0.0009*
Diethyl phthalate	84-66-2		x	5

IPCS = International Programme on Chemical Safety; CICAD = Concise International Chemical Assessment Documents

[a] Tolerable Daily Intake (TDI): 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.

Table G-2d. Chemicals reported to be detected in flowback or produced water, with available less-than-chronic RfVs and OSFs.

Chemicals are ranked by PPRTV subchronic reference dose (sRfD). The "--" symbol indicates that no value was available from the sources consulted. Additionally, an "x" indicates the availability of measured concentration data in flowback or produced water (see Appendix E) and physicochemical properties data from EPI Suite™ (see Appendix C). Italicized chemicals are found in both fracturing fluids and flowback/produced water.

Chemical name	CASRN	Concen-tration data available	Physico-chemical data available	PPRTV	ATSDR	
				sRfD[a] (mg/kg-day)	Acute oral MRL[b] (mg/kg-day)	Intermediate oral MRL[c] (mg/kg-day)
Aldrin	309-00-2		x	0.00004	0.002	--
Antimony	7440-36-0	x		0.0004	--	--
Vanadium	7440-62-2	x		0.0007	--	0.01
Lithium	7439-93-2	x		0.002	--	--
Cobalt	7440-48-4	x		0.003	--	0.01
2-Methylnaphthalene	91-57-6	x	x	0.004	--	--
Methyl bromide	74-83-9		x	0.005	--	0.003
Bromodichloromethane	75-27-4		x	0.008	0.04	--
1,2,3-Trichlorobenzene	87-61-6		x	0.008	--	--
Benzene	*71-43-2*	*x*	*x*	*0.01*	--	--
p-Cresol	106-44-5	x	x	0.02	--	--
Bromoform	75-25-2		x	0.03	0.7	0.2
Ethylbenzene	*100-41-4*	*x*	*x*	*0.05*	--	*0.4*
2,4-Dimethylphenol	105-67-9	x	x	0.05	--	--
Chlorodibromomethane	124-48-1		x	0.07	0.1	--
1,2,4-Trichlorobenzene	120-82-1		x	0.09	--	0.1
Butylbenzene	104-51-8		x	0.1	--	--
Benzyl alcohol	100-51-6	x	x	0.3	--	--
Pyrene	129-00-0	x	x	0.3	--	--
Xylenes	*1330-20-7*	*x*	*x*	*0.4*	*1*	*0.4*
Iron	*7439-89-6*	*x*		*0.7*	--	--
Toluene	*108-88-3*	*x*	*x*	*0.8*	*0.8*	*0.02*
Formic acid	*64-18-6*		*x*	*0.9*	--	--
1,2-Propylene glycol	*57-55-6*		*x*	*20*	--	--

Chemical name	CASRN	Concen-tration data available	Physico-chemical data available	PPRTV	ATSDR	
				sRfD[a] (mg/kg-day)	Acute oral MRL[b] (mg/kg-day)	Intermediate oral MRL[c] (mg/kg-day)
Acrolein	*107-02-8*		*x*	--	--	*0.004*
1,4-Dioxane	*123-91-1*	*x*	*x*	--	*5*	*0.5*
Ethylene glycol	*107-21-1*		*x*	--	*0.8*	*0.8*
Di(2-ethylhexyl) phthalate	*117-81-7*	*x*	*x*	--	--	*0.1*
Naphthalene	*91-20-3*	*x*	*x*	--	*0.6*	*0.6*
Phenol	*108-95-2*	*x*	*x*	--	*1*	--
Acetone	*67-64-1*	*x*	*x*	--	--	*2*
Arsenic	*7440-38-2*	*x*		--	*0.005*	--
Chromium (VI)	*18540-29-9*			--	--	*0.005*
Copper	*7440-50-8*	*x*		--	*0.01*	*0.01*
Zinc	*7440-66-6*	*x*		--	--	*0.3*
Aluminum	*7429-90-5*	*x*		--	--	*1*
Acrylonitrile	107-13-1		x	--	0.1	0.01
Dioctyl phthalate	117-84-0	x	x	--	3	0.4
Tetrachloroethylene	127-18-4		x	--	0.008	0.008
Fluoranthene	206-44-0	x	x	0.1	--	0.4
beta-Hexachlorocyclohexane	319-85-7		x	--	0.05	0.0006
Lindane	58-89-9		x	--	0.003	0.00001
Dieldrin	60-57-1		x	--	--	0.0001
Chloroform	67-66-3	x	x	--	0.3	0.1
Strontium	7440-24-6	x		--	--	2
Tin	7440-31-5	x		--	--	0.3
Barium	7440-39-3	x		--	--	0.2
Boron	7440-42-8	x		--	0.2	0.2
Cadmium	7440-43-9	x		--	--	0.0005
Carbon disulfide	75-15-0	x	x	--	0.01	--
Heptachlor	76-44-8		x	--	0.0006	0.0001
Phosphorus	7723-14-0	x		--	--	0.0002

Chemical name	CASRN	Concen-tration data available	Physico-chemical data available	PPRTV	ATSDR	
				sRfD[a] (mg/kg-day)	Acute oral MRL[b] (mg/kg-day)	Intermediate oral MRL[c] (mg/kg-day)
Diethyl phthalate	84-66-2		x	--	7	6
Dibutyl phthalate	84-74-2	x	x	--	0.5	--
Fluorene	86-73-7	x	x	--	--	0.4
Dichloromethane	*75-09-2*		*x*	--	*0.2*	--

[a] Reference dose (RfD): 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 no observed-adverse-effect level (NOAEL), lowest observed-adverse-effect level (LOAEL), or benchmark dose (BMD), with uncertainty factors generally applied to reflect limitations of the data used. The RfD is generally used in the EPA's noncancer health assessments. Subchronic RfD (sRFD): Duration of exposure is up to 10% of an average lifespan.

[b] Minimum risk level (MRL): An ATSDR 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), noncancerous 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. Acute MRL: Duration of exposure is 1 to 14 days.

[c] Minimum risk level (MRL): An ATSDR 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), noncancerous 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. Intermediate MRL: Duration of exposure is >14 to 364 days.

G.4. References for Appendix G

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Appendix H

Description of EPA Hydraulic Fracturing Study Publications Cited in This Assessment

Appendix H. Description of EPA Hydraulic Fracturing Study Publications Cited in This Assessment

Table H-1. Titles, descriptions, and citations for EPA hydraulic fracturing study publications cited in this assessment.

Research project	Description	Citations
Analysis of existing data		
Literature Review	Review and assessment of existing papers and reports, focusing on peer-reviewed literature	Literature review is incorporated into this document.
Spills Database Analysis	Characterization of hydraulic fracturing-related spills using information obtained from selected state and industry data sources	U.S. EPA (U.S. Environmental Protection Agency). (2015). Review of state and industry spill data: characterization of hydraulic fracturing-related spills [EPA Report]. (EPA/601/R-14/001). Washington, D.C.: Office of Research and Development, U.S. Environmental Protection Agency.
Service Company Analysis	Analysis of information provided by nine hydraulic fracturing service companies in response to a September 2010 information request on hydraulic fracturing operations	Analysis of data received is incorporated into this document.[1]
Well File Review	Analysis of information provided by nine oil and gas operators in response to an August 2011 information request for 350 well files	U.S. EPA (U.S. Environmental Protection Agency). (2015). Review of well operator files for hydraulically fractured oil and gas production wells: Well design and construction [EPA Report]. (EPA/601/R-14/002). Washington, D.C.: Office of Research and Development, U.S. Environmental Protection Agency. Analysis of data received is also incorporated into this document.[2]

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Research project	Description	Citations
FracFocus Analysis	Analysis of data compiled from FracFocus 1.0, the national hydraulic fracturing chemical registry operated by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission	U.S. EPA (U.S. Environmental Protection Agency). (2015). Analysis of hydraulic fracturing fluid data from the FracFocus chemical disclosure registry 1.0 [EPA Report]. (EPA/601/R-14/003). Washington, D.C.: Office of Research and Development, U.S. Environmental Protection Agency. http://www2.epa.gov/hfstudy/analysis-hydraulic-fracturing-fluid-data-fracfocus-chemical-disclosure-registry-1-pdf U.S. EPA (U.S. Environmental Protection Agency). (2015). Analysis of hydraulic fracturing fluid data from the FracFocus chemical disclosure registry 1.0: project database. Washington, D.C.: U.S. Environmental Protection Agency, Office of Research and Development. U.S. EPA (U.S. Environmental Protection Agency). (2015). Analysis of hydraulic fracturing fluid data from the FracFocus chemical disclosure registry 1.0: Data management and quality assessment report [EPA Report]. (EPA/601/R-14/006). Washington, D.C.: U.S. Environmental Protection Agency, Office of Research and Development. http://www2.epa.gov/sites/production/files/2015-03/documents/fracfocus_data_management_report_final_032015_508.pdf

Research project	Description	Citations
Scenario evaluations		
Subsurface Migration Modeling	Numerical modeling of subsurface fluid migration scenarios that explore the potential for fluids, including liquids and gases to move from the fractured zone to drinking water aquifers	Kim, J; Moridis, GJ. (2013). Development of the T+M coupled flow–geomechanical simulator to describe fracture propagation and coupled flow–thermal–geomechanical processes in tight/shale gas systems. Computers and Geosciences 60: 184-198. http://dx.doi.org/10.1016/j.cageo.2013.04.023 Kim, J; Moridis, GJ. (In Press). Numerical analysis of fracture propagation during hydraulic fracturing operations in shale gas systems. International Journal of Rock Mechanics and Mining Sciences. Kim, J; Um, ES; Moridis, GJ. (2014). Fracture Propagation, Fluid Flow, and Geomechanics of Water-Based Hydraulic Fracturing in Shale Gas Systems and Electromagnetic Geophysical Monitoring of Fluid Migration. SPE Hydraulic Fracturing Technology Conference, The Woodlands, Texas, USA. http://dx.doi.org/10.2118/168578-MS Reagan, MT; Moridis, GJ; Johnson, JN; Keen, ND. (2015). Numerical simulation of the environmental impact of hydraulic fracturing of tight/shale gas reservoirs on near-surface groundwater: background, base cases, shallow reservoirs, short-term gas and water transport. Water Resour Res 51: 1-31. http://dx.doi.org/10.1002/2014WR016086 Rutqvist, J; Rinaldi, AP; Cappa, F; Moridis, GJ. (2013). Modeling of fault reactivation and induced seismicity during hydraulic fracturing of shale-gas reservoirs. Journal of Petroleum Science and Engineering 107: 31-44. http://dx.doi.org/10.1016/j.petrol.2013.04.023 Rutqvist, J; Rinaldi, AP; Cappa, F; Moridis, GJ. (2015). Modeling of fault activation and seismicity by injection directly into a fault zone associated with hydraulic fracturing of shale-gas reservoirs. Journal of Petroleum Science and Engineering 127: 377-386. http://dx.doi.org/10.1016/j.petrol.2015.01.019
Surface Water Modeling	Modeling of concentrations of selected chemicals at public water supplies downstream from wastewater treatment facilities that discharge treated hydraulic fracturing wastewater to surface waters	Weaver, JW; Xu, J; Mravik, SC. (In Press) Scenario analysis of the impact on drinking water intakes from bromide in the discharge of treated oil and gas waste water. J Environ Eng.

Research project	Description	Citations
Water Availability Modeling	Assessment and modeling of current and future scenarios exploring the impact of water usage for hydraulic fracturing on drinking water availability in the Upper Colorado River Basin and the Susquehanna River Basin	U.S. EPA (U.S. Environmental Protection Agency). (2015). Case study analysis of the impacts of water acquisition for hydraulic fracturing on local water availability [EPA Report]. (EPA/600/R-14/179). Washington, D.C.
Laboratory studies		
Source Apportionment Studies	Identification and quantification of the source(s) of high bromide and chloride concentrations at public water supply intakes downstream from wastewater treatment plants discharging treated hydraulic fracturing wastewater to surface waters	U.S. EPA (U.S. Environmental Protection Agency). (2015). Sources contributing bromide and inorganic species to drinking water intakes on the Allegheny river in western Pennsylvania [EPA Report]. (EPA/600/R-14/430). Washington, D.C.
Analytical Method Development	Development of analytical methods for selected chemicals found in hydraulic fracturing fluids or wastewater	DeArmond, PD; DiGoregorio, AL. (2013). Characterization of liquid chromatography-tandem mass spectrometry method for the determination of acrylamide in complex environmental samples. Anal Bioanal Chem 405: 4159-4166. http://dx.doi.org/10.1007/s00216-013-6822-4 DeArmond, PD; DiGoregorio, AL. (2013). Rapid liquid chromatography-tandem mass spectrometry-based method for the analysis of alcohol ethoxylates and alkylphenol ethoxylates in environmental samples. J Chromatogr A 1305: 154-163. http://dx.doi.org/10.1016/j.chroma.2013.07.017

Research project	Description	Citations
Analytical Method Development (cont.)	Development of analytical methods for selected chemicals found in hydraulic fracturing fluids or wastewater (cont.)	U.S. EPA (U.S. Environmental Protection Agency). (2014). Development of rapid radiochemical method for gross alpha and gross beta activity concentration in flowback and produced waters from hydraulic fracturing operations [EPA Report]. (EPA/600/R-14/107). Washington, D.C. http://www2.epa.gov/hfstudy/development-rapid-radiochemical-method-gross-alpha-and-gross-beta-activity-concentration U.S. EPA (U.S. Environmental Protection Agency). (2014). The verification of a method for detecting and quantifying diethylene glycol, triethylene glycol, tetraethylene glycol, 2-butoxyethanol and 2-methoxyethanol in ground and surface waters [EPA Report]. (EPA/600/R-14/008). Washington, D.C. http://www2.epa.gov/hfstudy/verification-method-detecting-and-quantifying-diethylene-glycol-triethylene-glycol
Retrospective case studies *Investigations of whether reported drinking water impacts may be associated with or caused by hydraulic fracturing activities*		
Las Animas and Huerfano Counties, Colorado	Investigation of potential drinking water impacts from coalbed methane extraction in the Raton Basin	U.S. EPA (U.S. Environmental Protection Agency). (2015). Retrospective case study in the Raton Basin, Colorado: study of the potential impacts of hydraulic fracturing on drinking water resources [EPA Report]. (EPA 600/R-14/091). Washington, D.C.
Dunn County, North Dakota	Investigation of potential drinking water impacts from a well blowout during hydraulic fracturing for oil in the Bakken Shale	U.S. EPA (U.S. Environmental Protection Agency). (2015). Retrospective case study in Killdeer, North Dakota: study of the potential impacts of hydraulic fracturing on drinking water resources [EPA Report]. (EPA 600/R-14/103). Washington, D.C.
Bradford County, Pennsylvania	Investigation of potential drinking water impacts from shale gas development in the Marcellus Shale	U.S. EPA (U.S. Environmental Protection Agency). (2014). Retrospective case study in northeastern Pennsylvania: study of the potential impacts of hydraulic fracturing on drinking water resources [EPA Report]. (EPA 600/R-14/088). Washington, D.C.
Washington County, Pennsylvania	Investigation of potential drinking water impacts from shale gas development in the Marcellus Shale	U.S. EPA (U.S. Environmental Protection Agency). (2015). Retrospective case study in southwestern Pennsylvania: study of the potential impacts of hydraulic fracturing on drinking water resources [EPA Report]. (EPA 600/R-14/084). Washington, D.C.

Research project	Description	Citations
Wise County, Texas	Investigation of potential drinking water impacts from shale gas development in the Barnett Shale	U.S. EPA (U.S. Environmental Protection Agency). (2015). Retrospective case study in Wise County, Texas: study of the potential impacts of hydraulic fracturing on drinking water resources [EPA Report]. (EPA 600/R-14/090). Washington, D.C.

Appendix I

Unit Conversions

Appendix I. Unit Conversions

LENGTH

1 in (inch)	=	2.54 cm (centimeters)
		25.4 mm (millimeters)
		25,400 µm (microns)
1 ft (foot)	=	0.3048 m (meters)
		30.48 cm
1 mi (mile)	=	5,280 ft
		1,609.344 m
		1.6093 km (kilometers)

AREA

1 ft^2 (square foot)	=	0.0929 m^2 (square meters)
1 acre	=	43,560 ft^2
	=	0.0016 mi^2 (square miles)
	=	0.4047 ha (hectares)
	=	4,046.825 m^2
1 mi^2	=	639.9974 ac
	=	258.9988 ha
	=	2.5899 km^2 (square kilometers)

MASS

1 lb (pound)	=	453.5924 g (grams)
	=	0.4536 kg (kilograms)
1 ton (short ton, U.S.)	=	2,000 lbs
	=	907.185 kg
	=	0.9072 metric tons

VOLUME OR CAPACITY (LIQUID MEASURE)

1 bbl (barrel)	=	42 gal (gallons, U.S.)
	=	158.9873 L (liters)
1 gal	=	231 in^3 (cubic inches)
	=	0.1337 ft^3 (cubic feet)
	=	3.7854 L
	=	0.0039 m^3 (cubic meters)
	=	3.7854×10^{-9} Mm^3 (million cubic meters)
1 Mgal (million gallons)	=	1.3368×10^5 ft^3
1 ft^3	=	1,728 in^3
	=	7.4805 gal
	=	28.3169 L
	=	0.0283 m^3
1 mi^3 (cubic mile)	=	4.1682 km^3 (cubic kilometers)

CONCENTRATION

1 mg/L (milligram per liter)	=	1.0×10^{-6} kg/L (kilograms per liter)
	=	1.0×10^{-3} g/L (grams per liter)
	=	1,000 μg/L (micrograms per liter)
	=	1.001 ppm (parts per million)
	=	8.3454×10^{-6} lb/gal (pounds per gallon)
	=	6.2428×10^{-5} lb/ft^3 (pounds per cubic foot)

SPEED

1 mi/hr (mile per hour)	=	$1.466\overline{6}$ ft/s (feet per second)
	=	0.4470 m/s (meters per second)

DENSITY

1 g/mL	=	1,000 g/L
	=	1.0×10^6 mg/L

VOLUME PER UNIT TIME

1 ft^3/s (cubic foot per second)	=	448.8312 gpm (gallons per minute)
	=	0.6163 Mgpd (million gallons per day)
	=	28.3169 L/s (liters per second)
	=	0.0283 m^3/s (cubic meters per second)
1 ft^3/day (cubic feet per day)	=	0.0052 gpm
	=	7.4805 gpd
	=	0.0283 m^3/d (cubic meters per day)
1 bbl/day (barrel per day)	=	42 gpd
	=	158.9873 L/d (liters per day)

PRESSURE

1 psi (pound per square inch)	=	6,894.7573 Pa (pascals)
	=	0.068 atm (standard atmospheres)

RADIATION

Activity

1 Ci (curie)	=	3.7×10^{10} decays per second
1 Bq (becquerel)	≈	2.703×10^{-11} Ci
	≈	27.027 pCi (picocuries)
1 pCi	=	0.037 Bq
	=	0.037 decays per second
	=	2.22 decays per minute

Exposure

1 rem (röentgen equivalent in man)	=	0.01 Sv (sieverts)
1 Sv	=	1 J/kg (joule per kilogram)

ELECTRIC CONDUCTANCE

1 S (siemen)	=	1 Ω^{-1} (reciprocal of resistance)
	=	1 A/V (ampere per volt)
	=	1 $kg^{-1} \bullet m^{-2} \bullet s^3 \bullet A^2$ (second cubed- ampere squared per kilogram-square meter)
	=	1.0×10^6 μS (microsiemens)

TEMPERATURE

[°F (degrees, Fahrenheit) - 32] × 5/9 = °C (degrees, Celsius)

PERMEABILITY

1 cm^2	=	1.0×10^{-4} m^2
	≈	1.0×10^{8} D (darcys)
1 D	≈	1.0×10^{-12} m^2
	=	1,000 mD (millidarcys)
	=	1.0×10^{6} μD (microdarcys)

Appendix J

Glossary

Appendix J. Glossary

J.1. Glossary Terms and Definitions

Acid mine drainage: Flow of water from areas that have been mined for coal or other mineral ores. The water has a low pH because of its contact with sulfur-bearing material and is harmful to aquatic organisms. (U.S. EPA, 2013d)

Additive: A single chemical or chemical mixture designed to serve a specific purpose in the hydraulic fracturing fluid.[1]

Adsorption: Adhesion of molecules of gas, liquid, or dissolved solids to a surface. (U.S. EPA, 2013d)

Advection: A mechanism for moving chemicals in flowing water, where a chemical moves along with the flow of the water itself.

Aeration: A process that promotes biological degradation of organic matter in water. The process may be passive (as when waste is exposed to air) or active (as when a mixing or bubbling device introduces the air). (U.S. EPA, 2013d)

Aerobic mesophiles: Microorganisms that use oxygen for energy production and are tolerant of moderate temperatures.

Analyte: The element, ion, or compound that an analysis seeks to identify; the compound of interest. (U.S. EPA, 2013d)

Annulus: Refers to either the space between the casing of a well and the wellbore or the space between any two strings of tubing or casing. (U.S. EPA, 2013d)

API number: A unique identifying number for all oil and gas wells drilled in the United States. The system was developed by the American Petroleum Institute. (Oil and Gas Mineral Services, 2010)

Aquifer: An underground geological formation, or group of formations, containing water. A source of ground water for wells and springs. (U.S. EPA, 2013d)

Base fluid: The fluid into which additives and proppants are mixed to formulate a hydraulic fracturing fluid.

Basin: A depression in the crust of the earth, caused by plate tectonic activity and subsidence, in which sediments accumulate. Sedimentary basins vary from bowl-shaped to elongated troughs. Basins can be bounded by faults. Rift basins are commonly symmetrical; basins along continental margins tend to be asymmetrical. If rich hydrocarbon source rocks occur in combination with appropriate depth and duration of burial, then a petroleum system can develop within the basin.

[1] Definitions that have no associated citation in this glossary were developed for this assessment.

Most basins contain some amount of shale, thus providing opportunities for shale gas exploration and production. (Schlumberger, 2014)

Biogenic: Methane that is produced in shallower formations by bacterial activity in anaerobic conditions. It is the ultimate dissimilation product of microbially mediated reactions of organic molecules.

Blowout preventer (BOP): 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)

Brackish water: Mixed fresh and salt waters. Used here to qualitatively refer to water that contains higher total dissolved solids (TDS) than that typically used for fresh drinking water.

BTEX: An acronym for benzene, toluene, ethylbenzene, and xylenes. These chemicals are a group of single ringed aromatic hydrocarbon based on the benzene structure. These compounds are found in petroleum and are of specific importance because of their health effects.

Caliper log: A log that is used to check for any wellbore irregularities. It is run prior to primary cementing as a means of calculating the amount of cement needed. Also run in conjunction with other open hole logs for log corrections or run on cased holes to evaluate metal loss. (NYSDEC, 2011)

Capillarity: The action by which the surface of a liquid where it is in contact with a solid is elevated or depressed depending on the relative attraction of the molecules of the liquid for each other and for those of the solid. 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. (Adapted from Dake, 1978)

Casing: Steel pipe that is lowered into a wellbore. Casing extends from the bottom of the hole to the surface. (Schlumberger, 2014)

Casing inspection logs: An in situ record of casing thickness and integrity, to determine whether and to what extent the casing has undergone corrosion. The term refers to an individual measurement, or a combination of measurements using acoustic, electrical, and mechanical techniques, to evaluate the casing thickness and other parameters. The log is usually presented with the basic measurements and an estimate of metal loss. It was first introduced in the early 1960s. Today the terms casing-evaluation log and pipe-inspection log are used synonymously. (Schlumberger, 2014)

Cation exchange capacity: The total amount of cations (positively charged ions) that a soil can hold.

Cement: Material used to support and seal the well casing to the rock formations exposed in the borehole. Cement also protects the casing from corrosion and prevents movement of injectate up the borehole. (U.S. EPA, 2013d)

Cement squeeze: A remedial cementing operation designed to force cement into leak paths in wellbore tubulars. The required squeeze pressure is achieved by carefully controlling pump pressure. Squeeze cementing operations may be performed to repair poor primary cement jobs, isolate perforations, or repair damaged casing or liner. (Schlumberger, 2014)

Centralized waste treatment facility (CWT): any facility that treats (for disposal, recycling or recovery of material) any hazardous or non-hazardous industrial wastes, hazardous or non-hazardous industrial wastewater, and/or used material received from off-site. (U.S. EPA, 2012b)

Coalbed methane: Methane contained in coal seams. A coal seam is a layer or stratum of coal parallel to the rock stratification. (U.S. EPA, 2013d)

Collapse pressure: The pressure at which a tube, or vessel, will catastrophically deform as a result of differential pressure acting from outside to inside of the vessel or tube. (Schlumberger, 2014)

Collar: A threaded coupling used to join two lengths of pipe such as production tubing, casing, or liner. The type of thread and style of collar varies with the specifications and manufacturer of the tubing. (Schlumberger, 2014)

Combination truck: A truck tractor or a truck tractor pulling any number of trailers. (U.S. Department of Transportation, 2012)

Community water systems: Public water systems that supply water to the same population year-round. (U.S. EPA, 2013c)

Completion: 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.

Complexation: 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.

Compressive strength: Measure of the ability of a substance to withstand compression. (NYSDEC, 2011)

Conductor casing: This large diameter casing is usually the first string of casing in a well. It is set or driven into the unconsolidated material where the well will be drilled to keep the loose material from caving in. (NYSDEC, 2011)

Confidential business information (CBI): Information that contains trade secrets, commercial or financial information, or other information that has been claimed as confidential by the submitter. The EPA has special procedures for handling such information. (U.S. EPA, 2013d)

Contaminant: A substance that is either present in an environment where it does not belong or is present at levels that might cause harmful (adverse) health effects. (U.S. EPA, 2013d)

Conventional reservoir: A reservoir in which buoyant forces keep hydrocarbons in place below a sealing caprock. Reservoir and fluid characteristics of conventional reservoirs typically permit oil or natural gas to flow readily into wellbores. The term is used to make a distinction from shale and other unconventional reservoirs, in which gas might be distributed throughout the reservoir at the basin scale, and in which buoyant forces or the influence of a water column on the location of hydrocarbons within the reservoir are not significant. (Schlumberger, 2014)

Crosslinked gels: linear gels that are linked together by chemicals called crosslinkers, which may link two or more chains together.

Crude oil: A general term for unrefined petroleum or liquid petroleum. (Schlumberger, 2014)

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

Cumulative water use/cumulative water: Refers to the amount of water used or consumed by all hydraulic fracturing wells in a given area per year.

Cyclical stress: Refers to stress caused by frequent or rapid changes in temperature or pressure.

Deviated well: Any non-horizontal well in which the well bottom is intentionally located at a distance (e.g., hundreds of feet) laterally from the wellhead.

Discharge: Any emission (other than natural seepage), intentional or unintentional. Includes, but is not limited to, spilling, leaking, pumping, pouring, emitting, emptying, or dumping. (U.S. EPA, 2013d)

Disinfection byproduct (DBP): A compound formed by the reaction of a disinfectant such as chlorine with organic material in the water supply. (U.S. EPA, 2013d)

Domestic water use: Includes indoor and outdoor water uses at residences, and includes uses such as drinking, food preparation, bathing, washing clothes and dishes, flushing toilets, watering lawns and gardens, and maintaining pools. (USGS, 2015)

Drill bit: The tool used to crush or cut rock. Most bits work by scraping or crushing the rock as part of a rotational motion, while some bits work by pounding the rock vertically. (Schlumberger, 2014)

Drill collar: A component of a drill string that provides weight on the bit for drilling. Drill collars are thick-walled tubular pieces machined from solid bars of steel, usually plain carbon steel but sometimes of nonmagnetic nickel-copper alloy or other nonmagnetic premium alloys. (Schlumberger, 2014)

Drill cuttings: Ground rock produced by the drilling process.

Drill string: The combination of the drillpipe, the bottomhole assembly, and any other tools used to make the drill bit turn at the bottom of the wellbore. (Schlumberger, 2014)

Drilling fluid: Any of a number of liquid and gaseous fluids and mixtures of fluids and solids used when drilling boreholes. (Adapted from Schlumberger, 2014)

Drinking water resource: Any body of ground water or surface water that now serves, or in the future could serve, as a source of drinking water for public or private use (U.S. EPA, 2013d)

Dry gas: Refers to natural gas that occurs in the absence of liquid hydrocarbons. (Adapted from Schlumberger, 2014)

Effluent: Waste material being discharged into the environment, either treated or untreated. (U.S. EPA, 2013d)

Facultative anaerobes: Microorganisms that can use oxygen for energy production if it is present in their environment, but can also use alternatives for energy production if no oxygen is present.

Fault: A fracture or fracture zone along which there has been displacement of the sides relative to each other. (NYSDEC, 2011)

Field: Area of oil and gas production with at least one common reservoir for the entire area. (Oil and Gas Mineral Services, 2010)

Flowback: The term is defined multiple ways in the literature. In general, it is either fluids predominantly containing hydraulic fracturing fluid that return from a well to the surface or a process used to prepare the well for production.

Fluid: A substance that flows when exposed to an external pressure; fluids include both liquids and gases.

Fluid formulation: The entire suite of chemicals, proppant, and base fluid injected into a well during hydraulic fracturing. (U.S. EPA, 2013d)

Formation: A body of earth material with distinctive and characteristic properties and a degree of homogeneity in its physical properties. (U.S. EPA, 2013d)

Formation packer: 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 casing and formation, preventing migration of fluids.

Formation fluid: Fluid that occurs naturally within the pores of rock. These fluids consist primarily of water, with varying concentrations of total dissolved solids, but may also contain oil or gas. Sometimes referred to as native fluids, native brines, or reservoir fluids.

FracFocus Registry: A registry for oil and gas well operators to disclose information about hydraulic fracturing well locations, and water and chemical use during hydraulic fracturing

operations developed by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission.

Fracture: A crack or breakage surface within a rock.

Fracture geometry: Refers to characteristics of the fracture such as height and aperture (width).

Fresh water: Qualitatively refers to water with relatively low TDS that is most readily available for drinking water currently.

Gelled fluids: Fracturing fluids that are usually water-based with added gels to increase the fluid viscosity to aid in the transport of proppants. (Spellman, 2012; Gupta and Valkó, 2007)

Ground water: In the broadest sense, all subsurface water; more commonly that part of the subsurface water in the saturated zone. (Solley et al., 1998)

Halite: A soft, soluble evaporate mineral commonly known as salt or rock salt. Can be critical in forming hydrocarbon traps and seals because it tends to flow rather than fracture during deformation, thus preventing hydrocarbons from leaking out of a trap even during and after some types of deformation. (Schlumberger, 2014)

Hazard evaluation: A component of risk assessment that involves gathering and evaluating data on the types of health injuries or diseases (e.g., cancer) that may be produced by a chemical and on the conditions of exposure under which such health effects are produced.

Hazard identification: A process for determining if a chemical or a microbe can cause adverse health effects in humans and what those effects might be. (U.S. EPA, 2013d)

Henry's law constant: Ratio of a chemical's vapor pressure in the atmosphere to its solubility in water. The higher the Henry's law constant, the more volatile the compound will be from water. (NYSDEC, 2011)

Horizontal drilling: Drilling a portion of a well horizontally to expose more of the formation surface area to the wellbore. (Oil and Gas Mineral Services, 2010)

Horizontal well: A well that is drilled vertically up 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.

Hydraulic fracturing: A stimulation technique used to increase production of oil and gas. Hydraulic fracturing involves the injection of fluids under pressures great enough to fracture the oil- and gas-production formations. (U.S. EPA, 2011a)

Hydraulic fracturing fluids: Engineered fluids, typically consisting of a base fluid, additives, and proppant, that are pumped under high pressure into the well to create and hold open fractures in the formation.

Hydraulic fracturing wastewater: Flowback and 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.

Hydraulic fracturing water cycle: The cycle of water in the hydraulic fracturing process, encompassing the acquisition of water, chemical mixing of the fracturing fluid, injection of the fluid into the formation, the production and management of flowback and produced water, and the ultimate treatment and disposal of hydraulic fracturing wastewaters.

Hydraulic gradient: Slope of a water table or potentiometric surface. More specifically, change in the hydraulic head per unit of distance in the direction of the maximum rate of decrease. (U.S. EPA, 2013d)

Hydrocarbon: An organic compound containing only hydrogen and carbon, often occurring in petroleum, natural gas, and coal. (U.S. EPA, 2013d)

Hydrostatic pressure: The pressure exerted by a column of fluid at a given depth.

Imbibition: The displacement of a non-wet fluid (i.e., gas) by a wet fluid (typically water). (Adapted from Dake, 1978)

Immiscible: The chemical property in which two or more liquids or phases are incapable of attaining homogeneity. (U.S. EPA, 2013d)

Impact: Any observed change in the quality or quantity of drinking water resources, regardless of severity, that results from a mechanism.

Impact, potential: Any change in the quality or quantity of drinking water resources that could logically occur, but has not yet been observed, as the result of a mechanism or potential mechanism.

Induced fracture: A fracture created during hydraulic fracturing.

Injection well: A well into which fluids are being injected (40 CFR 144.3).

Integrated risk information system (IRIS): An electronic database that contains the EPA's latest descriptive and quantitative regulatory information about chemical constituents. Files on chemicals maintained in IRIS contain information related to both noncarcinogenic and carcinogenic health effects. (U.S. EPA, 2013d)

Intermediate casing: Casing that seals off intermediate depths and geologic formations that may have considerably different reservoir pressures than deeper zones to be drilled. (Devereux, 1998; Baker, 1979)

Karst: A type of topography that results from dissolution and collapse of carbonate rocks, such as limestone, dolomite, and gypsum, and that is characterized by closed depressions or sinkholes, caves, and underground drainage. (Solley et al., 1998)

Kill fluid: A weighted fluid with a density that is sufficient to overcome the formation pressure and prevent fluids from flowing up the wellbore.

Large truck: A truck with a gross vehicle weight rating greater than 10,000 pounds. (U.S. Department of Transportation, 2012)

Lateral: A horizontal section of a well.

Leakoff: The fraction of the injected fluid that infiltrates into the formation (e.g., through an existing natural fissure) and is not recovered during production.

Linear gel: a series of chemicals linked together so that they form a chain.

Liner: A casing string that does not extend to the top of the wellbore, but instead is anchored or suspended from inside the bottom of the previous casing string. (Schlumberger, 2014)

Lost cement: Refers to a failure of the cement to be circulated back to the surface, indicating that the cement has escaped into the formation.

Lowest-observable-adverse effect level (LOAEL): 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.

Maximum allowable daily level (MADL): 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.

Maximum contaminant level (MCL): The highest level of a contaminant that is allowed in drinking water. MCLs are enforceable standards. (U.S. EPA, 2014b)

Mechanical integrity: The absence of significant leakage within the injection tubing, casing, or packer (known as internal mechanical integrity), or outside of the casing (known as external mechanical integrity). (U.S. EPA, 2013d)

Mechanism: A means or series of events by which an activity within the hydraulic fracturing water cycle has been observed to change the quality or quantity of drinking water resources.

Mechanism, potential: A means or series of events by which hydraulic fracturing activities could logically or theoretically (for instance, based on modeling) change the quality or quantity of drinking water resources but one that has not yet been observed.

Mechanism, suspected: A means or series of events by which hydraulic fracturing activities could logically have resulted in an observed change in the quality or quantity of drinking water resources. Available evidence may or may not be sufficient to determine if it is the *only* mechanism that caused the observed change.

Metropolitan combined statistical area: A core urban area of 50,000 or more people. (U.S. Census Bureau, 2013)

Microaerophiles: Microorganisms that require small amounts of oxygen for energy production.

Microannuli: Very small channels that form in the cement and that may serve as pathways for fluid migration to drinking water resources.

Micropolitan combined statistical area: An urban core of at least 10,000, but less than 50,000, people. (U.S. Census Bureau, 2013)

Microseismic monitoring: A technique to track the propagation of a hydraulic fracture as it advances through a formation. (Schlumberger, 2014)

Minimum risk level (MRL): 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), noncancerous effects. MRLs are calculated for a route of exposure (inhalation or oral) over a specified time period (acute, intermediate, or chronic).

Mobility: The ratio of effective permeability to phase viscosity. The overall mobility is a sum of the individual phase viscosities. Well productivity is directly proportional to the product of the mobility and the layer thickness product. (Schlumberger, 2014)

National Pollution Discharge Elimination System (NPDES): A national program under Section 402 of the Clean Water Act for regulation of discharges of pollutants from point sources to waters of the United States. Discharges are illegal unless authorized by an NPDES permit. (U.S. EPA, 2013d)

National Secondary Drinking Water Regulations (NSDWR): Non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water (also referred to as secondary standards). (U.S. EPA, 2014b)

Natural gas: A naturally occurring mixture of hydrocarbon and nonhydrocarbon gases in porous formations beneath the earth's surface, often in association with petroleum. The principal constituent of natural gas is methane. (Schlumberger, 2014)

Natural organic matter (NOM): Complex organic compounds that are formed from decomposing plant animal and microbial material in soil and water. (U.S. EPA, 2013d)

Non-community water systems: Water systems that supply water to at least 25 of the same people at least six months per year, but not year-round. (U.S. EPA, 2013c)

Octanol-water partition coefficient (K_{ow}): A coefficient representing the ratio of the solubility of a compound in octanol (a nonpolar solvent) to its solubility in water (a polar solvent). The higher the K_{ow}, the more nonpolar the compound. Log K_{ow} is generally used as a relative indicator of the

tendency of an organic compound to adsorb to soil. Log K_{ow} values are generally inversely related to aqueous solubility and directly proportional to molecular weight. (U.S. EPA, 2013d)

Offset well: An existing wellbore close to a proposed well that provides information for planning the proposed well. (Schlumberger, 2014)

Open hole completion: A well completion that has no casing or liner set across the reservoir formation, allowing the produced fluids to flow directly into the wellbore. (Schlumberger, 2014)

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.

Organic carbon-water partition coefficient (K_{oc}): A coefficient representing the amount of a compound that is adsorbed to soil to the amount of a compound that is dissolved in water, normalized to the total organic carbon content of the soil. The higher the K_{oc}, the more likely a compound is to adsorb to soils and sediments, and the less likely it is to migrate with water. Along with log K_{ow}, log K_{oc} is used as a relative indicator of the tendency of an organic compound to adsorb to soil.

Orphaned well: An inactive oil or gas well with no known (or financially solvent) owner.

Overburden: Material of any nature, consolidated or unconsolidated, that overlies a deposit of useful minerals or ores. (U.S. EPA, 2013d)

Packer: A device that can be run into a wellbore with a smaller initial outside diameter that then expands externally to seal the wellbore. (Schlumberger, 2014)

Pad fluid: a mixture of base fluid, typically water and additives designed to create, elongate, and enlarge fractures along the natural channels of the formation when injected under high pressure.

Partial cementing: Cementing a casing string along only a portion of its length.

Passby flow: A prescribed, low-streamflow threshold below which withdrawals are not allowed. (U.S. EPA, 2015d)

Peer review: A documented critical review of a specific major scientific and/or technical work product. Peer review is intended to uncover any technical problems or unresolved issues in a preliminary or draft work product through the use of independent experts. This information is then used to revise the draft so that the final work product will reflect sound technical information and analyses. The process of peer review enhances the scientific or technical work product so that the decision or position taken by the EPA, based on that product, has a sound and credible basis. (U.S. EPA, 2013d)

Perforation: The communication tunnel created from the casing or liner into the reservoir formation through which injected fluids and oil or gas flows. Also refers to the process of creating communication channels, e.g., via the use of a jet perforating gun.

Permeability: The ability of a material (e.g., rock or soil) to transmit fluid to move through pore spaces.

Persistence: The length of time a compound stays in the environment, once introduced. A compound may persist for less than a second or indefinitely.

Physicochemical properties: The inherent physical and chemical properties of a molecule such as boiling point, density, physical state, molecular weight, vapor pressure, etc. These properties define how a chemical interacts with its environment. (U.S. EPA, 2013d)

Play: A set of oil or gas accumulations sharing similar geologic, geographic properties, such as source rock, hydrocarbon type, and migration pathways. (Oil and Gas Mineral Services, 2010)

Poisson's ratio: A ratio of transverse-to-axial (or latitudinal-to-longitudinal) strain; characterizes how a material is deformed under pressure.

Polar molecule: A molecule with a slightly positive charge at one part of the molecule and a slightly negative charge on another. The water molecule, H2O, is an example of a polar molecule, where the molecule is slightly positive around the hydrogen atoms and negative around the oxygen atom.

Porosity: A measure of pore space, or the percentage of the material (e.g., rock or soil) volume that can be occupied by oil, gas, or water.

Produced water: Water that flows from oil and gas wells.

Production casing: The deepest casing set and serves primarily as the conduit for producing fluids, although when cemented to the wellbore, this casing can also serve to seal off other subsurface zones including ground water resources. (Devereux, 1998; Baker, 1979)

Production well: A well that is used to bring fluids (such as oil or gas) to the surface.

Production zone: Refers to the portion of a subsurface rock zone that contains oil or gas to be extracted (sometimes using hydraulic fracturing). The production zone is sometimes referred to as the target zone.

Proppant/propping agent: A granular substance (sand grains, aluminum pellets, or other material) that is carried in suspension by the fracturing fluid and that serves to keep the cracks open when fracturing fluid is withdrawn after a fracture treatment. (U.S. EPA, 2013d)

Protected ground water resource: The deepest aquifer that the state or other regulatory agency requires to be protected from fluid migration through or along wellbores.

Public water system source: The source of the surface or ground water used by a public water system, including source wells, intakes, reservoirs, infiltration galleries, and springs.

Public water systems: Water systems that provide water for human consumption from surface or ground water 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. (Safe Drinking Water Act, 2002)

Publicly owned treatment works (POTW): Any device or system used in the treatment (including recycling and reclamation) of municipal sewage or industrial wastes of a liquid nature that is owned by a state or municipality. This definition includes sewers, pipes, or other conveyances only if they convey wastewater to a POTW providing treatment. (U.S. EPA, 2013d)

Quality assurance (QA): An integrated system of management activities involving planning, implementation, documentation, assessment, reporting, and quality improvement to ensure that a process, item, or service is of the type and quality needed and expected by the customer. (U.S. EPA, 2013d)

Quality assurance project plan (QAPP): A formal document describing in comprehensive detail the necessary quality assurance procedures, quality control activities, and other technical activities that need to be implemented to ensure that the results of the work performed will satisfy the stated performance or acceptance criteria. (U.S. EPA, 2013d)

Quality management plan: A document that describes a quality system in terms of the organizational structure, policy and procedures, functional responsibilities of management and staff, lines of authority, and required interfaces for those planning, implementing, documenting, and assessing all activities conducted. (U.S. EPA, 2013d)

Radioactive tracer log: A record of the presence of tracer material placed in or around the borehole to measure fluid movement in injection wells. (Schlumberger, 2014)

Radionuclide: Radioactive particle, man-made or natural, with a distinct atomic weight number. Emits radiation in the form of alpha or beta particles, or as gamma rays. Can have a long life as soil or water pollutant. Prolonged exposure to radionuclides increases the risk of cancer. (U.S. EPA, 2013d)

Reference dose (RfD): 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.

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. Reference value is a generic term not specific to a given route of exposure.

Relative permeability: A dimensionless property allowing for 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.

Reservoir: A porous and permeable geologic formation where hydrocarbons collect under pressure over geological time.

Residuals: The solids generated or retained during the treatment of wastewater. (U.S. EPA, 2013d)

Safe Drinking Water Act (SDWA): The act designed to protect the nation's drinking water supply by establishing national drinking water standards (maximum contaminant levels or specific treatment techniques) and by regulating underground injection control wells. (U.S. EPA, 2013d)

Sandstone: A clastic sedimentary rock whose grains are predominantly sand sized. The term is commonly used to imply consolidated sand or a rock made of predominantly quartz sand, although sandstones often contain feldspar, rock fragments, mica, and numerous additional mineral grains held together with silica or another type of cement. The relatively high porosity and permeability of sandstones make them good reservoir rocks. (Schlumberger, 2014)

Science Advisory Board (SAB): A federal advisory committee that provides a balanced, expert assessment of scientific matters relevant to the EPA. An important function of the Science Advisory Board is to review EPA's technical programs and research plans. (U.S. EPA, 2013d)

Service company: A company that assists well operators by providing specialty services, including hydraulic fracturing. (U.S. EPA, 2013d)

Shale: A fine-grained, fissile, detrital sedimentary rock formed by consolidation of clay- and silt-sized particles into thin, relatively impermeable layers. (Schlumberger, 2014)

Shale gas: Natural gas generated and stored in shale.

Shale oil: Oil present in unconventional oil reservoirs that are made up of shale.

Shut-in: The process of sealing off a well by either closing the valves at the wellhead, a downhole safety valve, or a blowout preventer.

Slickwater: A type of fracturing fluid that consists mainly of water with a very low portion of additives like polymers that serve as friction reducers to reduce friction loss when pumping the fracturing fluid downhole. (Barati and Liang, 2014)

Solubility: The amount of mass of a compound that will dissolve in a unit volume of solution. (U.S. EPA, 2013d)

Sorption: 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.

Source water: Surface or ground water, or reused wastewater, acquired for use in hydraulic fracturing. (U.S. EPA, 2013d)

Spacer fluid: A fluid pumped before the cement to clean drilling mud out of the wellbore.

Spud (spud a well): To start the well drilling process by removing rock, dirt, and other sedimentary material with the drill bit. (U.S. EPA, 2013d)

Stages (frac stages): A single reservoir interval that is hydraulically stimulated in succession with other intervals.

Stimulation: Refers to (1) injecting fluids to clear the well or pore spaces near the well of drilling mud or other materials that create blockage and inhibit optimal production (i.e., matrix treatment) and (2) injecting fluid to fracture the rock to optimize the production of oil or gas.

Stray gas: Refers to the phenomenon of natural gas (primarily methane) migrating into shallow drinking water resources or to the surface.

Strings: An assembled length of steel pipe configured to suit a specific wellbore.

Subsurface formation: A mappable body of rock of distinctive rock type(s), including the rock's pore volume (i.e., the void space within a formation that fluid flow can occur, as opposed to the bulk volume which includes both pore and solid phase volume), with a unique stratigraphic position.

Surface casing: The shallowest cemented casing, with the widest diameter. Cemented surface casing generally serves as an anchor for blowout protection equipment and to seal off drinking water resources. (Baker, 1979)

Surface water: All water naturally open to the atmosphere (rivers, lakes, reservoirs, ponds, streams, impoundments, seas, estuaries, etc.). (U.S. EPA, 2013d)

Surfactant: Used during the hydraulic fracturing process to decrease liquid surface tension and improve fluid passage through the pipes. (U.S. EPA, 2013d)

Sustained casing pressure: Refers to cases when the pressure in any well annulus that is measurable at the wellhead rebuilds after it is bled down, not caused solely by temperature fluctuations or imposed by the operator. 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). (Skjerven et al., 2011)

Technically recoverable resources: The volumes of oil and natural gas that could be produced with current technology, regardless of oil and natural gas prices and production costs. (EIA, 2013)

Temperature log: A log of the temperature of the fluids in the borehole; a differential temperature log records the rate of change in temperature with depth and is sensitive to very small changes. (U.S. EPA, 2013d)

Tensile strength: The force per unit cross-sectional area required to pull a substance apart. (Schlumberger, 2014)

Thermogenic: Methane that is produced by high temperatures and pressures in deep formations over geologic timescales. Thermogenic methane is formed by the thermal breakdown, or cracking, of organic material that occurs during deep burial of sediment.

Tight oil: Oil found in relatively impermeable reservoir rock. (Schlumberger, 2014)

Total dissolved solids (TDS): The quantity of dissolved material in a given volume of water. Total dissolved solids can include salts (e.g., sodium chloride), dissolved metals, radionuclides, and dissolved organics. (U.S. EPA, 2013d)

Toxicity: The degree to which a substance or mixture of substances can harm humans or animals. Acute toxicity involves harmful effects in an organism through a single or short-term exposure. Chronic toxicity is the ability of a substance or mixture of substances to cause harmful effects over an extended period, usually upon repeated or continuous exposure, sometimes lasting for the entire life of the exposed organism. Subchronic toxicity is the ability of the substance to cause effects for more than 1 year but less than the lifetime of the exposed organism. (U.S. EPA, 2013d)

Tubing: The narrowest casing set within a completed well, either hung directly from the wellhead or secured at its bottom using a packer. Tubing is not typically cemented in the well.

Unconventional reservoir: A reservoir characterized by lower permeability than conventional reservoirs. It can be the same formation where hydrocarbons are formed and also serve as the source for hydrocarbons that migrate and accumulate in conventional reservoirs. Unconventional reservoirs can include methane-rich coalbeds and oil- and/or gas-bearing shales and tight sands.

Unconventional resource: An umbrella term for oil and natural gas that is produced by means that do not meet the criteria for conventional production. What has qualified as unconventional at any particular time is a complex function of resource characteristics, the available exploration and production technologies, the economic environment, and the scale, frequency, and duration of production from the resource. Perceptions of these factors inevitably change over time and often differ among users of the term. At present, the term is used in reference to oil and gas resources whose porosity, permeability, fluid trapping mechanism, or other characteristics differ from conventional sandstone and carbonate reservoirs. Coalbed methane, gas hydrates, shale gas, fractured reservoirs, and tight gas sands are considered unconventional resources. (Schlumberger, 2014)

Underground Injection Control (UIC): The program under the Safe Drinking Water Act that regulates the use of wells to pump fluids into the ground. (U.S. EPA, 2013d)

Unsaturated zone: The soil zone above the water table that is only partially filled by water; also referred to as the "vadose zone."

Vapor pressure: The force per unit area exerted by a vapor in an equilibrium state with its pure solid, liquid, or solution at a given temperature. Vapor pressure is a measure of a substance's

propensity to evaporate. Vapor pressure increases exponentially with an increase in temperature. (U.S. EPA, 2013d)

Vertical well: A well in which the wellbore is vertical throughout its entire length, from the wellhead at the surface to the production zone.

Viscosity: A measure of the internal friction of a fluid that provides resistance to shear within the fluid, informally referred to as how "thick" a fluid is.

Volatile: Readily vaporizable at a relatively low temperature. (U.S. EPA, 2013d)

Volatilization: The process in which a chemical leaves the liquid phase and enters the gas phase.

Wastewater treatment: Chemical, biological, and mechanical procedures applied to an industrial or municipal discharge or to any other sources of contaminated water in order to remove, reduce, or neutralize contaminants. (U.S. EPA, 2013d)

Water availability: 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.

Water consumption: 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).

Water intensity: The amount of water used per unit of energy obtained. (Nicot et al., 2014; Laurenzi and Jersey, 2013)

Water reuse: Any hydraulic fracturing wastewater that is used to offset total fresh water withdrawals for hydraulic fracturing, regardless of the level of treatment required.

Water use: Water withdrawn for a specific purpose, part or all of which may be returned to the local hydrologic cycle.

Water withdrawal: Water removed from the ground or diverted from a surface-water source for use. (Nicot et al., 2014; Laurenzi and Jersey, 2013)

Well blowout: The uncontrolled flow of fluids out of a well.

Well communication: Refers to fractures intersecting abandoned or active (producing) offset wells near the well that is being stimulated.

Well logging: A continuous measurement of physical properties in or around the well with electrically powered instruments to infer formation properties. Measurements may include electrical properties (resistivity and conductivity), sonic properties, active and passive nuclear measurements, measurements of the wellbore, pressure measurement, formation fluid sampling, sidewall coring tools, and others. Measurements may be taken via a wireline, which is a wire or cable that is used to deploy tools and instruments downhole and that transmits data to the surface. (Adapted from Schlumberger, 2014)

Well operator: A company that controls and operates oil and gas wells. (U.S. EPA, 2013d)

Well pad: A temporary drilling site, usually constructed of local materials such as sand and gravel. After the drilling operation is over, most of the pad is usually removed or plowed back into the ground. (NYSDEC, 2011)

Wellbore: The drilled hole or borehole, including the open hole or uncased portion of the well.

Wet gas: Refers to natural gas that typically contains less than 85% methane along with ethane and more complex hydrocarbons.

Wetting/nonwetting: The preferential attraction of a fluid to the surface. In typical reservoirs, water preferentially wets the surface, and gas is nonwetting. (Adapted from Dake, 1978)

Workover: Refers to any maintenance activity performed on a well that involves ceasing operations and removing the wellhead.

Young's modulus: A ratio of stress to strain that is a measure of the rigidity of a material.

J.2. References for Appendix J

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