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Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources

PROGRESS REPORT

United States Environmental Protection Agency
Office of Research and Development

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Washington, DC

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Disclaimer

Table of Contents

Table of Contents

List of Tables

List of Tables

List of Tables

List of Figures

List of Figures

List of Acronyms and Abbreviations

ADQ	Audit of data quality
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
Br-DBP	Brominated disinfection byproduct
BTEX	Benzene, toluene, ethylbenzene, and xylene
CASRN	Chemical Abstracts Service Registration Number
CBI	Confidential business information
CBM	Coalbed methane
COGCC	Colorado Oil and Gas Conservation Commission
CWT	Centralized waste treatment facility
DBP	Disinfection byproduct
DSSTox	Distributed Structure-Searchable Toxicity Database Network
FORTRAN	Formula translation
GIS	Geographic information system
GWPC	Ground Water Protection Council
HAA	Haloacetic acid
HSPF	Hydrologic Simulation Program FORTRAN
IRIS	Integrated Risk Information System
LBNL	Lawrence Berkeley National Laboratory
LOAEL	Lowest observed adverse effect levels
MCL	Maximum contaminant level
MGD	Million gallons per day
MSDS	Material Safety Data Sheet
NAS	National Academy of Sciences
NDIC	North Dakota Industrial Commission
NEMS	National Energy Modeling System
NOM	Naturally occurring organic matter
NPDES	National Pollutant Discharge Elimination System
NRC	National Response Center
NYSDEC	New York State Department of Environmental Conservation
PADEP	Pennsylvania Department of Environmental Protection
POTW	Publicly owned treatment work
PPRTV	Provisional Peer-Reviewed Toxicity Value
PWS	Public water systems
QA	Quality assurance

List of Acronyms and Abbreviations

QAPP	Quality assurance project plan
QC	Quality control
RRC	Railroad Commission of Texas
SDWA	Safe Drinking Water Act
SOP	Standard operating procedure
SRB	Susquehanna River Basin
SRBC	Susquehanna River Basin Commission
SWAT	Soil and Water Assessment Tool
TDS	Total dissolved solids
THM	Trihalomethane
TOPKAT	Toxicity Prediction by Komputer Assisted Technology
TOUGH	Transport of Unsaturated Groundwater and Heat
TSA	Technical systems audit
TSCA	Toxic Substances Control Act
UCRB	Upper Colorado River Basin
UIC	Underground injection control
US EIA	US Energy Information Administration
US EPA	US Environmental Protection Agency
US FWS	US Fish and Wildlife Service
US GAO	US Government Accountability Office
US OMB	US Office of Management and Budget
USCB	US Census Bureau
USDA	US Department of Agriculture
USGS	US Geological Survey
USHR	US House of Representatives
WWTF	Wastewater treatment facility

Executive Summary

Natural gas plays a key role in our nation's clean energy future. The United States has vast reserves of natural gas that are commercially viable as a result of advances in horizontal drilling and hydraulic fracturing technologies, which enable greater access to gas in rock formations deep underground. These advances have spurred a significant increase in the production of both natural gas and oil across the country.

Responsible development of America's oil and gas resources offers important economic, energy security, and environmental benefits. However, as the use of hydraulic fracturing has increased, so have concerns about its potential human health and environmental impacts, especially for drinking water. In response to public concern, the US House of Representatives requested that the US Environmental Protection Agency (EPA) conduct scientific research to examine the relationship between hydraulic fracturing and drinking water resources (USHR, 2009).

In 2011, the EPA began research under its *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources.* The purpose of the study is to assess the potential impacts of hydraulic fracturing on drinking water resources, if any, and to identify the driving factors that may affect the severity and frequency of such impacts. Scientists are focusing primarily on hydraulic fracturing of shale formations to extract natural gas, with some study of other oil- and gas-producing formations, including tight sands, and coalbeds. The EPA has designed the scope of the research around five stages of the hydraulic fracturing water cycle. Each stage of the cycle is associated with a primary research question:

- 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 hydraulic fracturing fluid surface spills 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 flowback and produced water (collectively referred to as "hydraulic fracturing wastewater") surface spills 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 wastewater on drinking water resources?

This report describes 18 research projects underway to answer these research questions and presents the progress made as of September 2012 for each of the projects. Information presented as part of this report cannot be used to draw conclusions about potential impacts to drinking water resources from hydraulic fracturing. The research projects are organized according to five different types of research activities: analysis of existing data, scenario evaluations, laboratory studies, toxicity assessments, and case studies.

Analysis of Existing Data

Data from multiple sources have been obtained for review and analysis. Many of the data come directly from the oil and gas industry and states with high levels of oil and gas activity. Information on the chemicals and practices used in hydraulic fracturing has been collected from nine companies that hydraulically fractured a total of 24,925 wells between September 2009 and October 2010. Additional data on chemicals and water use for hydraulic fracturing are being pulled from over 12,000 well-specific chemical disclosures in FracFocus, a national hydraulic fracturing chemical registry operated by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission. Well construction and hydraulic fracturing records provided by well operators are being reviewed for 333 oil and gas wells across the United States; data within these records are being scrutinized to assess the effectiveness of current well construction practices at containing gases and liquids before, during, and after hydraulic fracturing.

Data on causes and volumes of spills of hydraulic fracturing fluids and wastewater are being collected and reviewed from state spill databases in Colorado, New Mexico, and Pennsylvania. Similar information is being collected from the National Response Center national database of oil and chemical spills.

In addition, the EPA is reviewing scientific literature relevant to the research questions posed in this study. A *Federal Register* notice was published on November 9, 2012, requesting relevant, peer-reviewed data and published reports, including information on advances in industry practices and technologies. This body of literature will be synthesized with results from the other research projects to create a report of results.

Scenario Evaluations

Computer models are being used to identify conditions that may lead to impacts on drinking water resources from hydraulic fracturing. The EPA has identified hypothetical, but realistic, scenarios pertaining to the water acquisition, well injection, and wastewater treatment and waste disposal stages of the water cycle. Potential impacts to drinking water sources from withdrawing large volumes of water in semi-arid and humid river basins—the Upper Colorado River Basin in the west and the Susquehanna River Basin in the east—are being compared and assessed.

Additionally, complex computer models are being used to explore the possibility of subsurface gas and fluid migration from deep shale formations to overlying aquifers in six different scenarios. These scenarios include poor well construction and hydraulic communication via fractures (natural and created) and nearby existing wells. As a first step, the subsurface migration simulations will examine realistic scenarios to assess the conditions necessary for hydraulic communication rather than the probability of migration occurring.

In a separate research project, concentrations of bromide and radium at public water supply intakes located downstream from wastewater treatment facilities discharging treated hydraulic fracturing wastewater are being estimated using surface water transport models.

Laboratory Studies

Laboratory studies are largely focused on identifying potential impacts of inadequately treating hydraulic fracturing wastewater and discharging it to rivers. Experiments are being designed to test how well common wastewater treatment processes remove selected contaminants from hydraulic fracturing wastewater, including radium and other metals. Other experiments are assessing whether or not hydraulic fracturing wastewater may contribute to the formation of disinfection byproducts during common drinking water treatment processes, with particular focus on the formation of brominated disinfection byproducts, which have significant health concerns at high exposure levels.

Samples of raw hydraulic fracturing wastewater, treated wastewater, and water from rivers receiving treated hydraulic fracturing wastewater have been collected for source apportionment studies. Results from laboratory analyses of these samples are being used to develop a method for determining if treated hydraulic fracturing wastewater is contributing to high chloride and bromide levels at downstream public water supplies.

Finally, existing analytical methods for selected chemicals are being tested, modified, and verified for use in this study and by others, as needed. Methods are being modified in cases where standard methods do not exist for the low-level detection of chemicals of interest or for use in the complex matrices associated with hydraulic fracturing wastewater. Analytical methods are currently being tested and modified for several classes of chemicals, including glycols, acrylamides, ethoxylated alcohols, disinfection byproducts, radionuclides, and inorganic chemicals.

Toxicity Assessments

The EPA has identified chemicals reportedly used in hydraulic fracturing fluids from 2005 to 2011 and chemicals found in flowback and produced water. Appendix A contains tables with over 1,000 of these chemicals identified. Chemical, physical, and toxicological properties are being compiled for chemicals with known chemical structures. Existing models are being used to estimate properties in cases where information is lacking. At this time, the EPA has not made any judgment about the extent of exposure to these chemicals when used in hydraulic fracturing fluids or found in hydraulic fracturing wastewater, or their potential impacts on drinking water resources.

Case Studies

Two rounds of sampling at five case study locations in Colorado, North Dakota, Pennsylvania, and Texas have been completed. In total, water samples have been collected from over 70 domestic water wells, 15 monitoring wells, and 13 surface water sources, among others. This research will help to identify the source of any contamination that may have occurred.

The EPA continues to work with industry partners to begin research activities at potential prospective case study locations, which involve sites where the research will begin before well construction. This will allow the EPA to collect baseline water quality data in the area. Water quality will be monitored for any changes throughout drilling, injection of fracturing fluids, flowback, and production. Samples of flowback and produced water will be used for other parts of the study, such as assessing the efficacy of wastewater treatment processes at removing contaminants in hydraulic fracturing wastewater.

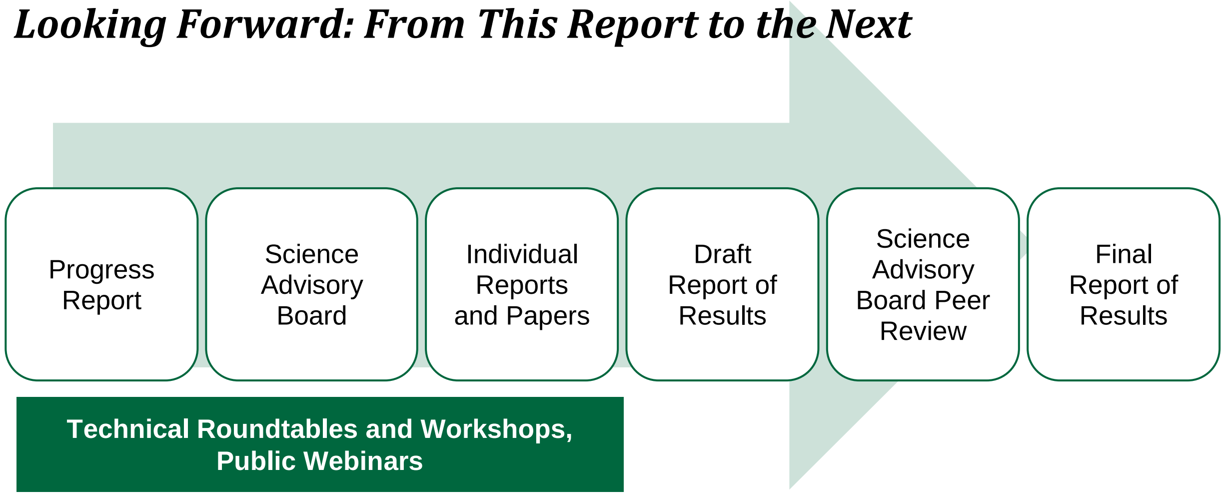
Invigorating the Research Study Through Consultation and Peer Review

The EPA is committed to conducting a study that uses the best available science, independent sources of information, and a transparent, peer-reviewed process that will ensure the validity and accuracy of the results. The agency is working in consultation with other federal agencies, state and interstate regulatory agencies, industry, non-governmental organizations, and others in the private and public sector. In addition to workshops held in 2011, stakeholders and technical experts are being engaged through technical roundtables and workshops, with the first set of roundtables held November 14–16, 2012. These activities will provide the EPA with ongoing access to a broad range of expertise and data, timely and constructive technical feedback, and updates on changes in industry practices and technologies relevant to the study. Technical roundtables and workshops will be followed by webinars for the general public and posting of summaries on the study's website. Increased stakeholder engagement will also allow the EPA to educate and inform the public of the study's goals, design, and progress.

To ensure scientifically defensible results, each research project is subjected to quality assurance and peer review activities. Specific quality assurance activities performed by the EPA make sure that the agency's environmental data are of sufficient quantity and quality to support the data's intended use. Research products, such as papers or reports, will be subjected to both internal and external peer review before publication, which make certain that the data are used appropriately. Published results from the research projects will be synthesized in a report of results that will inform the research questions associated with each stage of the hydraulic fracturing water cycle. The EPA has designated the report of results as a "Highly Influential Scientific Assessment," which will undergo peer review by the EPA's Science Advisory Board, an independent and external federal advisory committee that conducts peer reviews of significant EPA research products and activities. The EPA will seek input from individual members of an *ad hoc* expert panel convened under the auspices of the EPA Science Advisory Board. The EPA will consider feedback from the individual experts in the development of the report of results.

Ultimately, the results of this study are expected to inform the public and provide decision-makers at all levels with high-quality scientific knowledge that can be used in decision-making processes.

Looking Forward: From This Report to the Next



1. Introduction

Oil and natural gas provided more energy in the United States for residential and industrial use than any other energy source in 2010—37% and 25%, respectively (US EIA, 2011a). Advances in technology and new applications of existing techniques, as well as supportive domestic energy policy and economic developments, have recently spurred an increase in oil and gas production across a wide range of geographic regions and geologic formations in the United States. Hydraulic fracturing is a technique used to produce economically viable quantities of oil and natural gas, especially from unconventional reservoirs, such as shale, tight sands, coalbeds, and other formations. Hydraulic fracturing involves the injection of fluids under pressures great enough to fracture the oil- and gas-producing formations. The resulting fractures are held open using "proppants," such as fine grains of sand or ceramic beads, to allow oil and gas to flow from small pores within the rock to the production well.

As the use of hydraulic fracturing has increased, so have concerns about its potential impact on human health and the environment, especially with regard to possible impacts on drinking water resources.[1] These concerns have increased as oil and gas exploration and development has spread from areas with a long history of conventional production to new areas with unconventional reservoirs, such as the Marcellus Shale, which extends from New York through parts of Pennsylvania, West Virginia, eastern Ohio, and western Maryland.

In response to public concerns and anticipated growth in the oil and gas industries, the US Congress urged the US Environmental Protection Agency (EPA) to examine the relationship between hydraulic fracturing and drinking water resources (USHR, 2009):

> *The conferees urge the agency to carry out a study on the relationship between hydraulic fracturing and drinking water, using a credible approach that relies on the best available science, as well as independent sources of information. The conferees expect the study to be conducted through a transparent, peer-reviewed process that will ensure the validity and accuracy of the data. The Agency shall consult with other federal agencies as well as appropriate state and interstate regulatory agencies in carrying out the study, which should be prepared in accordance with the agency's quality assurance principles.*

In 2010, the EPA launched the planning of the current study and included multiple opportunities for the public and the Science Advisory Board[2] to provide input during the study planning process.[3] The EPA's *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*

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[1] Common concerns raised by stakeholders include potential impacts to air quality and ecosystems as well as sociologic effects (e.g., community changes). A more comprehensive list of concerns reported to the EPA during initial stakeholder meetings can be found in Appendix C of the EPA's *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (EPA/600/R-11/121).

[2] The Science Advisory Board is an independent and external federal advisory committee that conducts peer reviews of scientific matters for the EPA.

[3] During summer 2010, the EPA engaged stakeholders in a dialogue about the study through facilitated meetings. Summaries of these meetings are available at http://www.epa.gov/hfstudy/publicoutreach.html.

(subsequently referred to as the "Study Plan") was finalized in November 2011 (US EPA, 2011e). The purpose of the EPA's current study is to assess the potential impacts of hydraulic fracturing on drinking water resources,[4] if any, and to identify the driving factors that may affect the severity and frequency of such impacts. This study includes research on hydraulic fracturing to extract oil and gas from shale, tight sand, and coalbeds, focusing primarily on hydraulic fracturing of shale for gas extraction. It is intended to assess the potential impacts to drinking water resources from hydraulic fracturing as it is currently practiced and has been practiced in the past, and it is not intended to evaluate best management practices or new technologies. Emphasis is placed on identifying possible exposure pathways and hazards, providing results that can then be used to assess the potential risks to drinking water resources from hydraulic fracturing. Ultimately, results from the study are intended to inform the public and provide policymakers at all levels with high-quality scientific knowledge that can be used in decision-making.

The body of this progress report presents the research progress made by the EPA, as of September 2012, regarding the potential impacts of hydraulic fracturing on drinking water resources; information presented as part of this report cannot be used to draw conclusions about the proposed research questions. Chapters 3 through 7 provide project-specific updates that include background information on the research project, a description of the research methods, an update on the current status and next steps of the work, as well as a summary of the quality assurance (QA) activities to date;[5] these chapters are written for scientific and engineering professionals. All projects described in this progress report are currently underway, and nearly all are expected to be completed in the next few years. Results from individual projects will undergo peer review prior to publication. The EPA intends to synthesize the published results from these research projects in a report of results, described in more detail in Section 9.3.

1.1. Stakeholder Engagement

The EPA is committed to conducting this study in an open and transparent manner. During the development of the study, the EPA met with stakeholders from the general public; federal, state, regional and local agencies; tribes; industry; academia; and non-governmental organizations. Webinars and meetings with these separate groups were held to discuss the study scope, data gaps, opportunities for sharing data and conducting joint studies, current policies and practices for protecting drinking water resources, and the public engagement process.

In addition to webinars and meetings, the EPA held a series of technical workshops in early 2011 on four subjects integral to hydraulic fracturing and the study: chemical and analytical methods, well construction and operation, chemical fate and transport, and water resource management.[6] Technical experts from the oil and natural gas industry, academia, consulting firms, commercial laboratories, state and federal agencies, and environmental organizations were chosen to

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[4] For this study, "drinking water resources" are considered to be any body of water, ground or surface, that could (now or in the future) serve as a source of drinking water for public or private water supplies.

[5] QA activities include implementation of quality assurance project plans (QAPPs), technical systems audits (TSAs), and audits of data quality (ADQs). These activities are described further in Section 8.1.

[6] Proceedings from the four technical workshops are available at http://www.epa.gov/hfstudy/technicalworkshops.html.

participate in each of the workshops. The workshops gave EPA scientists the opportunity to interact with technical experts regarding current hydraulic fracturing technology and practices and to identify and design research related to the potential impacts of hydraulic fracturing on drinking water resources. Information presented during the workshops is being used to inform ongoing research.

The EPA has recently announced additional opportunities for stakeholder engagement. The goals of this enhanced engagement process are to improve public understanding of the study, ensure that the EPA is current on changes in industry practices and technologies so that the report of results reflects an up-to-date picture of hydraulic fracturing operations, and obtain timely and constructive feedback on ongoing research projects.

Stakeholders and technical experts are being engaged through the following activities:

- *Technical roundtables* with invited experts from diverse stakeholder groups to discuss the work underway to answer key research questions and identify possible topics for technical workshops. The roundtables also give the EPA access to a broad and balanced range of expertise as well as data from outside the agency.
- *Technical workshops* with experts invited to participate in more in-depth discussions and share expertise on discrete technical topics relevant to the study.
- *Information requests* through a *Federal Register* notice, requesting that the public submit relevant studies and data—particularly peer-reviewed studies—for the EPA's consideration, including information on advances in industry practices and technologies.
- *Study updates* to a wide range of stakeholders, including the general public, states, tribes, academia, non-governmental organizations, industry, professional organizations, and others.
- *Periodic briefings* with the EPA's Science Advisory Board to provide updates on the progress of the study.

These efforts will help:

- Inform the EPA's interpretation of the research being conducted as part of this study.
- Identify additional data and studies that may inform the report or results.
- Identify future research needs.

Additional information on the ongoing stakeholder engagement process can be found in Appendix B and online at http://www.epa.gov/hfstudy/. The website includes the presentations made by the EPA during the technical roundtables held in November 2012 as well as a list of roundtable participants. Readers are encouraged to check this website for up-to-date information on upcoming webinars for the general public and proceedings from technical workshops, which are currently scheduled for spring 2013.

2. Overview of the Research Program

The EPA's *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* is organized into five topics according to the potential for interaction between hydraulic fracturing and drinking water resources. These five topics—stages of the hydraulic fracturing water cycle—are illustrated in Figure 1 and include (1) water acquisition, (2) chemical mixing, (3) well injection, (4) flowback and produced water, and (5) wastewater treatment and waste disposal.

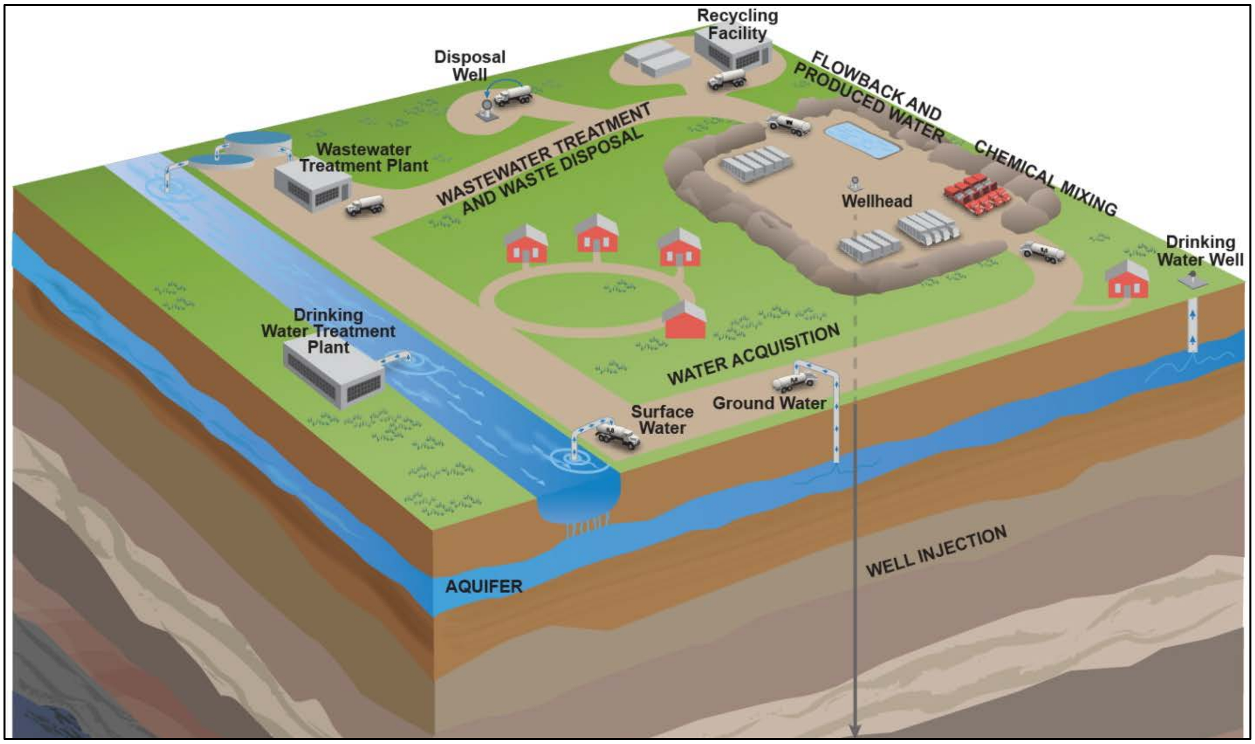

Figure 1. Illustration of the five stages of the hydraulic fracturing water cycle. The cycle includes the acquisition of water needed for the hydraulic fracturing fluid, onsite mixing of chemicals with the water to create the hydraulic fracturing fluid, injection of the fluid under high pressures to fracture the oil- or gas-containing formation, recovery of flowback and produced water (hydraulic fracturing wastewater) after the injection is complete, and treatment and/or disposal of the wastewater.

Figure 2 lists potential drinking water issues identified for each stage of the hydraulic fracturing water cycle.

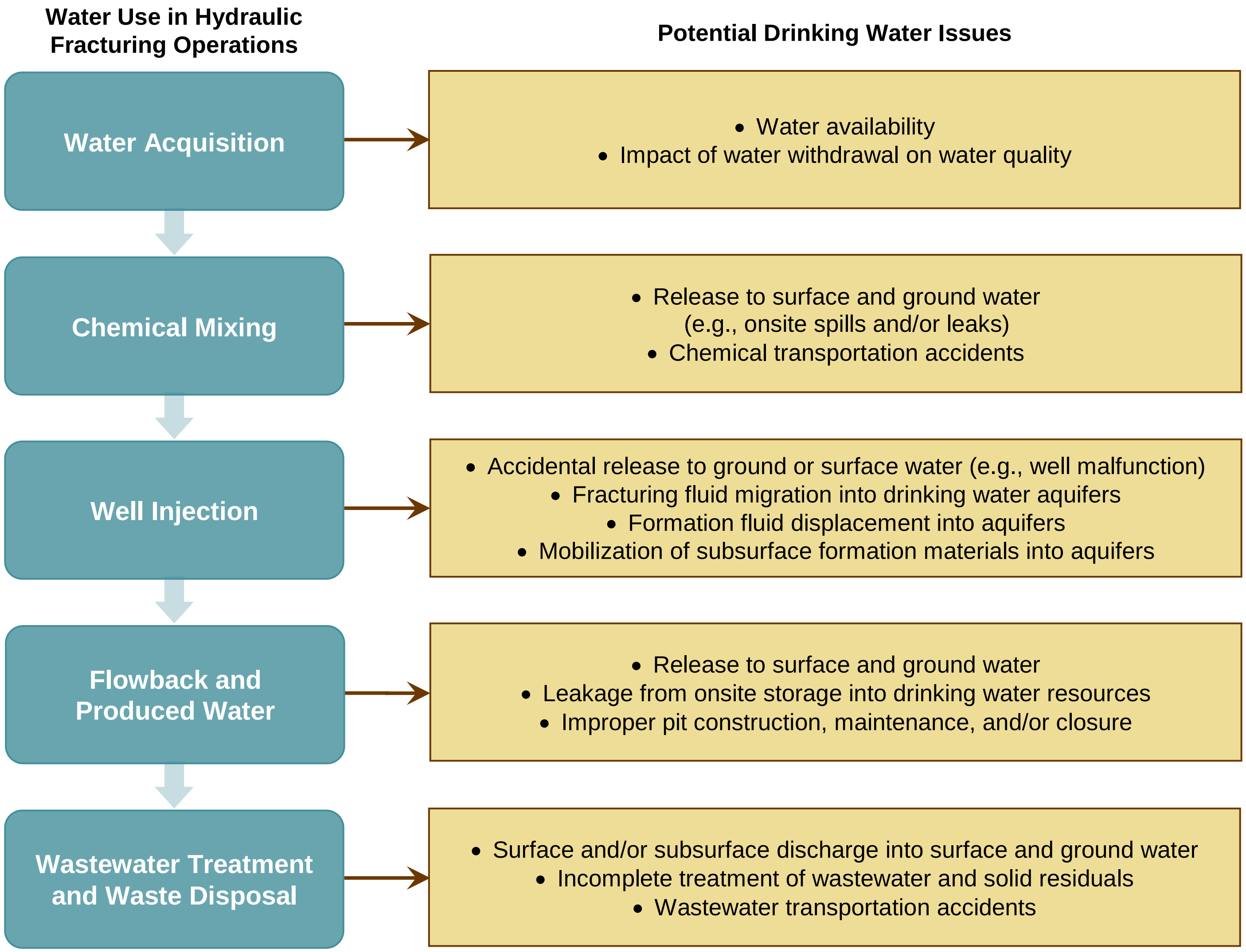

Figure 2. Potential drinking water issues associated with each stage of the hydraulic fracturing water cycle. The potential issues help to define the fundamental research questions. Figure reprinted from the Study Plan (US EPA, 2011e).

As described in the Study Plan, the potential issues led to the development of primary research questions that are supported by secondary research questions. The secondary research questions are addressed by the research projects listed in Table 1. Table 1 also provides short titles and descriptions of the research projects; these titles are used throughout the rest of the report.

Table 1. Titles and descriptions of the research projects conducted as part of the EPA's *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*. These titles are used throughout the rest of the report. Detailed descriptions of each project can be found in Chapters 3 through 7.

Research Project	Description
Analysis of Existing Data	
Literature Review	Review and assessment of existing papers and reports, focusing on peer-reviewed literature
Spills Database Analysis	Analysis of selected federal and state databases for information on spills of hydraulic fracturing fluids and wastewaters
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
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
FracFocus Analysis	Analysis of data compiled from FracFocus, the national hydraulic fracturing chemical registry operated by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission
Scenario Evaluations	
Subsurface Migration Modeling	Numerical modeling of subsurface fluid migration scenarios that explore the potential for gases and fluids to move from the fractured zone to drinking water aquifers
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
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
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
Wastewater Treatability Studies	Assessment of the efficacy of common wastewater treatment processes on removing selected chemicals found in hydraulic fracturing wastewater
Br-DBP Precursor Studies	Assessment of the ability of bromide and brominated compounds present in hydraulic fracturing wastewater to form brominated disinfection byproducts (Br-DBPs) during drinking water treatment processes
Analytical Method Development	Development of analytical methods for selected chemicals found in hydraulic fracturing fluids or wastewater

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Research Project	**Description**
	Toxicity Assessment
Toxicity Assessment	Toxicity assessment of chemicals reportedly used in hydraulic fracturing fluids or found in hydraulic fracturing wastewater
	Case Studies
Retrospective 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
Dunn County, North Dakota	Investigation of potential drinking water impacts from a well blowout during hydraulic fracturing for oil in the Bakken Shale
Bradford County, Pennsylvania	Investigation of potential drinking water impacts from shale gas development in the Marcellus Shale
Washington County, Pennsylvania	Investigation of potential drinking water impacts from shale gas development in the Marcellus Shale
Wise County, Texas	Investigation of potential drinking water impacts from shale gas development in the Barnett Shale
Prospective Studies	*Investigation of potential impacts of hydraulic fracturing through collection of samples from a site before, during, and after well pad construction and hydraulic fracturing*

Each project has been designed to inform answers to one or more of the secondary research questions with multiple projects informing answers to each secondary research question. The answers to the secondary research questions will then inform answers to the primary research questions. Figure 3 illustrates the relationship between water cycle stage, primary and secondary research questions, and research projects.

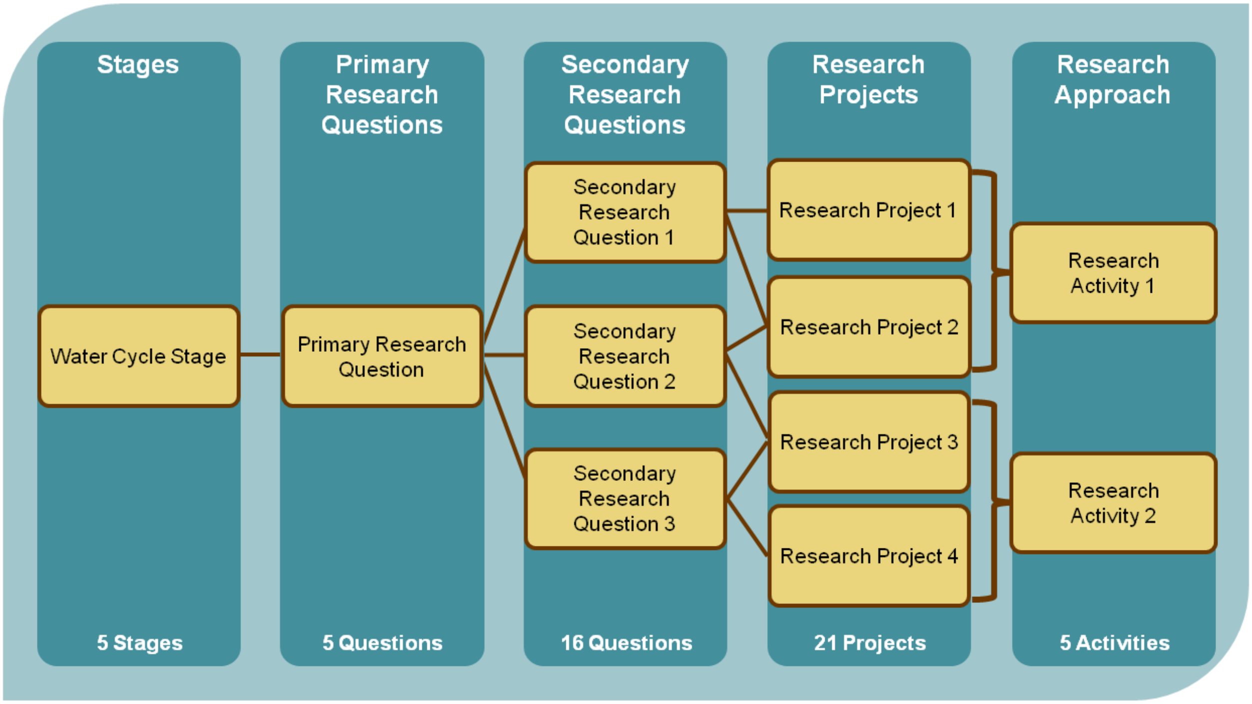

Figure 3. Illustration of the structure of the EPA's *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*. Results from multiple research projects may be used to inform answers to one secondary research question. Additionally, one research project may provide information to help answer multiple secondary research questions. Each research project falls under one type of research activity.

2.1. Research Questions

This section describes the activities that occur during each stage of the water cycle, potential drinking water issues, and primary research questions, which are listed in Figure 4.[7] It also introduces the secondary research questions and lists the associated research projects. This section is intended to offer a broad overview of the EPA's study and direct the reader to further information in subsequent chapters of this progress report. Later chapters (Chapters 3 through 7) contain detailed information about the progress of individual research projects listed in Tables 2 through 6 below.

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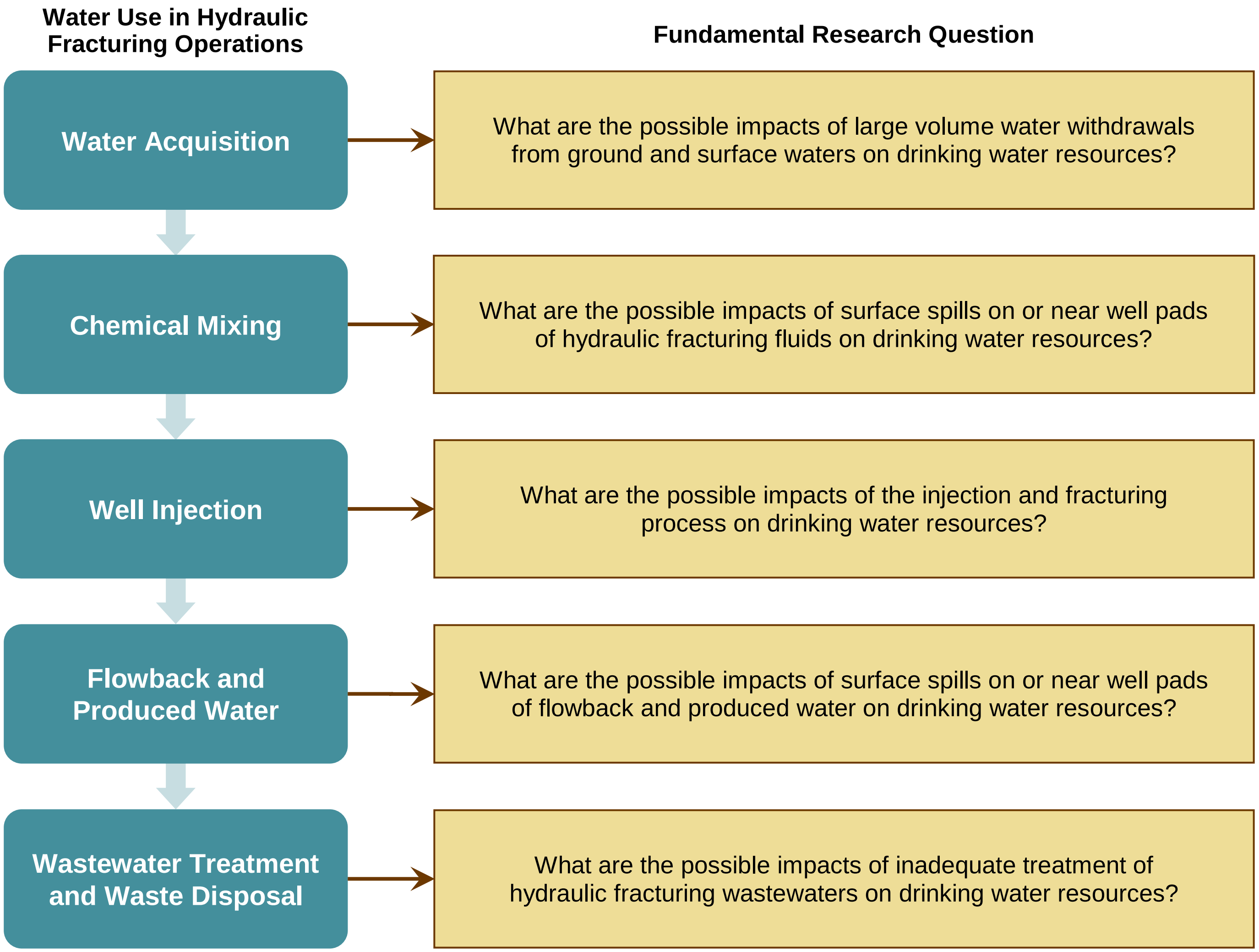
[7] Additional information on the hydraulic fracturing water cycle stages and research questions can be found in the Study Plan.



Water Use in Hydraulic Fracturing Operations	Fundamental Research Question
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 on or near well pads of hydraulic fracturing fluids 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 on or near well pads of flowback and produced water 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?

Figure 4. Fundamental research questions posed for each stage of the hydraulic fracturing water cycle. Figure reprinted from the Study Plan (US EPA, 2011e).

2.1.1. Water Acquisition: What are the possible impacts of large volume water withdrawals from ground and surface waters on drinking water resources?

Hydraulic fracturing fluids are usually water-based, with approximately 90% of the injected fluid composed of water (GWPC and ALL Consulting, 2009). Estimates of water needs per well have been reported to range from 65,000 gallons for coalbed methane (CBM) production up to 13 million gallons for shale gas production, depending on the characteristics of the formation being fractured and the design of the production well and fracturing operation (GWPC and ALL Consulting, 2009; Nicot et al., 2011). Five million gallons of water are equivalent to the water used by approximately 50,000 people for one day.[8] The source of the water may vary, but is typically ground water, surface water, or treated wastewater, as illustrated in Figure 5. Industry trends suggest a recent shift to using treated and recycled produced water (or other treated wastewaters) as base fluids in hydraulic fracturing operations.

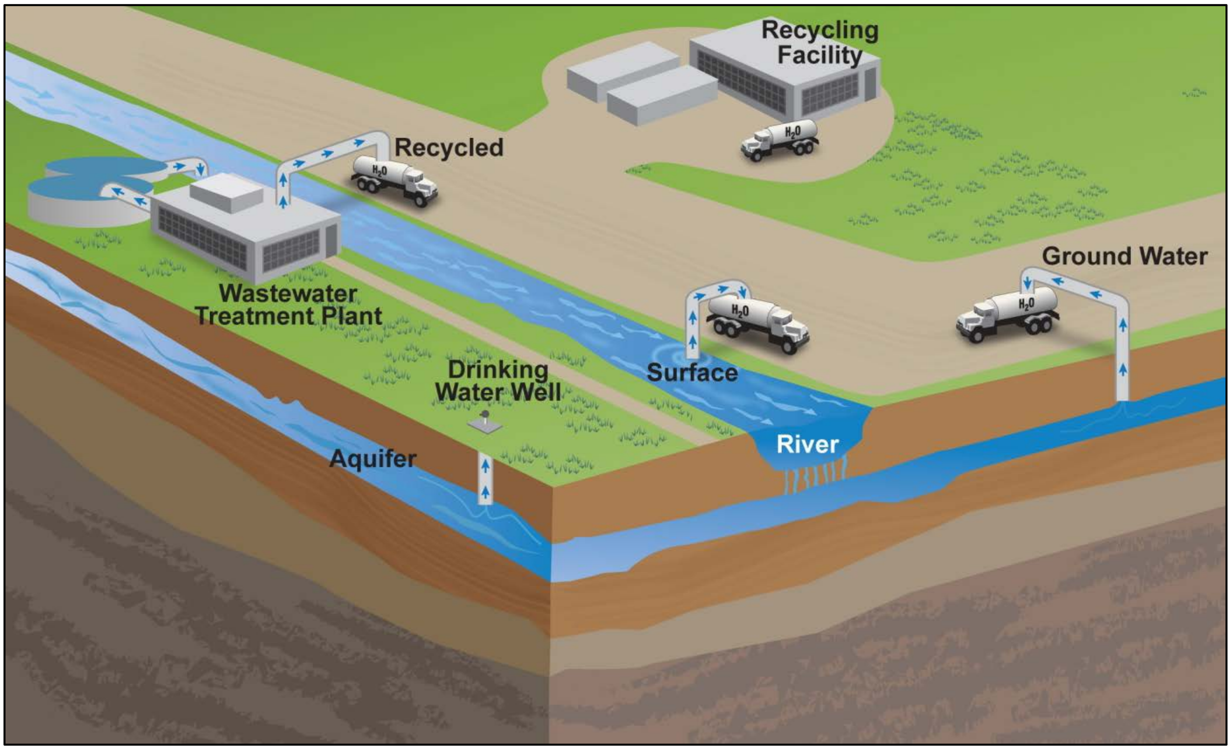


Figure 5. Water acquisition. Water for hydraulic fracturing can be drawn from a variety of sources including surface water, ground water, treated wastewater generated during previous hydraulic fracturing operations, and other types of wastewater.

The EPA is working to better characterize the amounts and sources of water currently being used for hydraulic fracturing operations, including recycled water, and how these withdrawals may impact local drinking water quality and availability. To that end, secondary research questions have been developed, as well as the research projects listed in Table 2.

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[8] This assumes that the average American uses approximately 100 gallons of water per day. See http://www.epa.gov/watersense/pubs/indoor.html.

Table 2. Secondary research questions and applicable research projects identified for the water acquisition stage of the hydraulic fracturing water cycle. The table also identifies the sections of this report that contain detailed information about the listed research projects.

Secondary Research Questions	Applicable Research Projects	Section
How much water is used in hydraulic fracturing operations, and what are the sources of this water?	Literature Review	3.1
	Service Company Analysis	3.3
	Well File Review	3.4
	FracFocus Analysis	3.5
	Water Availability Modeling	4.3
How might water withdrawals affect short- and long-term water availability in an area with hydraulic fracturing activity?	Literature Review	3.1
	Water Availability Modeling	4.3
What are the possible impacts of water withdrawals for hydraulic fracturing operations on local water quality?	Literature Review	3.1

2.1.2. Chemical Mixing: What are the possible impacts of surface spills on or near well pads of hydraulic fracturing fluids on drinking water resources?

Once onsite, water is mixed with chemicals to create the hydraulic fracturing fluid that is pumped down the well, as illustrated in Figure 6. The fluid serves two purposes: to create pressure to propagate fractures and to carry the proppant into the fracture. Chemicals are added to the fluid to change its properties (e.g., viscosity, pH) in order to optimize the performance of the fluid. Roughly 1% of water-based hydraulic fracturing fluids are composed of various chemicals, which is equivalent to 50,000 gallons for a shale gas well that uses 5 million gallons of fluid.

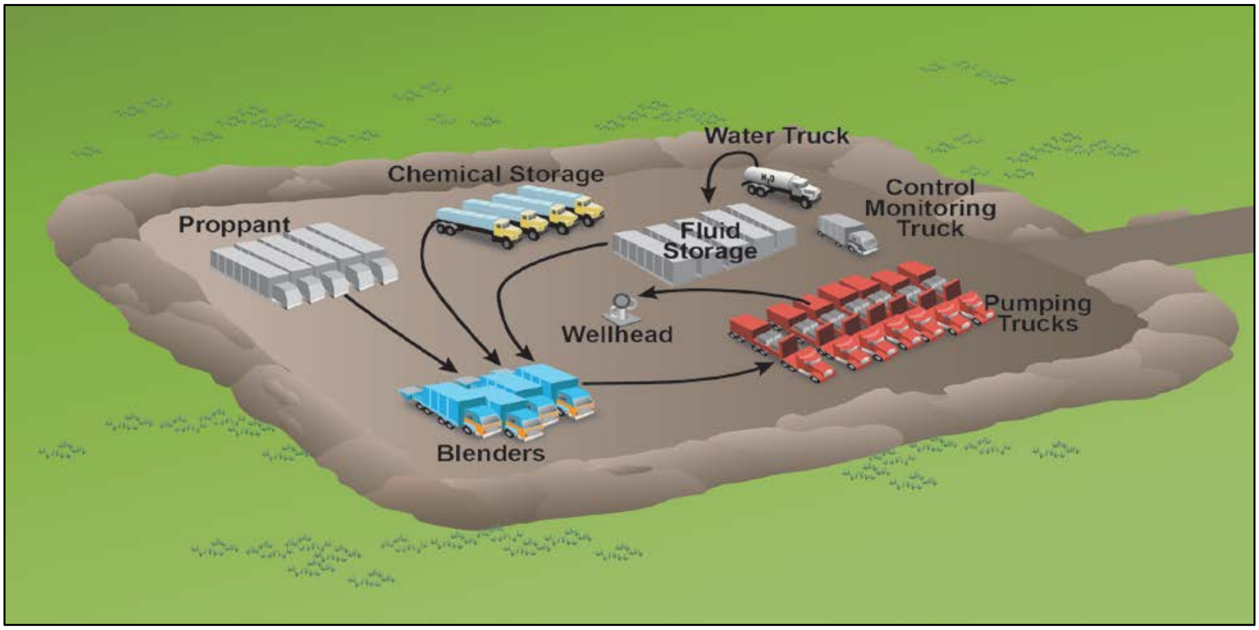

Figure 6. Chemical mixing. Water is mixed with chemicals and proppant onsite to create the hydraulic fracturing fluid immediately before injection.

Hydraulic fracturing operations require large quantities of supplies, equipment, water, and vehicles. Onsite storage, mixing, and pumping of hydraulic fracturing fluids may result in accidental releases, such as spills or leaks.[9] Released fluids could then flow into nearby surface water bodies or infiltrate into the soil and near-surface ground water, potentially reaching drinking water resources. In order to explore the potential impacts of surface releases of hydraulic fracturing fluids on drinking water resources, the EPA is: (1) compiling information on reported spills; (2) identifying chemical additives used in hydraulic fracturing fluids and their chemical, physical, and toxicological properties; and (3) gathering data on the environmental fate and transport of selected hydraulic fracturing chemical additives. These activities correspond to the secondary research questions and research projects described in Table 3.

Table 3. Secondary research questions and applicable research projects identified for the chemical mixing stage of the hydraulic fracturing water cycle. The table also identifies the sections of this report that contain detailed information about the listed research projects.

Secondary Research Questions	Applicable Research Projects	Section
What is currently known about the frequency, severity, and causes of spills of hydraulic fracturing fluids and additives?	Literature Review	3.1
	Spills Database Analysis	3.2
	Service Company Analysis	3.3
	Well File Review	3.4
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?	Literature Review	3.1
	Service Company Analysis	3.3
	FracFocus Analysis	3.5
	Analytical Method Development	5.4
What are the chemical, physical, and toxicological properties of hydraulic fracturing chemical additives?	Toxicity Assessment	6
If spills occur, how might hydraulic fracturing chemical additives contaminate drinking water resources?	Literature Review	3.1
	Retrospective Case Studies	7

2.1.3. Well Injection: What are the possible impacts of the injection and fracturing process on drinking water resources?

The hydraulic fracturing fluid is pumped down the well at pressures great enough to fracture the oil- or gas-containing rock formation, as shown in Figure 7 for both horizontal and vertical well completions. Production wells are drilled and completed in order to best and most efficiently drain the geological reservoir of its hydrocarbon resources. This means that wells may be drilled and completed vertically (panel b in Figure 7), vertically at the top and then horizontally at the bottom (panel a), or in other configurations deviating from vertical, known as "deviated wells."

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[9] As noted in the Study Plan, transportation-related spills of hydraulic fracturing chemical additives and wastewater are outside of the scope of the current study.

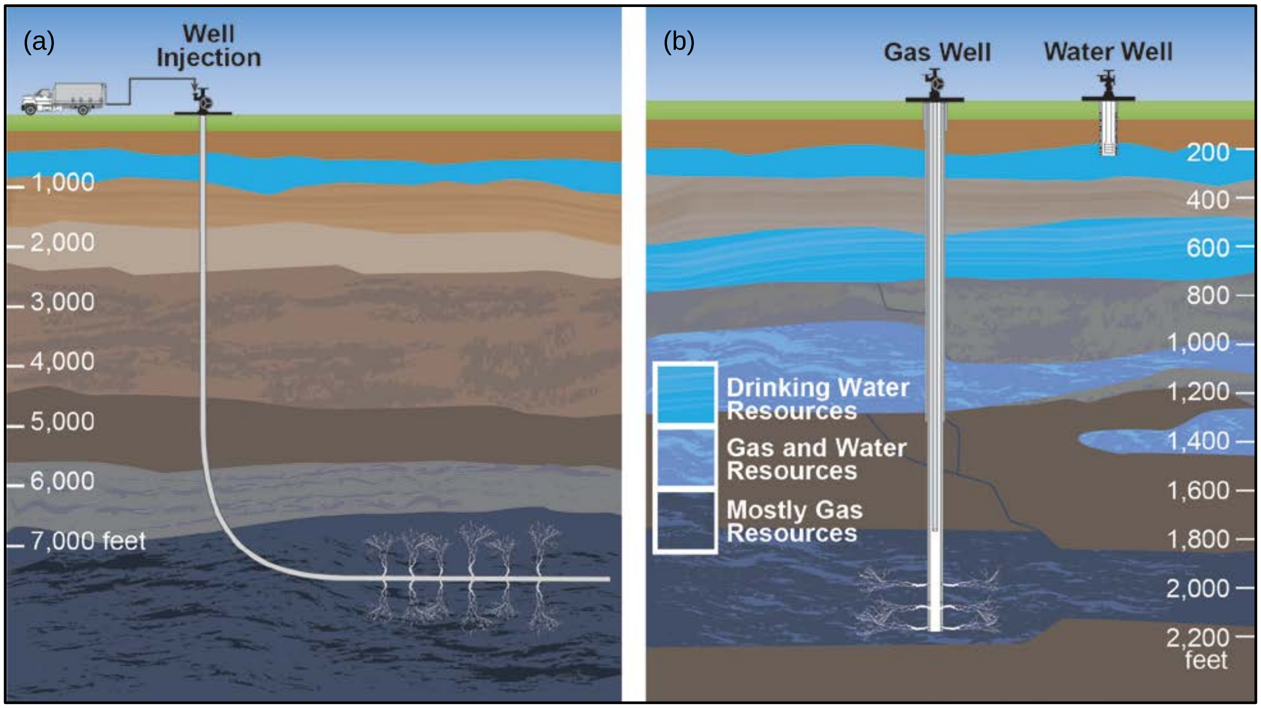

Figure 7. Well injection. During injection, hydraulic fracturing fluids are pumped into the well at high pressures, which are sustained until the fractures are formed. Hydraulic fracturing can be used with both (a) deep, horizontal well completions and (b) shallower, vertical well completions. Horizontal wells are typically used in formations such as tight sandstones, carbonate rock, and shales. Vertical wells are typically used in formations for conventional production and coalbed methane.

Within this stage of the hydraulic fracturing water cycle, the EPA is studying a number of scenarios that may lead to changes in local drinking water resources, including well construction failure and induced fractures intersecting existing natural (e.g., faults or fractures) or man-made (e.g., abandoned wells) features that may act as conduits for contaminant transport. Table 4 lists the secondary research questions and research projects that address these concerns.

Table 4. Secondary research questions and applicable research projects identified for the well injection stage of the hydraulic fracturing water cycle. The table also identifies the sections of this report that contain detailed information about the listed research projects.

Secondary Research Questions	Applicable Research Projects	Section
How effective are current well construction practices at containing gases and fluids before, during, and after fracturing?	Literature Review	3.1
	Service Company Analysis	3.3
	Well File Review	3.4
	Subsurface Migration Modeling	4.1
	Retrospective Case Studies	7
Can subsurface migration of fluids or gases to drinking water resources occur, and what local geologic or man-made features might allow this?	Literature Review	3.1
	Service Company Analysis	3.3
	Well File Review	3.4
	Subsurface Migration Modeling	4.1
	Retrospective Case Studies	7

2.1.4. Flowback and Produced Water: What are the possible impacts of surface spills on or near well pads of flowback and produced water on drinking water resources?

When the injection pressure is reduced, the direction of fluid flow reverses, leading to the recovery of flowback and produced water. For this study, “flowback” is the fluid returned to the surface after hydraulic fracturing has occurred, but before the well is placed into production, while “produced water” is the fluid returned to the surface after the well has been placed into production.[10] They are collectively referred to as “hydraulic fracturing wastewater” and may contain chemicals injected as part of the hydraulic fracturing fluid, substances naturally occurring in the oil- or gas-producing formation,[11] hydrocarbons, and potential reaction and degradation products.

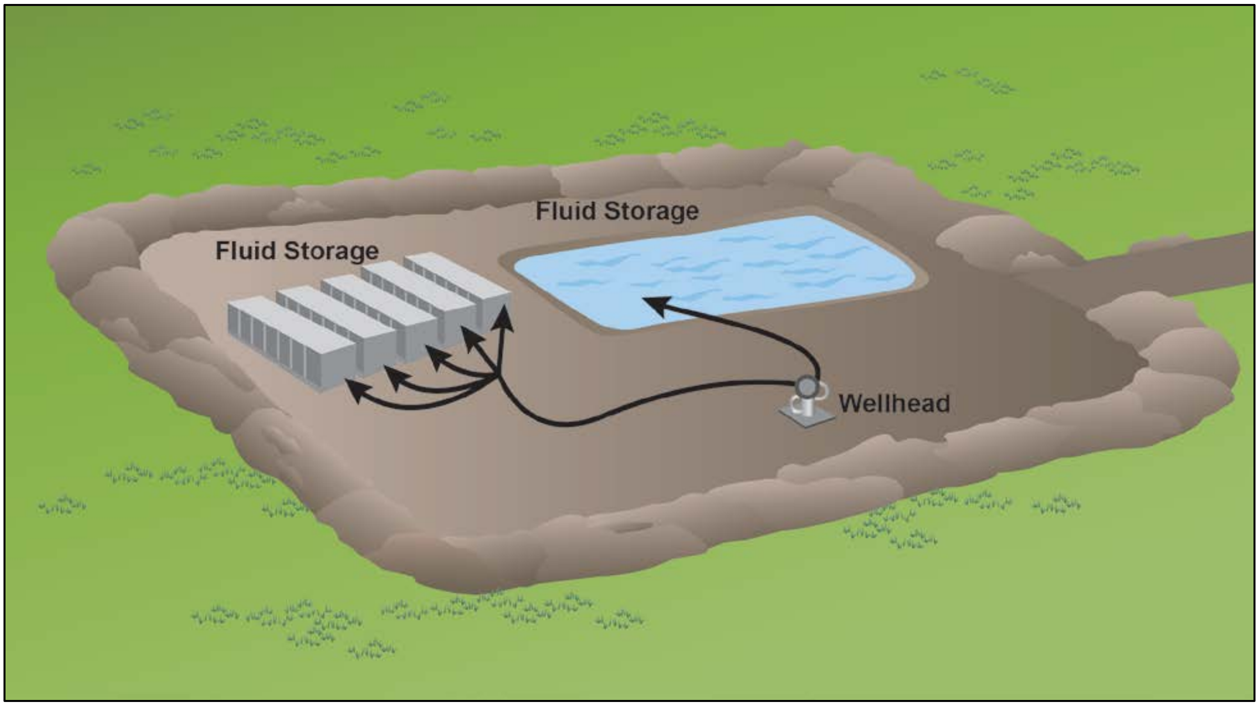

Figure 8. Flowback and produced water. During this stage, the pressure on the hydraulic fracturing fluid is reduced and the flow is reversed. The flowback and produced water contain hydraulic fracturing fluids, native formation water, and a variety of naturally occurring substances picked up by the wastewater during the fracturing process. The fluids are separated from any gas or oil produced with the water and stored in either tanks or an open pit.

As depicted in Figure 8, the wastewater is typically stored onsite in impoundment pits or tanks. Onsite transfer and storage of hydraulic fracturing wastewater may result in accidental releases, such as spills or leaks, which may reach nearby drinking water resources. The potential impacts to drinking water resources from flowback and produced water are similar to the potential impacts identified in the chemical mixing stage of the hydraulic fracturing water cycle, with the exception of different fluid compositions for injected fluids and wastewater. Therefore, the secondary research

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[10] Produced water is a product of all oil and gas wells, including wells that have not been hydraulically fractured.

[11] Substances naturally found in hydraulically fractured formations may include brines, trace elements (e.g., mercury, lead, arsenic), naturally occurring radioactive material (e.g., radium, thorium, uranium), gases (e.g., natural gas, hydrogen sulfide), and organic material (e.g., organic acids, polycyclic aromatic hydrocarbons, volatile organic compounds).

questions and associated research projects are similar. The secondary research questions and applicable research projects are listed in Table 5.

Table 5. Secondary research questions and applicable research projects identified for the flowback and produced water stage of the hydraulic fracturing water cycle. The table also identifies the sections of this report that contain detailed information about the listed research projects.

Secondary Research Questions	Applicable Research Projects	Section
What is currently known about the frequency, severity, and causes of spills of flowback and produced water?	Literature Review	3.1
	Spills Database Analysis	3.2
	Service Company Analysis	3.3
	Well File Review	3.4
What is the composition of hydraulic fracturing wastewaters, and what factors might influence this composition?	Literature Review	3.1
	Service Company Analysis	3.3
	Well File Review	3.4
	Analytical Method Development	5.4
What are the chemical, physical, and toxicological properties of hydraulic fracturing wastewater constituents?	Toxicity Assessment	6
If spills occur, how might hydraulic fracturing wastewater contaminate drinking water resources?	Literature Review	3.1
	Retrospective Case Studies	7

2.1.5. Wastewater Treatment and Waste Disposal: What are the possible impacts of inadequate treatment of hydraulic fracturing wastewaters on drinking water resources?

Estimates of the fraction of hydraulic fracturing wastewater recovered vary by geologic formation and range from 10% to 70% of the injected hydraulic fracturing fluid (GWPC and ALL Consulting, 2009; US EPA, 2011f). For a hydraulic fracturing job that uses 5 million gallons of hydraulic fracturing fluid, this means that between 500,000 and 3.5 million gallons of fluid will be returned to the surface. As illustrated in Figure 9, the wastewater is generally managed through disposal into deep underground injection control (UIC) wells,[12] treatment followed by discharge to surface water bodies,[13] or treatment followed by reuse.

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[12] Underground injection of fluids related to oil and gas production (including flowback and produced water) is authorized by the Safe Drinking Water Act.

[13] Treatment processes involving discharge to surface waters are authorized by the Clean Water Act and the National Pollutant Discharge Elimination System program.

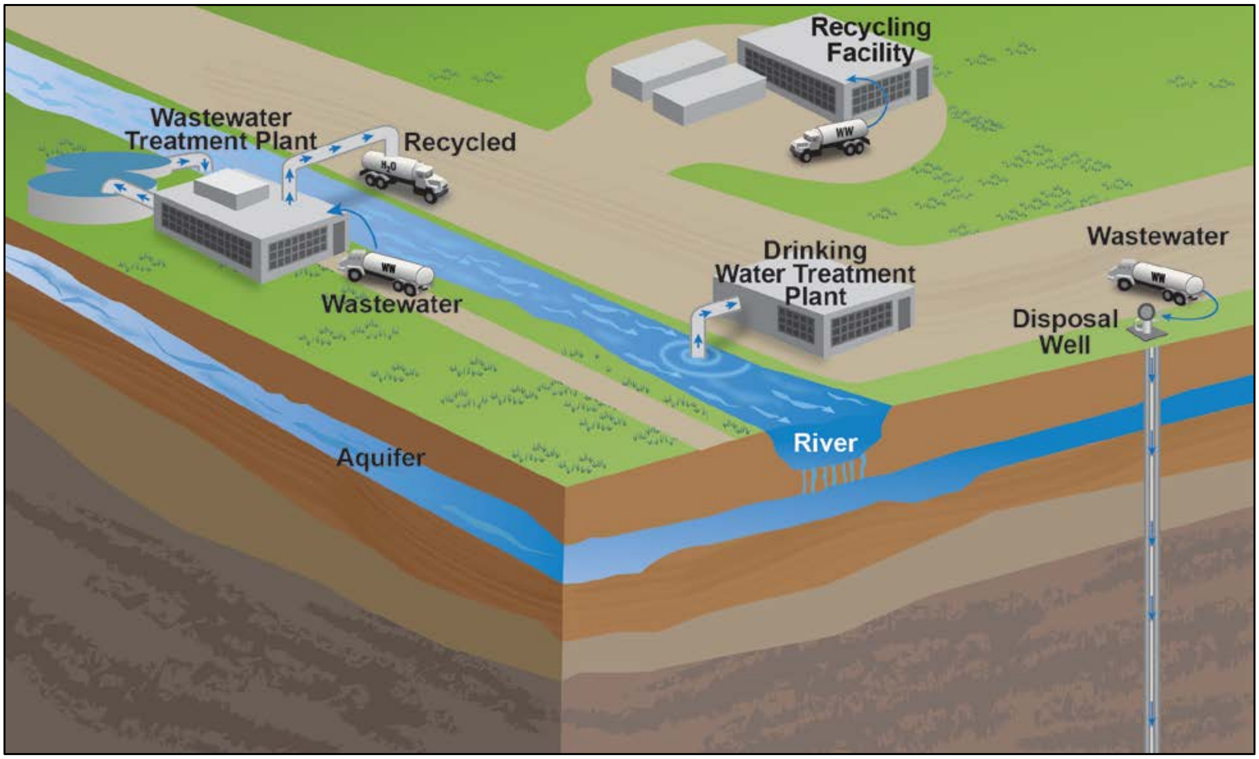

Figure 9. Wastewater treatment and waste disposal. Flowback and produced water is frequently disposed of in deep injection wells, but may also be trucked, or in some cases piped, to a disposal or recycling facility. Once treated, the wastewater may be reused in subsequent hydraulic fracturing operations or discharged to surface water.

Understanding the treatment, disposal, and reuse of flowback and produced water from hydraulic fracturing activities is important. For example, contaminants present in these waters may be inadequately treated at publicly owned treatment works (POTWs), discharges from which may threaten downstream drinking water intakes, as depicted in Figure 9.[14] Table 6 summarizes the secondary research questions and the applicable research projects for each question.

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[14] As noted in the Study Plan, this study does not propose to evaluate the potential impacts of underground injection or the associated potential impacts due to transport and storage leading up to ultimate disposal in a UIC well.

Table 6. Secondary research questions and applicable research projects identified for the wastewater treatment and waste disposal stage of the hydraulic fracturing water cycle. The table also identifies the sections of this report that contain detailed information about the listed research projects.

Secondary Research Questions	Applicable Research Projects	Section
What are the common treatment and disposal methods for hydraulic fracturing wastewater, and where are these methods practiced?	Literature Review	3.1
	Well File Review	3.4
	FracFocus Analysis	3.5
How effective are conventional POTWs and commercial treatment systems in removing organic and inorganic contaminants of concern in hydraulic fracturing wastewater?	Literature Review	3.1
	Wastewater Treatability Studies	5.2
What are the potential impacts from surface water disposal of treated hydraulic fracturing wastewater on drinking water treatment facilities?	Literature Review	3.1
	Surface Water Modeling	4.2
	Source Apportionment Studies	5.1
	Br-DBP Precursor Studies	5.3

2.2. *Environmental Justice*

Environmental justice is the fair treatment and meaningful involvement of all people regardless of race, color, national origin, or income, with respect to the development, implementation, and enforcement of environmental laws, regulations, and policies.[15]

During the planning process, some stakeholders raised concerns about environmental justice and hydraulic fracturing, while others stated that hydraulic fracturing–related activities provide benefits to local communities. In its review of the draft Study Plan, the EPA's Science Advisory Board supported the inclusion in the study of an environmental justice analysis as it pertains to the potential impacts on drinking water resources. The EPA, therefore, attempted to conduct a screening to provide insight into the research questions in Table 7.

Table 7. Research questions addressed by assessing the demographics of locations where hydraulic fracturing activities are underway.

Fundamental Research Question	Secondary Research Questions
Does hydraulic fracturing disproportionately occur in or near communities with environmental justice concerns?	• Are large volumes of water being disproportionately withdrawn from drinking water resources that serve communities with environmental justice concerns? • Are hydraulically fractured oil and gas wells disproportionately located near communities with environmental justice concerns? • Is wastewater from hydraulic fracturing operations being disproportionately treated or disposed of (via POTWs or commercial treatment systems) in or near communities with environmental justice concerns?

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[15] The EPA's definition of environmental justice can be found at http://www.epa.gov/environmentaljustice/basics/index.html and was informed by E.O. 12898.

Environmental justice screening uses easily obtained environmental and demographic information to highlight locations where additional review (i.e., information collection or analysis) may be warranted (US EPA, 2012c). Screenings do not examine whether co-location of specific activities and communities with certain demographics (e.g., low-income, non-white minority, young children, and elderly subpopulations) may lead to any positive or negative impacts on a given community.

Nationwide data on the locations of water withdrawals and wastewater treatment associated with hydraulic fracturing activities are difficult to obtain. The EPA was not able to identify comprehensive data sources that identify the locations of water withdrawals associated with hydraulic fracturing or facilities receiving hydraulic fracturing wastewaters. Geographic data on hydraulic fracturing-only water use (rather than general oil and gas water use) are limited, and the available data are aggregated by regions too large for an environmental justice analysis. Data on commercial and publicly owned treatment works accepting hydraulic fracturing wastewater were found to be inconsistent between states or difficult to obtain.

Data on the locations of hydraulically fractured oil and gas production wells considered for the environmental justice screen are available from two sources: data provided to the EPA from nine hydraulic fracturing service companies (see Section 3.3) and data obtained from FracFocus (Section 3.5). The service company data set includes county-level locations of approximately 25,000 oil and gas wells hydraulically fractured between September 2009 and October 2010. In total, 590 of the 3,221 counties in the United States contained wells hydraulically fractured by the nine service companies during the period under analysis. In comparison, the FracFocus data set includes latitude/longitude and county-level information on the location of roughly 11,000 wells hydraulically fractured between January 2009 and February 2012. In total, only 251 of the 3,221 counties in the United States contained wells reported to FracFocus during this time period.

The county-level resolution provided by the service company data set is insufficient for determining whether hydraulic fracturing activities are occurring in communities that possess characteristics associated with environmental justice populations. Finer resolution is needed since counties can contain a multitude of communities, townships, and even cities, with diverse populations. Data obtained from FracFocus provide well locations at finer resolution (i.e., specific latitude/longitude coordinates), which may provide further opportunity for either state- or nationwide environmental justice screens.

2.3. Changes to the Research Program

The EPA has significantly modified some of the research projects since the publication of the Study Plan. These modifications are discussed below.

FracFocus Analysis. In early 2011, the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission jointly launched a new national registry for chemicals used in hydraulic fracturing, called FracFocus. This registry is an online repository where oil and gas well operators can upload information regarding the chemical composition of hydraulic fracturing fluids used in specific oil and gas production wells. Extracting data from FracFocus allows the EPA to gather publicly available, nationwide data on the water volumes and chemicals used in hydraulic fracturing operations, as reported by oil and gas operating companies. These data are being analyzed to identify chemicals used in hydraulic fracturing fluids as well as the geographic distribution of water and chemical use.

Prospective Case Studies. The EPA identified the location of one of the prospective case studies as De Soto Parish, Louisiana, in the Haynesville Shale. Due to scheduling conflicts, the location in De Soto Parish is no longer being considered for a prospective case study.

The EPA continues to work with industry partners to identify locations and develop research activities for prospective case studies. As part of these case studies, the EPA intends to monitor local water quality for up to a year or more after hydraulic fracturing occurs. It is likely, therefore, that the prospective case studies will be completed after the report of results. In that event, results from any prospective case studies will be published in a follow-up report.

Chemical Prioritization. As part of the toxicity assessment research project, the EPA is compiling chemical, physical, and toxicological properties for chemicals reportedly used in hydraulic fracturing fluids and/or detected in flowback and produced water. One aspect of the planned second phase of this work was to include prioritizing a subset of these chemicals for future toxicity screening using high throughput screening assays. However, consistent with recommendations of the Science Advisory Board, the agency will not conduct high throughput screening assays at this time on a subset of these chemicals, but will continue efforts to identify, evaluate, and prioritize existing toxicity data.

Reactions Between Hydraulic Fracturing Fluids and Shale. Based on research already being conducted by the US Department of Energy and academic institutions on the interactions between hydraulic fracturing fluids and various rock formations,[16] the EPA has decided to discontinue its work in this area. The EPA continues to believe in the importance of research to address research questions associated with this project, but has decided to rely upon work being conducted by another federal agency.

Therefore, the EPA has removed two research questions associated with this project:

- How might hydraulic fracturing fluids change the fate and transport of substances in the subsurface through geochemical interactions?
- What are the chemical, physical, and toxicological properties of substances in the subsurface that may be released by hydraulic fracturing operations?

2.4. Research Approach

The research projects listed in Table 1 and discussed in detail in Chapters 3 through 7 of this progress report require a broad range of scientific expertise in environmental and petroleum engineering, ground water hydrology, fate and transport modeling, and toxicology, as well as many other disciplines. Consequently, the EPA is using a transdisciplinary research approach that

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[16] See, for example, research underway by the US Department of Energy's National Energy Technology Laboratory (http://www.netl.doe.gov/publications/factsheets/rd/R%26D166.pdf) and Penn State 3S Laboratory (http://3s.ems.psu.edu/research.html).

integrates various types of expertise from inside and outside the agency. The research projects fall into five categories: analysis of existing data, case studies, scenario modeling and evaluation, laboratory studies, and toxicology assessments. Table 8 summarizes the five main types of research activities occurring as part of this study and their objectives. Figure 3 illustrates the relationship between the research activities and the research projects and questions.

Table 8. Research activities and objectives. Each research project falls under one type of research activity.

Activity	Objective
Analysis of existing data	Gather and summarize existing data from various sources to provide current information on hydraulic fracturing activities; includes information requested of hydraulic fracturing service companies and oil and gas operators*
Scenario evaluations	Use computer modeling to assess the potential for hydraulic fracturing to impact drinking water resources
Laboratory studies	Conduct targeted experiments to test and develop analytical detection methods and to study the fate and transport of selected chemicals during wastewater treatment and discharge to surface water
Toxicity assessment	Identify chemicals used in hydraulic fracturing fluids or reported to be in hydraulic fracturing wastewater and compile available chemical, physical, and toxicological properties
Case studies	
Retrospective	Study sites with reported contamination to understand the underlying causes and potential impacts to drinking water resources
Prospective	Develop understanding of hydraulic fracturing processes and their potential impacts on drinking water resources

* For more information on the information requests, see http://www.epa.gov/hfstudy/analysis-of-existing-data.html.

3. Analysis of Existing Data

The objective of this approach is to gather and summarize data from many sources to provide current information on hydraulic fracturing activities. The EPA is collecting and analyzing data on chemical spills, surface water discharges, and chemicals found in hydraulic fracturing fluids and wastewater, among others. These data have been collected from a variety of sources, including state and federal agencies, industry, and public sources. Included among these sources is information received after the September 2010 letter requesting data from nine hydraulic fracturing service companies and the August 2011 letter requesting well files from nine oil and gas well operators.[17] This chapter includes progress reports for the following projects:

3.1. Literature Review 25
Review and assessment of existing papers and reports, focusing on peer-reviewed literature

3.2. Spills Database Analysis 31
Analysis of selected federal and state databases for information on spills of hydraulic fracturing fluids and wastewaters

3.3. Service Company Analysis 39
Analysis of information provided by nine hydraulic fracturing service companies in response to a September 2010 information request on hydraulic fracturing operations

3.4. Well File Review 46
Analysis of information provided by nine oil and gas operators in response to an August 2011 information request for 350 well files

3.5. FracFocus Analysis 54
Analysis of data compiled from FracFocus, the national hydraulic fracturing chemical registry operated by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission

3.1. Literature Review

3.1.1. Relationship to the Study

The EPA is gathering and assessing literature relevant to all secondary research questions.

3.1.2. Project Introduction

An extensive review of existing literature is an important component of the EPA's study of the relationship between hydraulic fracturing and drinking water resources. The objective of this literature review is to identify and analyze data and literature relevant to all secondary research questions. This objective will be met by reviewing a wide range of information sources on the five stages of the hydraulic fracturing water cycle. Sources identified through the literature review are subject to a quality review to support decisions regarding their inclusion in the EPA's report of

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[17] Copies of these information requests are available at http://www.epa.gov/hfstudy/analysis-of-existing-data.html.

results. Information gathered during the literature review will be synthesized with results from the other research projects described in this progress report to answer the research questions posed in the Study Plan and summarized in Chapter 2.

3.1.3. Research Approach

Existing literature and data is being identified through a variety of methods, including conducting a search of published documents, searching online databases such as OnePetro[18] and Web of Knowledge℠ [19] and reviewing materials provided to the EPA through technical workshops, comment submissions, and the Science Advisory Board's review of the draft study plan.[20] Once identified, sources are classified as shown in Table 9.

Table 9. Classifications of information sources with examples. Once identified, existing literature and data sources are classified according to the following categories.

Source Classification	Examples
Peer-reviewed literature	Journal publications, reports, and white papers developed by federal and state agencies
Non-peer-reviewed literature	Non-peer-reviewed government documents; congressional documents and hearing proceedings; workshop proceedings; Ph.D. theses; non-peer-reviewed reports and white papers from industry, associations, and non-governmental organizations
Unpublished data	Online databases, personal communications, unpublished manuscripts, unpublished government data

Once sources are grouped into the categories shown in Table 9 above, assessment factors are used to further evaluate their merit. Five assessment factors are being used to evaluate the quality of existing data and information: soundness, applicability and utility, clarity and completeness, uncertainty and variability, and evaluation and review (US EPA, 2003a). These factors are described in more detail in Table 10.

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[18] OnePetro is an online library of technical literature for the oil and gas exploration and production industry. It can be accessed at http://www.onepetro.org/.

[19] Thomson Reuters Web of Knowledge℠ is a research platform that provides access to objective content and powerful tools to search, track, measure, and collaborate in the sciences, social sciences, arts, and humanities. It can be accessed at http://wokinfo.com/.

[20] A list of literature recommended by the Science Advisory Board can be found on pages 29–34 of the Science Advisory Board's review of the draft Study Plan, available at http://yosemite.epa.gov/sab/sabproduct.nsf/0/2BC3CD632FCC0E99852578E2006DF890/$File/EPA-SAB-11-012-unsigned.pdf.

Table 10. Description of factors used to assess the quality of existing data and information compiled during the literature review. The assessment factors are identified in (US EPA, 2003a).

Factors	Description
Soundness	The extent to which the scientific and technical procedures, measures, methods, or models employed to generate the information are reasonable for, and consistent with, the intended application
Applicability and utility	The extent to which the information is relevant for the agency's intended use
Clarity and completeness	The degree of clarity and completeness with which the data, assumptions, methods, quality assurance, sponsoring organizations, and analyses employed to generate the information are documented
Uncertainty and variability	The extent to which the variability and uncertainty (quantitative and qualitative) in the information or in the procedures, measures, methods or models are evaluated and characterized
Evaluation and review	The extent of independent verification, validation, and peer review of the information or of the procedures, measures, methods, or models

Information included in the report of results will be drawn primarily from peer-reviewed publications. Peer-reviewed publications contain the most reliable information, although some portions of the report may contain compilations of data from a variety of sources and source classifications. Non-peer-reviewed and unpublished sources will not form the sole basis of any conclusions presented in the report of results. Generally, these sources will be used to support results presented from peer-reviewed work, enhance understanding based on peer-reviewed sources, identify promising ideas of investigation, and discuss further in-depth work needed.

The criteria in Table 10 are applied to all sources to ensure that the EPA is using high-quality data. In some cases, these data may not strictly meet the quality guidelines outlined in Table 10, though they still provide valuable information. Principal investigators on this project are responsible for deciding whether to include these data and providing all available background information in order to place these results in the appropriate context.

3.1.4. Status and Preliminary Data

The literature review is currently underway. Water acquisition, chemical mixing, and flowback and produced water are the only stages of the hydraulic fracturing water cycle for which specific updates are available at this time.

Water Acquisition. The water acquisition literature review is intended to complement the analysis of existing data on hydraulic fracturing fluid source water resources from nine service companies (see Section 3.3) and nine oil and gas operators (Section 3.4), as well as the analysis of existing data from FracFocus (Section 3.5). Work at this stage is directed at answering three secondary research questions:

- How much water is used in hydraulic fracturing operations, and what are the sources of this water?
- How might water withdrawals affect short- and long-term water availability in an area with hydraulic fracturing activity?

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

To date, work has focused on the first question regarding the volumes and sources of water acquired for use in hydraulic fracturing. The literature review focuses on the major basins where hydraulic fracturing is prevalent in order to present a national perspective on water use. Hydrocarbon plays that will be highlighted include the Barnett, Eagle Ford, and Haynesville Shales in the South, the Bakken Shale in the Midwest, and the Marcellus and Utica Shales in the East.

The Barnett, Eagle Ford, and Haynesville Shales have undergone the most thorough analysis as reflected by the availability of peer-reviewed literature pertaining to the Texas oil and gas basins and to the water resources in the southern United States. The Bakken Shale has also been investigated extensively, although very little peer-reviewed literature was available for analysis as of July 2012. Instead, information on volumes and sources of water in the Bakken Shale comes largely from news articles. Water acquisition in the Marcellus and Utica Shales has not yet been analyzed, but water withdrawal data is expected to be available.

Chemical Mixing and Flowback and Produced Water. Existing scientific literature is being reviewed to identify how chemicals used in hydraulic fracturing fluids or present in hydraulic fracturing wastewaters may contaminate drinking water resources as a result of surface spills of these fluids. Relevant information from the literature review will help address the research questions listed below:

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

The EPA has identified chemicals for further review based on publicly available information on hazard and frequency of use. Tables 11 and 12 identify a subset of chemicals used in hydraulic fracturing fluids as reported to the US House of Representatives' Committee on Energy and Commerce by 14 hydraulic fracturing service companies as being used in hydraulic fracturing fluids between 2005 and 2009 (USHR, 2011). Table 11 lists chemicals that are known or suspected carcinogens, regulated by the Safe Drinking Water Act (SDWA), or listed as Clean Air Act hazardous air pollutants. The Committee included the hazardous air pollutant designation for listed chemicals because some may impact drinking water (e.g., methanol and ethylene glycol). Table 12 lists the chemical components appearing most often in over 2,500 hydraulic fracturing products used between 2005 and 2009, according to the information reported to the Committee.

Table 11. Chemicals identified by the US House of Representatives Committee on Energy and Commerce as known or suspected carcinogens, regulated under the Safe Drinking Water Act (SDWA) or classified as hazardous air pollutants (HAP) under the Clean Air Act. The number of products containing each chemical is also listed. These chemicals were reported by 14 hydraulic fracturing service companies to be in a total of 652 different products used between 2005 and 2009. Reproduced from USHR (2011).

Chemicals	Category	No. of Products
Methanol	HAP	342
Ethylene glycol	HAP	119
Naphthalene	Carcinogen, HAP	44
Xylene	SDWA, HAP	44
Hydrochloric acid	HAP	42
Toluene	SDWA, HAP	29
Ethylbenzene	SDWA, HAP	28
Diethanolamine	HAP	14
Formaldehyde	Carcinogen, HAP	12
Thiourea	Carcinogen	9
Benzyl chloride	Carcinogen, HAP	8
Cumene	HAP	6
Nitrilotriacetic acid	Carcinogen	6
Dimethyl formamide	HAP	5
Phenol	HAP	5
Benzene	Carcinogen, SDWA, HAP	3
Di (2-ethylhexyl) phthalate	Carcinogen, SDWA, HAP	3
Acrylamide	Carcinogen, SDWA, HAP	2
Hydrofluoric acid	HAP	2
Phthalic anhydride	HAP	2
Acetaldehyde	Carcinogen, HAP	1
Acetophenone	HAP	1
Copper	SDWA	1
Ethylene oxide	Carcinogen, HAP	1
Lead	Carcinogen, SDWA, HAP	1
Propylene oxide	Carcinogen, HAP	1
p-Xylene	HAP	1

Table 12. Chemical appearing most often in hydraulic fracturing in over 2,500 products reported by 14 hydraulic fracturing service companies as being used between 2005 and 2009. Reproduced from USHR (2011).

Chemical	No. of Products
Methanol	342
Isopropanol	274
Crystalline silica	207
2-Butoxyethanol	126
Ethylene glycol	119
Hydrotreated light petroleum distillates	89
Sodium hydroxide	80

Existing scientific literature is also being reviewed for the chemicals identified as part of the analytical method development research project (see Table 45 in Section 5.4). This table includes chemicals associated with injected hydraulic fracturing fluids and wastewater.

Literature searches have found papers describing impacts from spills of produced water (Healy et al., 2011; Healy et al., 2008), although the emphasis is often on ecosystem impacts rather than drinking water impacts. Produced water has the greatest number of literature publications for reported spills compared to hydraulic fracturing fluids and flowback, because produced water must be managed in both conventional and unconventional oil and gas production. Papers describing impacts from spills of produced water from conventional oil and gas production wells are being considered as part of the literature review because the chemical composition of flowback and produced water from hydraulically fractured formations is similar to that of conventional reservoirs (Hayes, 2009). Publications about impoundment leaks or other types of surface impoundment failures are also included within the scope of the flowback and produced water literature review.

Because some of the chemicals commonly used in hydraulic fracturing fluid are ubiquitous, a very large numbers of papers have been found. To narrow the scope, recent review papers on environmental impacts and other published summaries on transport of chemicals or classes of chemicals are being sought. Information on the chemicals listed in Tables 11, 12, and 45 has been collected primarily by searching peer-reviewed literature using keyword searches of major databases, including Web of Knowledge℠, Proquest,[21] and OnePetro. Review papers describing impacts from spills of hydraulic fracturing fluids containing benzene, toluene, ethylbenzene, and xylenes (Farhadian et al., 2008; Seagren and Becker, 2002; Seo et al., 2009); ethylene glycol (Staples et al., 2001); phenol (Van Schie and Young L.Y., 2000); surfactants (Scott and Jones, 2000; Sharma et al., 2009; Soares A. et al., 2008; Van Ginkel, 1996); and napthalenes (Haritash and Kaushik, 2009; Rogers et al., 2002) have been identified. Other sources of information include the Government Accountability Office report on federal research on produced water (US GAO, 2012); toxicological profiles from the Agency for Toxic Substances and Disease Registry, which often contain brief summaries of information on transport and transformation;[22] EPA software systems (US EPA, 2012b); and chemical reference handbooks (Howard, 1989; Howard et al., 1991; Montgomery, 2000). Specific discussion of abiotic transformations is included in some of these references, including the Agency for Toxic Substances and Disease Registry Toxicological Profiles, environmental organic chemistry references (Schwarzenbach et al., 2002), and review papers (Stangroom et al., 2010).

Chemical and physical properties of most of the organic chemicals listed in Tables 11 and 12 have been summarized, and the analysis is nearly complete. As more chemicals of interest are identified throughout the study, the number of chemicals may expand. Fewer publications exist for less

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[21] ProQuest can be accessed at http://www.proquest.com.

[22] See, for example, pages 258–259 of ATSDR (2007).

common chemicals, however, and obtaining enough data to characterize these chemicals' potential to affect drinking water resources may not be feasible.

3.1.5. Next Steps

Next steps include completing the literature review for questions pertaining to sources, volumes, and impacts of large volume water withdrawals on local water quality and water availability. Further review of the water acquisition and quantity literature will specifically address the volumes and sources of water used in the Marcellus and Utica Shales. The literature review on chemical mixing and flowback and produced water for information that may answer the secondary research questions for those water stages will be completed. The EPA will also review relevant literature on all the remaining secondary research questions.

3.1.6. Quality Assurance Summary

The quality assurance project plan (QAPP) for the literature review, "Data and Literature Evaluation for the EPA's *Study of the Potential Impacts of Hydraulic Fracturing (HF) on Drinking Water Resources* (Version 0)," was approved on September 4, 2012 (US EPA, 2012f). Links to the all of the QAPPs are provided in Appendix C.

3.2. Spills Database Analysis

3.2.1. Relationship to the Study

The primary research questions for the chemical mixing and flowback and produced water stages of the hydraulic fracturing water cycle focus on the potential for hydraulic fracturing fluids and wastewaters to be spilled on the surface, possibly impacting nearby drinking water resources. This project searches various data sources in order to answer the research questions listed in Table 13.

Table 13. Secondary research questions addressed by reviewing existing databases that contain data relating to surface spills of hydraulic fracturing fluids and wastewater.

Water Cycle Stage	Applicable Research Questions
Chemical mixing	What is currently known about the frequency, severity, and causes of spills of hydraulic fracturing fluids and additives?
Flowback and produced water	What is currently known about the frequency, severity, and causes of spills of flowback and produced water?

3.2.2. Project Introduction

Hydraulic fracturing operations require large quantities of chemical additives, equipment, water, and vehicles, which may create risks of accidental releases, such as spills or leaks. Surface spills or releases can occur as a result of events such as tank ruptures, equipment or surface impoundment failures, overfills, vandalism, accidents, ground fires, or improper operations. Released fluids might flow into nearby surface water bodies or infiltrate into the soil and near-surface ground water, potentially reaching drinking water aquifers (NYSDEC, 2011).

Over the past few years, there have been numerous media reports of spills of hydraulic fracturing fluids and wastewater (US EPA, 2011e). While the media reports have highlighted specific surface spills of hydraulic fracturing fluids and wastewaters, the frequency and typical causes of these spills remain unclear. Additionally, these reports may tend to highlight severe spills and may not accurately reflect the distribution, number, and severity of spills across the country. The EPA is compiling information on surface spills of hydraulic fracturing fluids and wastewaters as reported in federal and state databases to assess the frequency, severity, and causes of spills associated with hydraulic fracturing. Hydraulic fracturing fluid and wastewater spill information was also collected from nine hydraulic fracturing service companies and nine oil and gas operators, as discussed in Sections 3.3 and 3.4, respectively. Together, these data are being used to describe spills of hydraulic fracturing fluids and wastewater and to identify factors that may lead to potential impacts on drinking water resources.

3.2.3. Research Approach

There is currently no national repository or database that contains spill data focusing primarily on hydraulic fracturing operations. In the United States, spills relating to oil and gas operations are reported to the National Response Center (NRC) and various state regulatory entities. For example, in Colorado, spills are reported to the Oil and Gas Conservation Commission, within the Department of Natural Resources, while in Texas, oil and gas related spills are reported to the Texas Railroad Commission and the Texas Commission on Environmental Quality, depending on which agency has jurisdiction. The EPA has identified one federal database and databases in five states for review, as listed in Table 14. The NRC database was selected because it is the only nationwide source of information on releases of hazardous substances and oil. Spill databases from Colorado, New Mexico, Pennsylvania, Texas, and Wyoming were chosen for further consideration due to the large number of hydraulically fractured oil and gas wells found in those states.[23]

Table 14. Oil and gas-related spill databases used to compile information on hydraulic fracturing-related incidents.

Source	Website
National Response Center Freedom of Information Act data	http://www.nrc.uscg.mil/foia.html
Colorado Oil and Gas Information System	http://www.cogcc.state.co.us
New Mexico Energy, Minerals and Natural Resources Department	https://wwwapps.emnrd.state.nm.us/ocd/ocdpermitting/Data/Incidents/Spills.aspx http://www.emnrd.state.nm.us/ocd/Statistics.html
Pennsylvania Department of Environmental Protection Compliance Reporting Database	http://www.depreportingservices.state.pa.us/ReportServer/Pages/ReportViewer.aspx?/Oil_Gas/OG_Compliance
Texas Railroad Commission and Texas Commission on Environmental Quality	Consolidated Compliance and Enforcement Data System (not publicly available online)
Wyoming Department of Environmental Quality Water Quality Enforcement Actions	http://deq.state.wy.us/out/WQenforcementactions.htm

Each of the publicly available databases identified in Table 14 has been searched for spill incidents related to hydraulic fracturing operations. The search timeframe is limited to incidents between January 1, 2006, and April 30, 2012, in order to encompass the increase in hydraulic fracturing

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[23] Based on data provided by nine hydraulic fracturing service companies of oil and gas wells fractured between 2009 and 2010. See Figure 10 in Section 3.3.

activity seen during that period. To the extent that data are publicly available, electronically accessible, and readily searchable for spill-related data, the following information is being compiled about specific hydraulic fracturing-related spill incidents:

- Data source
- Location
- Chemicals/products spilled
- Estimated/reported volume of spill
- Cause of spill
- Reported impact to nearby water resources
- Proximity of the spill to the well or well pad

The information obtained from the NRC and state databases is being reviewed with information received in response to the EPA's September 2010 information request to nine hydraulic fracturing service companies (see Section 3.3) and the EPA's August 2011 information request to nine oil and gas operators (Section 3.4). The resulting list of unique spill incidents is being queried to identify common causes of hydraulic fracturing-related spills, chemicals spilled, the ranges of volumes spilled, and the potential impacts of these spills to drinking water sources. Because the main focus of this study is to identify hydraulic fracturing-related spills on the well pad that may impact drinking water resources, the following topics are not included in the scope of this project:

- Transportation-related spills (except when tanker trucks act as mobile portable storage containers for chemicals, products, and hydraulic fracturing wastewater used on drilling sites)
- Drilling mud spills
- Air releases
- Spills associated with disposal through underground injection control wells
- Erosion and sediment control issues
- Spill drills and exercise events (per NRC data)
- Well construction and permitting violations
- Leaks from pipes transporting flowback and produced water from one site to another for reuse

3.2.4. Status and Preliminary Data

The EPA has initiated work on all publicly available databases listed in Table 14. This section summarizes the type of information available in each database and lists the criteria being used to search each database.

National Response Center Freedom of Information Act Data. This database contains nationwide data on releases of hazardous substances and oil that trigger the federal notification requirements under several laws. The NRC is the sole federal point of contact for reporting of all hazardous substances releases and oil spills. Its information comes from people who arrive on the scene or discover a spell, then call the NRC hotline or submit a Web-based report form. The information collected by the NRC during the initial notification call may include the suspected responsible party; the incident location by county, state, and nearest city; the released material and volume or quantity released; and a description of the incident, incident causes, affected media, initial known damages, and remedial actions taken. This information is often based on the estimates made by persons responding to a spill and may be incomplete. More accurate information may be available once a response is complete, but this database is not updated with such information.

The data fields that can be used to query the NRC database are listed in Table 15. Many of these fields only allow searches from a fixed (i.e., drop-down) list, although several of the data fields are open to any input. None of the search terms in the fixed lists are specific to hydraulic fracturing or oil and gas exploration and production.

Table 15. Data fields available in the NRC Freedom of Information Act database. "Fixed list data fields" contain a fixed list of search terms form which the user can choose. "Open data fields" can receive any input from the user.

Fixed List Data Fields	Open Data Fields
Type of call	NRC report number
Incident date range	Nearest city
State	Suspected responsible company
County	Material name
Incident type	
Incident cause	
Medium affected	

Given the query restrictions, broad searches are being conducted using the listed responsible company, material name, and incident date range fields (i.e., leaving other fields blank).

The resulting spills are being examined to determine their relevance to this study. Since the database includes only initial incident reports, information is frequently missing or estimated, such as total volume spilled. Also, misspellings in the reports or the use of different vocabulary can cause the search engine to miss relevant incidents.

Colorado. The Colorado Oil and Gas Conservation Commission gathers data regarding pits, spills/releases, and complaints relating to oil and gas exploration and production. Oil and gas operators are required to report spills and releases that occur as a result of oil and gas operations, in accordance with Colorado Oil and Gas Conservation Commission Rule 906 (COGCC, 2011). Reported information is entered into the Colorado Oil and Gas Information System Inspection/Incident Database. Each report documents the type of facility, volume spilled and/or recovered, ground water impacts, depth to shallowest ground water, surface water impacts, distance to nearest surface water, cause of spill, and a detailed description of the incident. The database is searchable by API number,[24] complainant, operator, facility/lease, location, remediation project number, and document number. Since there is no searchable data field in the database to indicate whether the spill is related to hydraulic fracturing, the database was queried for all spill/release reports. Only reports dated from January 1, 2006, to April 30, 2012, were selected for further review. This search returned over 2,500 reports that are currently being evaluated to identify incidents related to hydraulic fracturing activities.

New Mexico. The Oil Conservation Division of the State of New Mexico Energy, Minerals and Natural Resources Department tracks information, in two separate databases, on both spill incidents and incidents where liquids in pits have contaminated ground water. Release Notification and Corrective Action forms are submitted to the Oil Conservation Divisions District offices. Spills can be reported by industry representatives or state agency personnel.

The spills database is searchable by facility and well names, incident type, operator, location, lease type, spilled material, spill cause, spill source, and the spill referrer (person who reported the incident). The database was initially searched using the spill material, spill cause, and spill source data fields. Each of these fields can only be searched using the preset search terms listed in Table 16. The initial search was conducted using the search terms in bold in Table 16. The EPA is currently examining the resulting list of spills to determine their relevancy to this study and is considering running additional queries to collect more information.

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[24] The API (American Petroleum Institute) number is a unique, permanent, numeric identifier assigned to each well drilled for oil and gas in the United States.

Table 16. Preset search terms available for the spill material, spill cause, and spill source data fields in the New Mexico Oil Conservation Division Spills Database. Terms in bold have been searched.

Spill Material	Spill Cause	Spill Source
All	All	All
Acid	**Blowout**	Coupling
Brine water	Corrosion	Gas compression station
B.S. & W (basic sediment & water)	Equipment failure	Dump line
Chemical (specify)	Fire	Motor
Condensate	Freeze	Flowline—injection
Diesel	Human error	Flowline—production
Drilling mud/fluid	Lightning	**Frac tank**
Glycol	Other	Fitting
Gasoline	Normal operations	Injection header
Gelled brine (frac fluid)	Vandalism	Other (specify)
Hydrogen sulfate	Vehicular accident	**Pit (specify)**
Crude oil		Pipeline (any)
Motor oil		Production tank
Natural gas (methane)		Pump
Natural gas liquids		Separator
Lube oil		Transport
Other (specify)		Unknown
Produced water		Valve
Unknown		Well
		Water tank

The database containing information regarding contamination of ground water due to pits tracks only the current company, facility name, tracking number, county, location, and status of the contamination incidents. Details regarding the contamination incident and the relation of the event to hydraulic fracturing are not included. Additional research is needed to determine if the pit information is related to hydraulic fracturing.

Pennsylvania. The Pennsylvania Department of Environmental Protection's Compliance Reporting Database provides information on oil and gas inspections, violations, enforcement actions, and penalties assessed and collected. Users can search the database according to the following fixed-variable data fields: county, municipality, date inspected, operator, Marcellus only,[25] inspections with violations only, and resolved violations only.

Table 17 displays the total number of incidents retrieved for four different queries, all using a date range of January 1, 2006, to April 30, 2012.

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[25] This data field was recently changed to "unconventional only" (last accessed July 6, 2012).

Table 17. Total number of incidents retrieved from the Pennsylvania Department of Environmental Protection's Compliance Reporting Database by varying inputs in the "Marcellus only" and inspections with "violations only data fields." In all cases, "no" was entered in the "resolved violations only" field.

Marcellus Only	Inspections with Violations Only	Total Number of Incidents Retrieved
Yes	No	25,687
Yes	Yes	4,319
No	Yes	18,700
No	No	Unknown*

* Error message received when formatting results of this query.

The queries shown in Table 17 returned information collected during inspections that found violations and/or when spills are reported. An incident or inspection may have multiple violations, leading to a large total number of violations retrieved from the database. The EPA's initial effort focused on the query that returned the fewest violations, which totaled 4,319 inspections with violations specific to the Marcellus Shale region. Inspection and violation comment fields for each incident are being reviewed to identify incidents related to hydraulic fracturing activities.

Texas. Representatives of the Railroad Commission of Texas, the Texas Commission on Environmental Quality, and the Texas General Land Office have confirmed that there is no central database in Texas on hydraulic fracturing-related spills. In Texas, a memorandum of understanding between the Railroad Commission and Commission on Environmental Quality identifies the jurisdiction of these agencies over waste materials resulting from exploring, developing, producing, and refining oil and gas. Pursuant to this understanding, oil and gas operators are required to report spills to the Railroad Commission, which maintains a publicly available database of spills of petroleum, oil, and condensate. The EPA has reviewed this database and determined that it does not include chemical spills; most of the spills reported in the database are crude oil spills. Therefore, there will be no further analysis of this database.

The Commission on Environmental Quality is Texas' lead agency in responding to spills of all hazardous substances that may cause pollution or lower air quality pursuant to the Texas Hazardous Substances Spill Prevention and Control Act (Texas Water Code §26.261). The Commission on Environmental Quality may generate an investigation, inspection, or complaint report in response to emergency spill notifications. These reports are submitted to the state's Consolidated Compliance and Enforcement Data System. However, the investigation and inspection reports in this database are not available electronically on the Texas Commission on Environmental Quality's website or at their Central Files Room.

Other attempts were made to obtain information on potential ground water contamination incidents related to hydraulic fracturing by examining the Joint Groundwater Monitoring and Contamination Reports prepared by the Texas Groundwater Protection Committee; this effort was unsuccessful in getting the relevant incident details. The abovementioned searches for hydraulic fracturing spill-related data may not be an exhaustive investigation of all available information from Texas' state agencies or organizations, but other publicly available sources of information have not been located at this time.

Wyoming. The Wyoming Department of Environmental Quality maintains a publicly available database of water quality enforcement actions. This database includes reports of water quality violations categorized by the year they occurred, from 2006 to 2012. None of the reports differentiate between hydraulic fracturing-related incidents and those due to other stages of oil and gas development. Many of the oil and gas-related violations were for CBM produced water discharges, such as to surface water. Due to the lack of information to differentiate between hydraulic fracturing-related incidents and other oil and gas-related incidents, there will be no further analysis of this dataset.

The spills database analysis has several important limitations:

- *Potential underreporting.* This affects the EPA's ability to assess the number or frequency of hydraulic fracturing-related spill incidents, since it is likely that some spills are not reported to the NRC or state agencies.
- *Variation in reporting requirements for different sources.* This makes it difficult to categorize reported spills as hydraulic fracturing-related and to comprehensively identify the causes, chemical identity, and volumes of hydraulic fracturing-related spills.
- *The lack of electronic accessibility of some state-reported data on oil and gas-related spills and emergency responses.* This also significantly impacts the comprehensiveness of the available information.

3.2.5. Next Steps

As noted, the EPA is reviewing the list of spill incidents generated by searching the NRC, Colorado, New Mexico, and Pennsylvania databases to identify incidents related to hydraulic fracturing activities. Spill incidents identified through this review will be combined with data received from nine hydraulic fracturing service companies (see Section 3.3) and nine oil and gas operators (Section 3.4) to create a master database of hydraulic fracturing-related spills from these sources. The compiled information will be examined to identify, where possible, common causes of hydraulic fracturing-related spills, chemicals spilled, and ranges of volumes spilled. Specific steps will then include:

- Creating a reference table of information gathered from all incidences determined to be related to hydraulic fracturing.
- Reviewing this reference table for trends in the causes and volumes of hydraulic fracturing-related spills.

3.2.6. Quality Assurance Summary

The QAPP for the analysis of publicly available information on surface spills related to hydraulic fracturing, "Hydraulic Fracturing (HF) Surface Spills Data Analysis (Version 1)," was approved on August 6, 2012 (US EPA, 2012l). The project underwent a technical systems audit (TSA) by the designated EPA QA Manager on August 27, 2012. The methods and products being developed under the project adhered to the approved QAPP, and no corrective actions were identified.

3.3. *Service Company Analysis*

3.3.1. Relationship to the Study

The EPA asked nine hydraulic fracturing service companies for information about hydraulic fracturing operations conducted from 2005 to 2010. The data are being analyzed for information that can be used to inform answers to the research questions in Table 18.

Table 18. Secondary research questions addressed by analyzing data received from nine hydraulic fracturing service companies.

Water Cycle Stage	Applicable Research Questions
Water acquisition	• How much water is used in hydraulic fracturing operations, and what are the sources of this water?
Chemical mixing	• What is currently known about the frequency, severity, and causes of spills of hydraulic fracturing fluids and 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?
Well injection	• How effective are current well construction practices at containing gases and fluids before, during, and after fracturing? • Can subsurface migration of fluids or gases to drinking water resources occur and what local geologic or man-made features may allow this? • How might hydraulic fracturing fluids change the fate and transport of substances in the subsurface through geochemical interactions?
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 wastewaters, and what factors might influence this composition?

3.3.2. Project Introduction

Hydraulic fracturing is typically performed by a service company under a contract with the oil or gas production well operator. The service companies possess detailed information regarding the implementation of hydraulic fracturing, from design through fracturing. In September 2010, the EPA requested information from nine companies on the chemical composition of hydraulic fracturing fluids used from 2005 to 2010, standard operating procedures (SOPs), impacts of chemicals on human health and the environment, and the locations of oil and gas wells hydraulically fractured in 2009 and 2010. The EPA is analyzing the information received from the service companies to better understand current hydraulic fracturing operating practices and to answer the research questions listed above.

Service Companies Selected. Nine service companies received the information request: BJ Services Company, Complete Production Services, Halliburton, Key Energy Services, Patterson-UTI Energy, RPC, Schlumberger, Superior Well Services, and Weatherford International. These companies reflect a range of industry market share and variation in company size. The EPA estimated that BJ Services Company, Halliburton, and Schlumberger performed approximately 95% of hydraulic fracturing services in the United States in 2003 (US EPA, 2004b), and the three companies reported the highest annual revenues for 2009 of the nine companies selected for the information request.[26] The remaining six companies represent mid-sized and small companies performing hydraulic fracturing services between 2005 and 2009.[27] Table 19 shows the annual revenue, number of employees, and company services reported by the companies to the US Securities and Exchange Commission in the 2009 Form 10-K.

Table 19. Annual revenue and approximate number of employees for the nine service companies selected to receive the EPA's September 2010 information request. The companies reflect a range of industry market share and company sizes. Information was obtained from Form 10-K, filed with the US Securities and Exchange Commission in 2009.

Company	Annual Revenue for 2009 (Millions)	Number of Employees (Approximate)
BJ Services Company*	$4,122	14,400
Complete Production Services	$1,056	5,200
Halliburton	$14,675	51,000
Key Energy Services	$1,079	8,100
Patterson-UTI Energy	$782	4,200
RPC	$588	2,000
Schlumberger	$22,702	77,000
Superior Well Services	$399	1,400
Weatherford International	$8,827	52,000

* BJ Services reports on a fiscal year calendar ending on September 30.

Three of the nine service companies that reported information to the EPA were acquired by other companies since 2010. Baker Hughes completed the purchase of BJ Services Company in April 2010, Patterson-UTI Energy purchased Key Energy Services in October 2010, and Superior Well Services acquired Complete Production Services in February 2012.

3.3.3. Research Approach

The EPA received responses to the September 2010 information request from each of the nine service companies. Data and information relevant to the research questions posed above were collected and organized in Microsoft Excel spreadsheets and Microsoft Access databases. Each company reported information in various organizational formats and using different descriptive terms; therefore, the EPA has put all nine datasets into a consistent format for analysis and resolving any issues associated with terminology, data gaps, or inconsistencies. This selection of information serves as the basis for targeted queries and data summaries described below. The queries and data summaries have been designed to answer the secondary research questions listed in Table 18.

Much of the data and information received by the EPA was claimed to be confidential business information (CBI) under the Toxic Substances Control Act (TSCA). Five of the nine companies,

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[26] Information was obtained from the 2009 Form 10-K, filed with the US Securities and Exchange Commission.

[27] Annual revenue and number of employees were used as indicators of company size.

however, also provided non-confidential information.[28] Because the majority of the information has been claimed as CBI, the analyses described below are being conducted in accordance with the procedures outlined in the EPA's TSCA CBI Protection Manual (US EPA, 2003b). All results are treated as CBI until determinations are made or until masking has been done to prevent disclosure of CBI information.

Summary of Service Company Operations. The EPA is using information provided by the companies to write a narrative description of the range of their operations, which includes information on the role of the service companies in each stage of the hydraulic fracturing water cycle.

Information has been compiled on the number and location of wells hydraulically fractured by the nine service companies between September 2009 and October 2010, resulting in a map that displays the number of wells fractured per county as reported by the companies. This information is intended to illustrate the intensity and geographic distribution of hydraulic fracturing activities by these companies.

Water Acquisition. The following information from the service company data on volumes, quality, and sources of water used in hydraulic fracturing fluids is being summarized and will include:

- *Water use by shale play*. The range of water volumes used based on the shale play in which the well is located. (The companies did not provide information on geologic formations other than shale.)
- *Procedures and considerations relating to water acquisition.* Summary of any SOPs, water quality requirements, water source preferences, and decision processes described in the submissions from the nine service companies.

Chemical Mixing. The following information collected from the service companies is being assembled to identify the composition of different hydraulic fracturing fluid formulations and the factors that influence formulation composition:

- Chemical name
- Chemical formula
- Chemical Abstracts Service Registration Number (CASRN)
- Material Safety Data Sheets (MSDSs) for each fluid product
- Concentration of each chemical in each fluid product
- Manufacturer of each product and chemical
- Purpose and use of each chemical in each fluid product

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[28] The non-confidential information is available on the federal under docket number EPA-HQ-ORD-2010-0674 or via http://www.regulations.gov/#!searchResults;rpp=10;po=0;s=epa-hq-ord-2010-0674.

For the purposes of the analysis, the EPA defines a "product" as an additive composed of a single chemical or several chemicals. A "chemical" is an individual chemical included in a product. A "fluid formulation" is the entire suite of products and carrier fluid injected into a well during hydraulic fracturing. The following information from the service company data on chemicals, products, and fluid formulations is being summarized:

- *Formulations, products, and product function.* The formulations reported by the nine service companies and the number and types of products used in those formulations.
- *Products, chemicals in those products and concentrations, and manufacturer of each product.* The chemicals used in each product may be used in conjunction with the formulations data (described in the previous bullet) to discern the chemicals used in each formulation. The manufacturer of each product will also be included.
- *Number of products reported for a given product function and the frequency with which a product function is reported in the formulations data.* The product function with the greatest number of products and the product function that is most often used in formulations.
- *Number of products and chemicals for each type of formulation.* The chemicals and products for various types of formulations and a description of the average number of products and chemicals for each formulation type, as well as the sample size for each population and common product functions for each formulation type.
- *Typical loadings for each group of products of a given product function and for each fluid formulation type.* The typical proportion of a product in a formulation. Typical loading values (e.g., gallons per thousand gallons) indicate an amount or volume of a product added to a volume of fracturing fluids rather than an accurate representation of the concentration of a particular product or the chemical constituents of a product in a fluid formulation.

Information provided by the companies relating to surface spills of hydraulic fracturing fluids and chemicals has been compiled, resulting in a table of specific spill incidences. The table includes information on the location, composition, volume, cause, and any reported impacts of each spill. This information will be used in the larger analysis of surface spills reported in federal and state databases (Section 3.2).

Well Injection. The EPA requested information regarding the hydraulic fracturing service companies' procedures for establishing well integrity, procedures used during well injections, and response plans to address unexpected circumstances (e.g., unexpected pressure changes during injection). Information provided by the companies will be used to write a narrative description of the range of operations conducted by this sample of service companies.

Flowback and Produced Water. Although this information was not requested, the EPA received some documents and information that referenced flowback and produced water, including policies, practices, and procedures employed by companies to determine estimated volumes and management options. The EPA has reviewed this information as well as information relevant to the frequency, severity, and causes of flowback and produced water spills and the composition of hydraulic fracturing wastewaters. The outputs of the analysis will include the following:

- *Reported spills of flowback and produced water.* Information on the composition of the fluid spilled, the volume spilled, the reported cause of the spill, and any reported impacts to nearby water resources. This information will be integrated into the larger analysis of surface spills reported in federal and state databases (see Section 3.2).
- *Reported compositions of hydraulic fracturing wastewater.* Information on the chemical and physical properties of hydraulic fracturing wastewater, such as the identities of analytes of interest and reported concentration ranges. To the extent possible, this information will be organized according to geologic and geographic location as well as time after fluid injection.
- *Flowback and produced water management.* Where possible, information about the role of hydraulic fracturing service companies in handling flowback and produced water will be described.

3.3.4. Status and Preliminary Data

Preliminary data analyses of service company operations, water acquisition, chemical mixing, and flowback and produced water has been completed and the analysis of well injection information has begun. The EPA has met with representatives from each of the nine hydraulic fracturing service companies to discuss their responses to the September 2010 information request. Information gathered during these meetings has been used to inform the data analysis and to ensure that confidential information is protected. As of September 2012, the EPA continues to clarify the information reported and to work with the nine hydraulic fracturing service companies to release information originally designated as CBI without compromising trade secrets.

Service Company Operations. As a group, the nine service companies reported that they hydraulically fractured 24,925 wells in the United States in 2009 and 2010. The companies reported the number of wells per county, which is displayed for all companies in Figure 10.

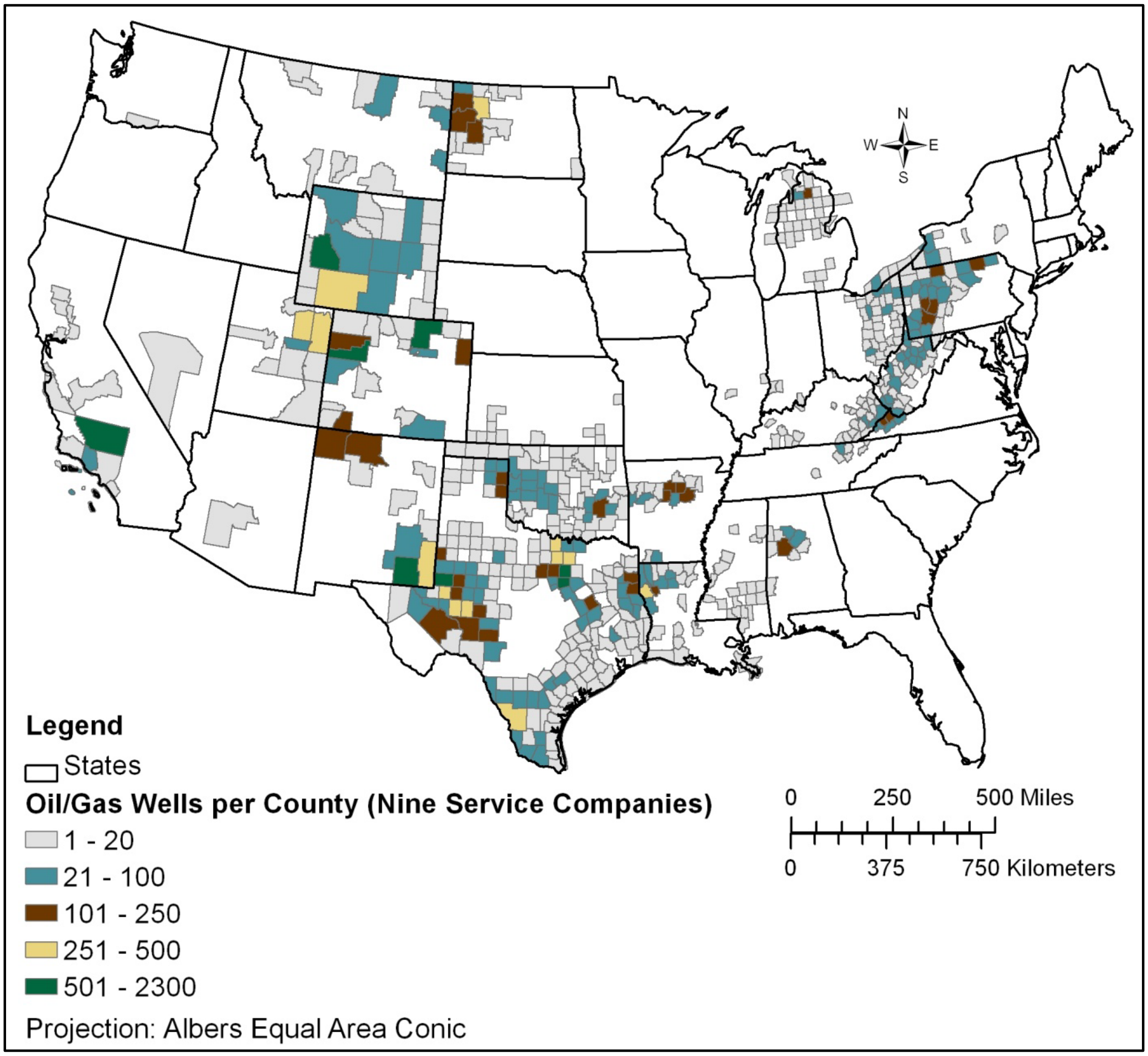

Figure 10. Locations of oil and gas production wells hydraulically fractured between September 2009 and October 2010. The information request to service companies (September 2010) resulted in county-scale locations for 24,925 wells. The service company wells represented in this map include only 24,879 wells because the EPA did not receive locational information for 46 of the 24,925 reported wells. (ESRI, 2010a, b; US EPA, 2011a)

Chemical Mixing. The service companies reported a total of 114 example formulations and 1,858 unique producets, which consist of 677 unique chemicals, used by the service companies between September 2005 and 2010.[29] Table 20 shows the number of formulations, products, and chemicals reported by each of the nine service companies; the totals for products and chemical constituents in Table 20 reflect use by multiple companies and are therefore greater than the sum of unique products and chemical constituents. The formulations reported to the EPA are not comprehensive, as each service company chose them as examples of the fluids they use.

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[29] Products and chemical constituents noted here are unique and may have been reported multiple times by the service companies.

Table 20. Formulations, products, and chemicals reported as used or distributed by the nine service companies between September 2005 and September 2010.

Company	Formulations	Products*	Chemical Constituents[†]
BJ Services	37	401	118
Key Energy Services	16	180	119
Halliburton	15	450	304
RPC	13	182	128
Schlumberger	11	110	61
Patterson-UTI Energy	10	67	67
Weatherford International	6	214	180
Complete Production Services	3	122	92
Superior Well Services	3	312	117

* Companies reported examples of formulations, which did not contain all of the products reported to the EPA.

[†] Not all products have reported chemicals.

Non-confidential hydraulic fracturing chemicals reported by the companies appear in Appendix A, along with chemicals reported from publicly available sources.

Well Injection. Seven service companies reported 231 protocols to the EPA. The protocols describe the procedures used by the companies for many aspects of field and laboratory work, including site and infrastructure planning, chemical mixing and design of fracturing fluid formulations, health and safety practices, well construction, and hydraulic fracturing. The EPA is analyzing the information to assess how hydraulic fracturing service companies use SOPs, to better understand how well integrity is established prior to fracturing, and to evaluate procedures used during well injection.

Flowback and Produced Water. Data provided by the companies indicate that the company conducting the fracturing is often not the same company that manages the flowback process. Five of the companies responded that they do not provide flowback services, although one of these companies provides analytical support to operators for the testing of flowback water for potential reuse. Two of the nine stated that they provide flowback services independent of their hydraulic fracturing services. For another two companies, the EPA received no information clearly describing role regarding flowback services. Only one company provided detailed information on flowback management.

3.3.5. Next Steps

All analyses will undergo a QA review before being compiled in a final report. The EPA will continue to work with each of the nine companies to determine how best to summarize the results so that CBI is protected while providing information in a transparent manner.

3.3.6. Quality Assurance Summary

The QAPP for the analysis of data received from nine service companies, “Analysis of Data Received from Nine Hydraulic Fracturing (HF) Service Companies (Version 1),” was approved on August 1, 2012 (US EPA, 2012h). A TSA on the work was conducted by designated EPA QA Manager on August 28, 2012, to review the methods being used and work products being developed with the data. The work accurately reflected what is described in the QAPP, and no corrective actions were identified. In addition, the EPA's contractor, Eastern Research Group, has been involved with collecting and compiling data submitted from the nine hydraulic fracturing service companies. Eastern Research Group's QAPP was approved on January 19, 2011 (Eastern Research Group Inc., 2011).

3.4. Well File Review

3.4.1. Relationship to the Study

The well file review provides an opportunity to assess well construction and hydraulic fracturing operations, as reported by the companies that own and operate oil and gas production wells. Results from the review will inform answers to the secondary research questions listed in Table 21.

Table 21. Secondary research questions addressed by the well file review research project.

Water Cycle Stage	Applicable Research Questions
Water acquisition	• How much water is used in hydraulic fracturing operations, and what are the sources of this water?
Chemical mixing	• What is currently known about the frequency, severity, and causes of spills of hydraulic fracturing fluids and 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? • If spills occur, how might hydraulic fracturing chemical additives contaminate drinking water resources?
Well injection	• How effective are current well construction practices at containing gases and fluids before, during, and after fracturing? • Can subsurface migration of fluids and gases to drinking water resources occur and what local geologic or man-made features may allow this?
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 wastewaters, and what factors might influence this composition? • If spills occur, how might hydraulic fracturing wastewater contaminate drinking water resources?
Wastewater treatment and waste disposal	• What are the common treatment and disposal methods for hydraulic fracturing wastewaters, and where are these methods practiced?

3.4.2. Project Introduction

The process of planning, designing, permitting, drilling, completing, and operating oil and gas wells involves many steps, all of which are ultimately controlled by the company that owns or operates the well, referred to as the "operator." Assisting the operator are service companies that provide specialty services, such as seismic surveys, lease acquisition, road and pad building, well drilling, logging, cementing, hydraulic fracturing, water and waste hauling, and disposal. Some operators can perform some of these services on their own and some rely exclusively on service companies.

During the development and production of oil and gas wells, operators receive documentation from service companies about site preparation and characteristics, well design and construction, hydraulic fracturing, oil and gas production, and waste management. Operators typically maintain much of this information in an organized file, which cumulatively represents the history of the well. The EPA refers to this file as a "well file." Some of the information in a well file may be required by law to be reported to state oil and gas agencies, and some of the information may be considered CBI by the operator.

For this project, the EPA is scrutinizing actual well files from hydraulic fracturing operations in different geographic areas that are operated by companies of various sizes. These wells include vertical, horizontal, and deviated wells that produce oil, gas, or both from differing geological environments. This review is providing information that can be used to identify practices that may impact drinking water resources**.**

3.4.3. Research Approach

While a portion of the data needed for this project is reported to state oil and gas agencies, the complete dataset is available only in the well files compiled by oil and gas operators.[30] Further, different states have different reporting requirements. As a result, the EPA selected 350 well identifiers believed to represent oil and gas production wells hydraulically fractured by the nine hydraulic fracturing service companies and requested the corresponding well files from operators associated with those wells.[31] This section describes the process used by the EPA to select well files for review, the information requested, and the planned analyses.

Well File Selection. The EPA used a list of hydraulically fractured oil and gas wells provided to the agency by the nine hydraulic fracturing service companies (referred to hereafter as the "service company well list") to select 350 specific well identifiers associated with nine oil and gas operators.[32] The service company well list obtained by the EPA contains 24,925 well identifiers associated with wells that were reported to have been hydraulically fractured between September 2009 and October 2010 (Figure 10) and identifies 1,146 oil and gas operators. This compiled list includes, for each well, a well identifier, the operator's name, and the well's state and county location.

Counties containing the 24,925 well identifiers were grouped into four geographic regions according to a May 9, 2011, map of current and prospective shale gas plays within the lower 48 states (US EIA, 2011c).[33] If any portion of a county was within one of the shale gas plays defined on the map, the entire county was assigned to that shale play and the corresponding geographic region. The four regions—East, South, West, and Other—are shown in Figure 11 with the corresponding number of wells in each region. Counties outside the shale gas plays were grouped

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[30] The EPA analyzed several state oil and gas agency websites and estimated that it would find less than 15% of the necessary data from websites to answer the research questions.

[31] Oil and gas production wells are generally assigned API numbers by state oil and gas agencies, a unique 10-digit number. Wells may also be commonly identified by a well name that is designated by the operator. The EPA considers both of these to be well identifiers.

[32] The EPA used the service company well list because it is unaware of the existence of a single list showing all oil and gas production wells in the United States, their operators, and whether each well has been hydraulically fractured.

[33] Wells within a designated shale play on the map are not guaranteed to be producing from that shale; they could be producing from rock formations within the same stratigraphic column.

into the Other region, which includes areas where oil and gas is produced from a variety of rock formations.[34] This grouping process allowed the EPA to select wells that reflect the geographic distribution of hydraulically fractured oil and gas wells.

A list of operators and their corresponding total well count was sorted by well count from highest to lowest. Operators with fewer than 10 well identifiers were removed, resulting in a final list of 266 operators and 22,573 wells. The resulting operators were categorized as “large,” “medium,” or “small.” Large operators were defined as those that accounted for the top 50% of the well identifiers on the list, medium operators for the next 25% and small operators for the last 25%. As a result, there were 17 large operators, 86 medium operators, and 163 small operators. To ensure that the final selected well identifiers would have geographic diversity among large operators, each large operator was assigned to one geographic region that contained a large number of its well identifiers.

One large operator was randomly chosen from each of the regions (i.e., one large operator from each of the East, South, West, and Other regions), for a total of four large operators. Two medium operators and three small operators were also chosen, with no preference for geographic region. This resulted in the selection of nine operators: Clayton Williams Energy, ConocoPhillips, EQT Production, Hogback Exploration, Laramie Energy, MDS Energy, Noble Energy, SandRidge Energy, and Williams Production.

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[34] Forty-six well identifiers had unknown counties and have been included in the Other region for the purposes of this analysis.

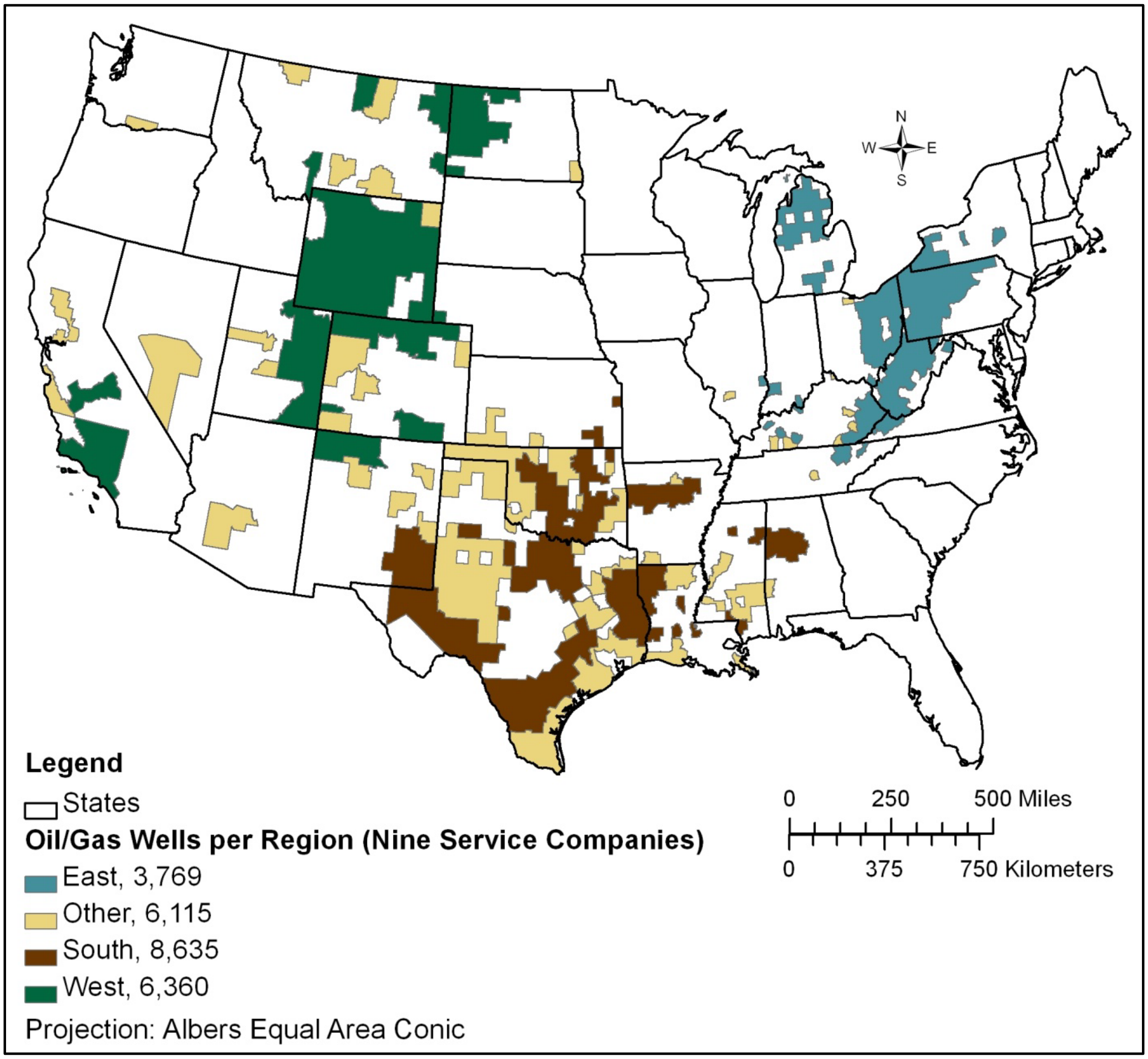

Figure 11. Locations of oil and gas production wells hydraulically fractured from September 2009 through October 2010. The information request to service companies (September 2010) resulted in county-scale locations for 24,925 wells. The service company wells are represented above as regional well summaries and summarize only 24,879 wells because the EPA did not have locational information for 46 of the 24,925 reported wells. (ESRI, 2010a, b; US EPA, 2011a)

The nine operators were associated with 2,455 well identifiers. The EPA initially chose 400 of those 2,455 well identifiers to request the associated well files for its analysis. The selection of 400 well identifiers required balancing goals of maximizing the geographic diversity of wells and maximizing the precision of any forthcoming statistical estimates. The well identifiers were chosen using an optimization algorithm that evaluated the statistical precision given different allocations across operating company/shale play combinations. The algorithm identified a solution given four constraints:

- Select all well identifiers for the three small operators whose total number of well identifiers was fewer than 35. For all other operators, keep the number of selected well identifiers between 35 and 77.
- Have at least two well identifiers (or one if there is only one) from each combination of a large operator and geographic region.
- Keep the regional distribution of sampled well identifiers close to the regional distribution of all 24,925 well identifiers on the initial service company well list.
- Keep the expected sampling variance due to unequal weights relatively small.

Due to resource and time constraints, the EPA subsequently decided to review 350 well files, so 50 of the 400 selected well identifiers were randomly removed. This sample size is large enough to be considered reasonably representative of the total number of wells hydraulically fractured by the nine service companies in the United States during the specified time period.

Data Requested. An information request letter was sent in August 2011 to the nine operators identified above, asking for 24 distinct items organized into five topic areas: (1) geologic maps and cross sections; (2) drilling and completion information; (3) water quality, volume, and disposition; (4) hydraulic fracturing; and (5) environmental releases.[35] Table 22 shows the potential relationship between the five topic areas and the stages of the hydraulic fracturing water cycle.

Table 22. The potential relationship between the topic areas in the information request and the stages of the hydraulic fracturing water cycle.

Water Cycle Stage	Information Request Topic Areas				
	Geologic Maps and Cross Sections	Drilling and Completion Information	Water Quality, Volume, and Disposition	Hydraulic Fracturing	Environmental Releases
Water acquisition			✓	✓	
Chemical mixing		✓	✓	✓	✓
Well injection	✓	✓	✓	✓	✓
Flowback and produced water			✓	✓	✓
Wastewater treatment and waste disposal			✓	✓	

Well File Review and Analysis. The EPA received responses to the August 2011 information request from each of the nine operators. Data and information contained in the well files is being extracted from individual well files and compiled in a single Microsoft Access database. All data in the database are linked by the well's API number; this process is described in more detail in the QAPP for this research project (US EPA, 2012j).

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[35] See the text of the information request for the specific items requested under each topic area. The information request can be found at http://www.epa.gov/hfstudy/August_2011_request_letter.pdf.

Information in the database is being used to design queries that will inform answers to the research questions listed in Table 21. Examples of queries being designed include:

- What sources and volumes of water are used for hydraulic fracturing fluids?
- How many well files contain reports of chemicals spilled during hydraulic fracturing, and do the reports show whether the spills led to any impacts to drinking water resources?
- How many wells have poor cement bonds immediately above the uppermost depth being hydraulically fractured? This may indicate that the cement sheath designed to isolate the target zone being stimulated may fail, potentially leading to gas and fluid migration up the wellbore.
- How many well files contain reports of flowback or produced water spilled, and do the reports show whether the spills lead to any impacts to drinking water resources?
- What are the reported treatment and/or disposal methods for the wastewater generated from hydraulic fracturing?

3.4.4. Status and Preliminary Data

Of the 350 well identifiers selected for analysis, the EPA received information on 334 wells. One of these was never drilled, ultimately providing the EPA with well files for 333 drilled wells.[36] Table 23 lists the number of wells for which valid data were provided by each operator and their designated company size.

Table 23. Number of wells for which data were provided by each operator. Company size, as determined for this analysis, is also listed. The nine operators provided data on a total of 333 oil and gas production wells.

Operator	Company Size	Number of Wells
Noble Energy	Large	67
ConocoPhillips	Large	57
Williams Production	Large	50
Clayton Williams Energy	Medium	36
SandRidge Energy	Medium	35
EQT Production	Large	29
MDS Energy	Small	24
Laramie Energy	Small	21
Hogback Exploration	Small	14
Total		333

Figure 12 shows a map of the 333 well locations. The well locations are distributed within 13 states: Arkansas, Colorado, Kentucky, Louisiana, New Mexico, North Dakota, Oklahoma, Pennsylvania, Texas, Utah, Virginia, West Virginia, and Wyoming.

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[36] Sixteen of the 350 well identification numbers were not valid for this project: 13 were duplicate entries, one was in Canada, one was not a well, and one was not actually owned by the selected operator. In total, roughly 5% of the 350 well identifiers chosen for review by the EPA do not correspond to oil and gas wells that have been hydraulically fractured. This provides a rough assessment of the accuracy of the original data received from the nine hydraulic fracturing service companies (the service company well list).

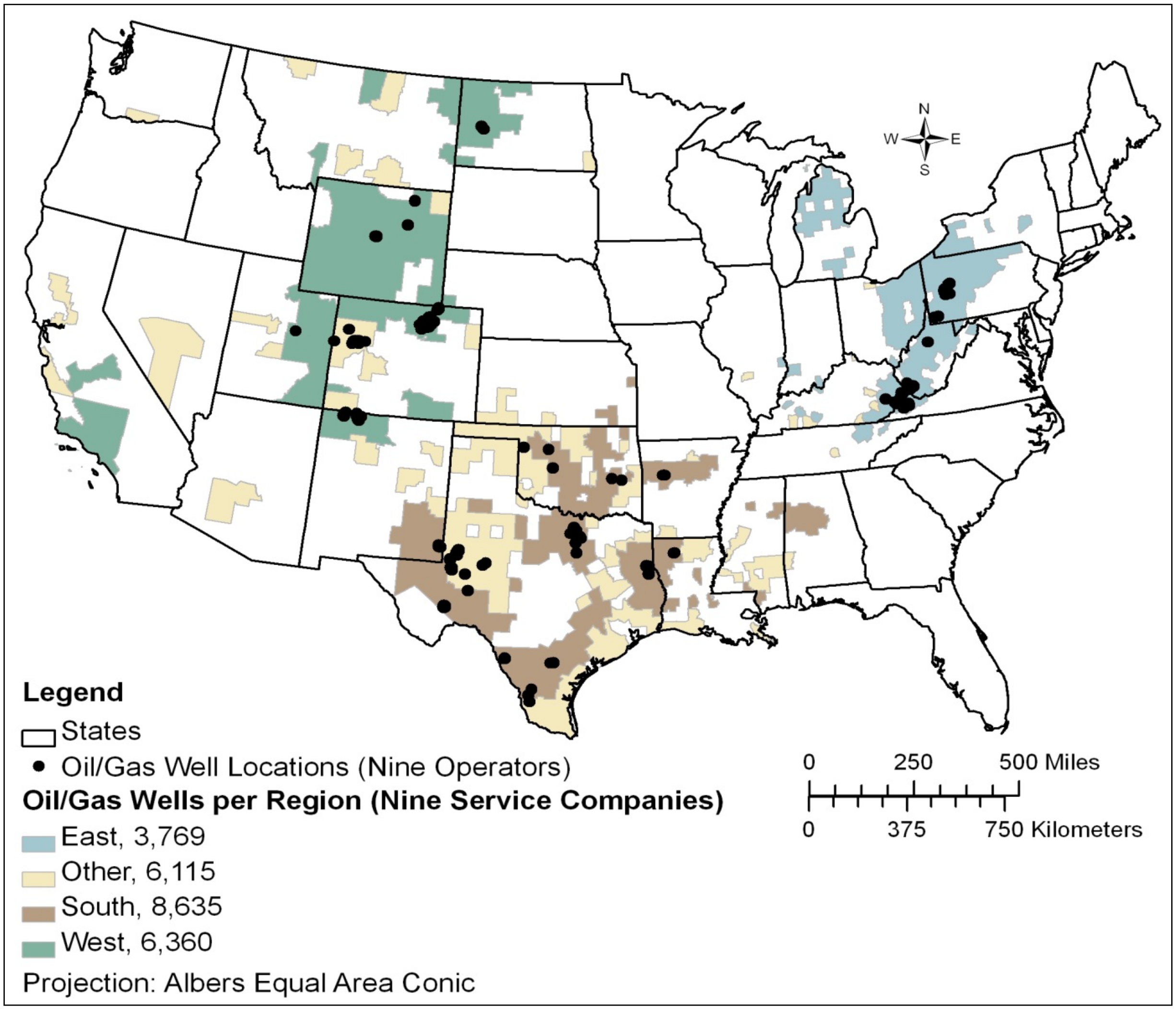

Figure 12. Locations of 333 wells (black points) selected for the well file review. Also shown are the locations of oil and gas production wells hydraulically fractured from September 2009 through October 2010. The information request to service companies (September 2010) resulted in county-scale locations for 24,925 wells. The service company wells are represented above as regional well summaries and summarize only 24,879 wells because the EPA did not have locational information for 46 of the 24,925 reported wells. (ESRI, 2010a, b; US EPA, 2011a, d)

The EPA received approximately 9,670 electronic files in response to the August 2011 information request. The amount of information received varied from one well file to another. Some well files included nearly all of the information requested, while others were missing information on entire topical areas. Some of the data received were claimed as CBI under TSCA. The EPA has contacted all nine of the oil and gas operators to clarify its understanding of the data, where necessary, and to discuss how to depict the well file data while still protecting confidential information. The analyses described in the previous section are being performed according to CBI procedures (US EPA, 2003b), and the results are considered CBI until determinations are made or until data masking has been done to prevent release of CBI information.

The EPA is extracting available data from the well files that can be used to answer research questions related to all stages of the hydraulic fracturing water cycle. As of September 2012, the

EPA had extracted, and continues to extract, the following available information from all of the well files:

- Open-hole log analysis of lithology, hydrocarbon shows, and water salinity
- Chemical analyses of various water samples
- Well construction data
- Cement reports
- Cased-hole logs, including identifying cement tops and bond quality

Other data to be extracted includes the following:

- Source of water used for hydraulic fracturing
- Well integrity pressure testing
- Fluid volumes injected during well stimulation and type and amount of additives and proppant used
- Pressures used during hydraulic fracturing
- Fracture growth data including that predicted and that observed
- Flowback and produced water data following hydraulic fracturing including volume, disposition, and duration

The EPA is creating queries on the extracted data that are expected to determine whether drinking water resources were protected from hydraulic fracturing operations. The results of these queries may indicate the frequency and variety of construction and fracturing techniques that could lead to impacts on drinking water resources. The results may provide, but may not be limited to, information on the following:

- Sources of water used for hydraulic fracturing
- Vertical distance between hydraulically fractured zones and the top of cement sheaths
- Quality of cementing near hydraulic fracturing zones, as determined by a cement bond index
- Number of well casing intervals left uncemented and whether there are aquifers in those intervals
- Distribution of depths of hydraulically fractured zones from the surface
- Frequency with which various tests are conducted, including casing shoe pressure tests and casing pressure tests
- Types of rock formations hydraulically fractured
- Types of well completions (e.g., vertical, horizontal)
- Types and amounts of proppants and chemicals used during hydraulic fracturing
- Amounts of fracture growth

- Distances between wells hydraulically fractured and geologic faults
- Proportions of fluid flowed back to the surface following hydraulic fracturing and the disposition of the flowback

3.4.5. Next Steps

Additional Database Analysis. The EPA plans to conduct further reviews of the well files to extract information relating to water acquisition for hydraulic fracturing, hydraulic fracturing fluid injection, and wastewater management.

Statistical Analysis. Once the data analysis has been completed, where possible, extrapolation of the results will be performed to the sampled universe of 24,925 wells, using methods consistent with published statistical practices (Kish, 1965).

Confidential Business Information. The EPA is working with the oil and gas operators to determine how best to summarize the results so that CBI is protected while upholding the agency's commitment to transparency.

3.4.6. Quality Assurance Summary

The EPA and its contractor, The Cadmus Group, Inc., are evaluating the well file contents. The QAPP associated with this project, "National Hydraulic Fracturing Study Evaluation of Existing Production Well File Contents (Version 1)," was approved on January 4, 2012 (US EPA, 2012j). A supplemental QAPP developed by Cadmus was approved on March 6, 2012 (Cadmus Group Inc., 2012b). Each team involved in the well file review underwent a separate TSA by the designated EPA QA Manager to ensure compliance with the approved QAPP. The audits occurred between April and August of 2012. No corrective actions were identified.

Westat, under contract with the EPA, is providing statistical support for the well file analysis. A QAPP, "Quality Assurance Project Plan v1.1 for Hydraulic Fracturing," was developed by Westat and approved on July 15, 2011 (Westat, 2011).

3.5. FracFocus Analysis

3.5.1. Relationship to the Study

Extracting data from FracFocus allows the EPA to gather publicly available, nationwide information on the water volumes and chemicals used in hydraulic fracturing operations, as reported by oil and gas operating companies. Data compiled from FracFocus are being used to help inform answers to the research questions listed in Table 24.

Table 24. Secondary research questions addressed by extracting data from FracFocus, a nationwide hydraulic fracturing chemical registry.

Water Cycle Stage	Applicable Research Questions
Water acquisition	How much water is used in hydraulic fracturing operations, and what are the sources of this water?
Chemical mixing	What are the identities and quantities of chemicals used in hydraulic fracturing fluids, and how might this composition vary at a given site and across the country?

3.5.2. Project Introduction

At the time the draft study plan was written in early 2011, the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission jointly launched a new national registry for chemicals used in hydraulic fracturing, called FracFocus (http://www.fracfocus.org; (GWPC, 2012b)). This registry, which has become widely accepted as the national hydraulic fracturing chemical registry, is an online repository where oil and gas well operators can upload information regarding the chemical compositions of hydraulic fracturing fluids used in specific oil and gas production wells. It has become one of the largest sources of data and information on chemicals used in hydraulic fracturing and may be the largest single source of publicly disclosed data for these chemicals. The registry also contains information on well locations, well depth, and water use. Confidential business information is not disclosed in FracFocus to protect proprietary or sensitive information.

FracFocus began as a voluntary program on January 1, 2011. Since its introduction, the amount of data in FracFocus has been steadily increasing. As of May 2012, the registry contained information on nearly 19,000 wells for which hydraulic fracturing fluid disclosures were entered (GWPC, 2012b). Seven states require operators to use FracFocus to report the chemicals used in hydraulic fracturing operations. In addition, many states are expected to pass or are working on legislation to require reporting with FracFocus.[37]

Although it represents neither a random sample nor a complete representation of the wells fractured during this time period, the number of well disclosures in FracFocus may constitute a large portion of the number of wells hydraulically fractured in the United States for this time period. For comparison, nine hydraulic fracturing service companies reported that nearly 25,000 wells were fractured between September 2009 and October 2010, as described in Section 3.3.

This analysis is gathering information on water and chemical use in hydraulic fracturing operations and attempts to answer the following questions:

- What are the patterns of water usage in hydraulic fracturing operations reported in FracFocus?
- What are the different sources of water reported in FracFocus, and is it possible to determine the relative proportions by volume or mass of these different sources of water?
- What are the identities of chemicals used in hydraulic fracturing fluids reported in FracFocus?
- Which chemicals are reported most often in FracFocus?
- What is the geographic distribution of the most frequently reported chemicals in FracFocus?

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[37] The seven states requiring disclosure to FracFocus are Colorado, Louisiana, Montana, North Dakota, Oklahoma, Pennsylvania, and Texas. As of September 2012, the EPA is aware of eight more states considering the use of FracFocus: Alaska, California, Illinois, Kansas, Kentucky, New Mexico, Ohio, and West Virginia.

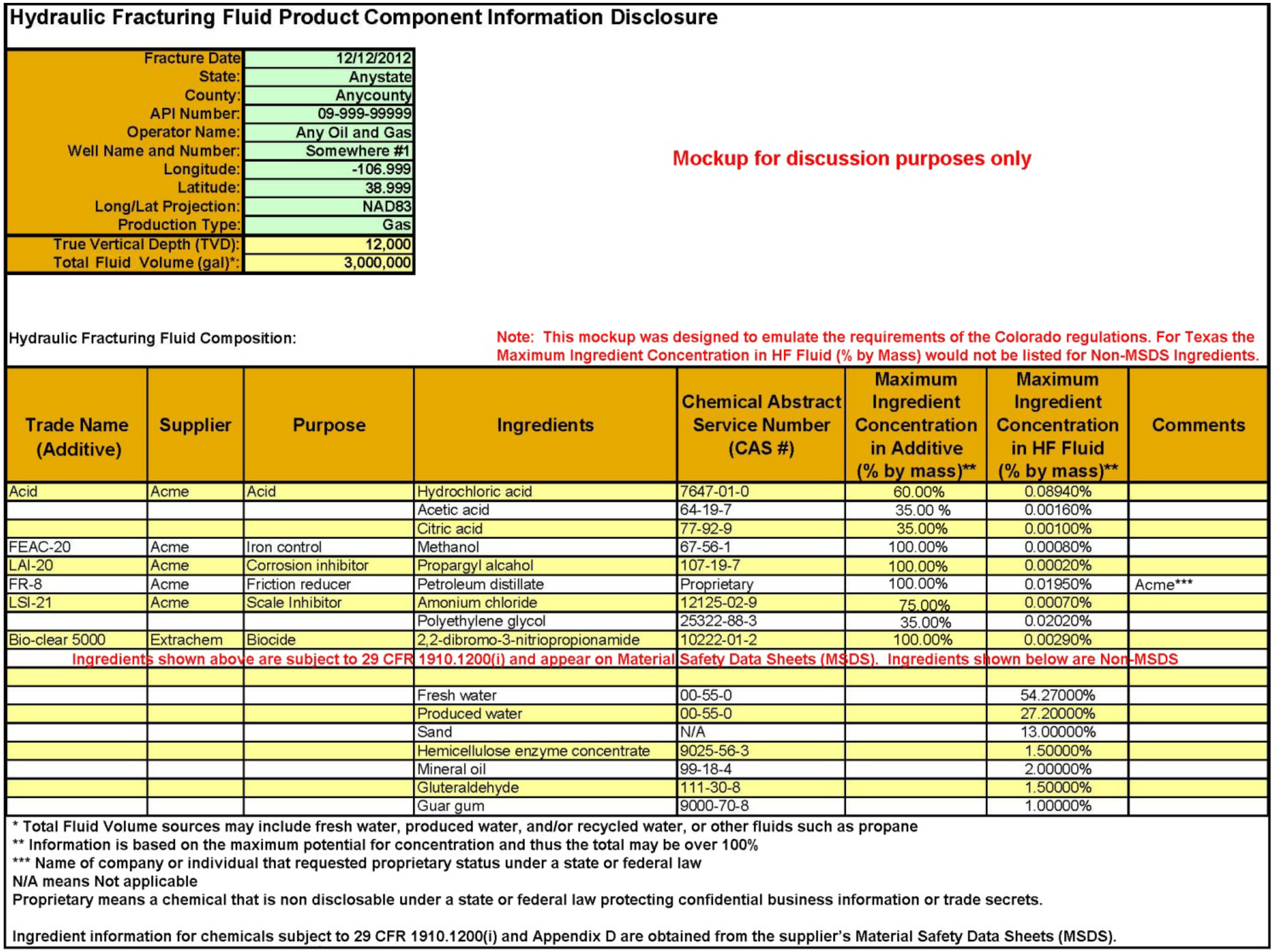
3.5.3. FracFocus Data

All data in FracFocus are entered by oil and gas companies that have agreed to "disclose the information in the public interest" (GWPC, 2012b). The Ground Water Protection Council, the organization that administers the registry, makes no specific claim about data quality in FracFocus. There is considerable variability in the posted data because they are uploaded by many different companies, including operator and service companies. Although FracFocus uses some built-in QA checks during the data upload process, several data quality issues are not addressed by these protocols. As a result, the EPA conducted a QA review of the data, as described in the next section.

Data in FracFocus are presented in individual PDF formats for individual wells; an example PDF is provided in Figure 13. Individual wells can be searched using a Google Maps application programming interface. In addition, well disclosure records can be searched by state, county, and operator. Results are returned by listing links to individual PDF files. Because only single well disclosure records are downloadable, systematic analysis of larger datasets is more challenging. Data must be extracted and transformed into more appropriate formats (e.g., a Microsoft Access database) for this type of analysis.

Data in FracFocus can be classified into two general types: well or "header" data and chemical- or ingredient-specific data. Header data describe information about each well, including the fracture date, API number, operator, well location, and total fluid volume, as shown in Figure 13. Chemical-specific data provide the trade names of ingredients, the chemicals found in these ingredients, and the concentrations used in the hydraulic fracturing fluid. Some well disclosures include information on the type or source of water in the chemical-specific data table.

The EPA has downloaded data in FracFocus on wells hydraulically fractured during 2011 and the beginning of 2012. It is beyond the scope of this project to evaluate the quality or representativeness on a national scale of the data submitted to FracFocus by oil and gas operators. The data cannot be assumed to be a complete or statistically representative of all hydraulically fractured wells. However, because FracFocus contains several thousands of well disclosures distributed throughout the United States, the EPA believes that the data in FracFocus are generally indicative of hydraulic fracturing activities during the time period covered. Therefore, it may be possible to find geographic patterns of occurrence or usage, including volume of water, frequency of chemical usage, and amounts of chemicals used, assuming that data in FracFocus meet quality requirements.



Hydraulic Fracturing Fluid Product Component Information Disclosure

Fracture Date	12/12/2012
State:	Anystate
County:	Anycounty
API Number:	09-999-99999
Operator Name:	Any Oil and Gas
Well Name and Number:	Somewhere #1
Longitude:	-106.999
Latitude:	38.999
Long/Lat Projection:	NAD83
Production Type:	Gas
True Vertical Depth (TVD):	12,000
Total Fluid Volume (gal)*:	3,000,000

Mockup for discussion purposes only

Hydraulic Fracturing Fluid Composition:

Note: This mockup was designed to emulate the requirements of the Colorado regulations. For Texas the Maximum Ingredient Concentration in HF Fluid (% by Mass) would not be listed for Non-MSDS Ingredients.

Trade Name (Additive)	Supplier	Purpose	Ingredients	Chemical Abstract Service Number (CAS #)	Maximum Ingredient Concentration in Additive (% by mass)**	Maximum Ingredient Concentration in HF Fluid (% by mass)**	Comments
Acid	Acme	Acid	Hydrochloric acid	7647-01-0	60.00%	0.08940%	
			Acetic acid	64-19-7	35.00 %	0.00160%	
			Citric acid	77-92-9	35.00%	0.00100%	
FEAC-20	Acme	Iron control	Methanol	67-56-1	100.00%	0.00080%	
LAI-20	Acme	Corrosion inhibitor	Propargyl alcahol	107-19-7	100.00%	0.00020%	
FR-8	Acme	Friction reducer	Petroleum distillate	Proprietary	100.00%	0.01950%	Acme***
LSI-21	Acme	Scale Inhibitor	Amonium chloride	12125-02-9	75.00%	0.00070%	
			Polyethylene glycol	25322-88-3	35.00%	0.02020%	
Bio-clear 5000	Extrachem	Biocide	2,2-dibromo-3-nitriopropionamide	10222-01-2	100.00%	0.00290%	
Ingredients shown above are subject to 29 CFR 1910.1200(i) and appear on Material Safety Data Sheets (MSDS). Ingredients shown below are Non-MSDS							
			Fresh water	00-55-0		54.27000%	
			Produced water	00-55-0		27.20000%	
			Sand	N/A		13.00000%	
			Hemicellulose enzyme concentrate	9025-56-3		1.50000%	
			Mineral oil	99-18-4		2.00000%	
			Gluteraldehyde	111-30-8		1.50000%	
			Guar gum	9000-70-8		1.00000%	

* Total Fluid Volume sources may include fresh water, produced water, and/or recycled water, or other fluids such as propane

** Information is based on the maximum potential for concentration and thus the total may be over 100%

*** Name of company or individual that requested proprietary status under a state or federal law

N/A means Not applicable

Proprietary means a chemical that is non disclosable under a state or federal law protecting confidential business information or trade secrets.

Ingredient information for chemicals subject to 29 CFR 1910.1200(i) and Appendix D are obtained from the supplier's Material Safety Data Sheets (MSDS).

Figure 13. Example of data disclosed through FracFocus. Data included in each PDF can be classified into two general types: well or "header" data and chemical- or ingredient-specific data. Header data are located in the top table, and ingredient-specific data are found in the bottom table. Provided by Ground Water Protection Council.

3.5.4. Research Approach

Data were first extracted from the FracFocus website, put into more appropriate formats for QA review, and then organized into a final database for analysis of fracturing fluid chemicals and water usage and source. The geographic coordinates provided for wells will be linked to both the chemical and water data (Figure 13) to determine if regional patterns exist. A QA review was performed following the data extraction and initial processing. The last stage of this project involves the quantitative analyses of the QA-reviewed data. These three stages are described in more detail below.

3.5.4.1. Data Extraction and Organization

Records for 12,306 wells hydraulically fractured from January 1, 2011, through February 27, 2012, were extracted from FracFocus PDF files and converted to XML using Adobe Acrobat Pro X software. Header- and chemical-specific data were mined from the XML files using text recognition software (Cadmus Group Inc., 2012b).[38] Using this technique, data representing 12,173 (>98% of the downloaded records) well records were compiled. Once fully processed, the data records were organized into two working files: one file containing header data that included well-specific geography, fracturing fluid volume, and well depth and one file containing chemical-specific data. The working files are linked by unique well identification numbers assigned by the contractor that developed the database for EPA.

3.5.4.2. Data Quality Assurance Review

Manual and automated methods were used to assess the data quality and make necessary adjustments. Records in the header data working file were flagged according to the following criteria: duplicate records, as identified by identical API numbers; fracture dates outside the January 1, 2011, to February 27, 2012, time period; anomalously large or small volumes of water; and anomalously deep or shallow true vertical depths. These records were kept in the working files, but flagged in order to exclude them from future analyses. Half of the duplicate records were excluded from all queries and analyses.

Spatial data from the well records include three sources, which can be used to perform quality checks: state and county names, latitude and longitude coordinates, and the state and county information encoded in the first five digits of the API Well Number (Figure 13). To validate the location of the wells, the state and county information from each of the locational fields was compared. State and county information (ESRI, 2010a, b) was assigned to the latitude and longitude coordinates by spatially joining the data in ArcGIS (ESRI, version 10). Validated spatial location was available for 12,163 wells (>99% of records extracted) (Cadmus Group Inc., 2012b).

Chemical names in the "Ingredients" field of chemical-specific data table were standardized according to the CASRN provided in the associated "Chemical Abstract Service Number" field

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[38] The text recognition software is highly sensitive to inconsistencies in reporting. If an operator departs from the general template when creating the well record, the record will be passed over or data will be extracted incorrectly. The contractor was able to convert data from 12,173 of the 12,302 well records into a more useable format (Cadmus Group Inc., 2012b).

(Figure 13). As described in Chapter 6, the EPA has compiled and curated a list of chemicals reported to be used in hydraulic fracturing fluids from many data sources. This list was used to standardize the chemical names provided in FracFocus by matching CASRNs.[39]

Water sources were also identified from the "Ingredients" field. Data were first organized to identify wells where water has been listed as a trade name or ingredient and has been used as a "carrier" or "base" fluid, excluding records that indicated the water has been used as a solvent for hydraulic fracturing chemicals. Additionally, records listing the CASRN for water (7732-18-5) and an additive concentration of 70% to 100% were identified.

3.5.4.3. Data Analysis

Following the QA review, all data were organized into four data tables: locational data for each well disclosure, the original chemical-specific data for each well disclosure, the QA-reviewed chemical-specific data for each well disclosure, and records with water as ingredient. These four tables have been imported into a database and linked together using key fields, where they can be used for the analyses described below. The raw, pre-QA data values for well disclosures and chemical ingredients as they were exported from FracFocus have also been imported into the database for baseline reference data to prevent any loss of original operator data.

Water Acquisition. Total water volume data that meet the QA requirements are being used to analyze general water usage patterns on national, state, and county scales of interest. Additional queries may be run that analyze water usage by operator and by production type (oil or gas).

Data will be summarized by water source or type for records where this information is provided. Concentrations of water by source type are generally found in the "Maximum Ingredient Concentration in HF (hydraulic fracturing) Fluid" field (Figure 13), which is reported as a percentage by mass, not percentage by total water volume. In some situations, there will be enough information in FracFocus to calculate water volumes by type (V_{H2O}^{i}), whether fresh water (e.g., surface water) or non-fresh water (e.g. recycled/produced, saline, seawater or brine). Given the FracFocus-reported total water volume (V_{H2O}^{total}) (US gallons) and assuming that volumes are effectively additive, and where *n* is the number of water types,

$$V_{H2O}^{total} \cong \sum_{i=1}^{n} V_{H2O}^{i} \qquad (1)$$

using the FracFocus-reported maximum water concentration in the hydraulic fracturing fluid (percent by mass for each water type, x_{H2O}^{i}), and assuming an average density for each water type (ρ_{H2O}^{i}) (lb/US gallons), the volume of each water type is expressed as:

$$V_{H2O}^{i} = \frac{x_{H2O}^{i}}{\rho_{H2O}^{i}} m_{total} \quad \text{(i = 1, n)} \qquad (2)$$

With *n* equations and *n* unknowns represented by equations (1) and (2), the unknown total mass of the hydraulic fracturing fluid (m_{total}) (lb) can be calculated:

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[39] CASRNs not already found on the EPA's list of chemicals reported to be used in hydraulic fracturing fluids were added to the list following the process outlined in Chapter 6.

$$m_{total} = \frac{V_{H2O}^{total}}{\sum_{i=1}^{n} \frac{x_{H2O}^{i}}{\rho_{H2O}^{i}}} \tag{3}$$

and the volume of each water type (V_{H2O}^{i}) back-calculated using equation (2).[40]

This calculation can only be made in the situation where the density of the fluid is known or reported. For example, in the situation where a FracFocus ingredient is clearly labeled fresh (surface) water and carrier or base fluid, a water density may be assumed between 8.34 lb/US gallon at 32 °F and 8.24 lb/US gallon at 100 °F (Lide, 2008). In other situations, the density for the carrier or base fluid may be reported in the FracFocus comment field.

Chemical Usage. Queries of the FracFocus data will include the total number of unique chemical records nationally, by state, per production type (oil or gas), fracture date, and operator represented. Additionally, the data may be queried to identify the frequency or number of well disclosures in which each chemical is used nationally, by state, per production type, within a fracture date range, and by operator represented. Lists of the top 20 to 30 most frequently used chemicals in hydraulic fracturing are likely to be generated at the nation, region, or state level. Some of the most frequently occurring chemicals will be mapped to show distribution of occurrence. Since chemicals claimed as CBI or proprietary do not have to be reported in FracFocus, the number of chemicals disclosed is likely to be lower than the total number of chemicals used.

3.5.5. Status and Preliminary Data

The data have been extracted from FracFocus, reviewed for quality issues, and organized in a database for analysis. Draft queries have been developed for water usage and chemical frequency occurrence nationwide using the database. Preliminary analyses have been conducted as of November 2012. Table 25 summarizes, by state, the well data that were downloaded from FracFocus in early 2012.

Table 25. Number of wells, by state, with data in FracFocus as of February 2012. These data represent wells fractured and entered into FracFocus between January 1, 2011, and February 27, 2012.

State	Number of Wells
Alabama	54
Alaska	24
Arkansas	807
California	79
Colorado	2,307
Kansas	22
Louisiana	621
Mississippi	1
Montana	28
New Mexico	421

State	Number of Wells
North Dakota	359
Ohio	11
Oklahoma	414
Pennsylvania	1,050
Texas	4,859
Utah	409
Virginia	23
West Virginia	93
Wyoming	591
Total	*12,173*

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[40] The EPA recognizes that volume is not a conserved quantity and estimates that the error introduced by assuming that volumes are additive is, in this case, negligible when compared to expected volume and density reporting errors.

During the QA review of the data, the EPA identified 422 pairs of potential duplicate well disclosure records (844 total records). A total of 277,029 chemicals were reported in all of the well disclosure records. This number includes chemicals listed multiple times (either for the same well or in many wells) and 12,464 instances where "water" was listed as an ingredient in the chemical-specific data table. The QA review of the chemicals identified 347 unique ingredients that match the EPA CASRN list of chemicals and approximately 60 CASRNs that were not previously known to be used in hydraulic fracturing fluids. One hundred eighty-four well records had ingredient lists that fully matched the EPA CASRN list. Chemical entries in FracFocus that contained "CBI," "proprietary," or "trade secret" as an ingredient were only 1.3% (3,534 of 277,029) of all chemical ingredients reported in FracFocus. Operators reported at least one chemical ingredient as "CBI," "proprietary," or "trade secret" in 1,924 well records.

Water was identified as a carrier or base fluid in 10,700 well records (88% of the 12,173 well records successfully extracted from FracFocus). Seven categories of source water were identified: fresh, surface, sea, produced, recycled, brine, and treated. Definitions for the categories are not provided by operators or FracFocus and some categories appear to overlap or may be synonymous. Only 1,484 well records identified a water source for those wells that used water as a carrier or base fluid.

3.5.6. Next Steps

The EPA will complete its analysis of the FracFocus data that have already been downloaded. In addition, the EPA plans to complete another data download in order to obtain a second year's worth of data. Once the second round of data has been extracted, the EPA will conduct a QA review and data analysis similar to the one described for the first round of downloaded data.

3.5.7. Quality Assurance Summary

The EPA and its contractor, The Cadmus Group, Inc., are extracting and analyzing data from FracFocus. The QAPP associated with this project, "Analysis of Data Extracted from FracFocus (Version 1)," was approved in early August 2012 (US EPA, 2012g). A TSA of the analysis was conducted by the designated EPA QA Manager shortly after on August 15, 2012; no corrective actions were identified. A supplemental QAPP developed by Cadmus was approved March 6, 2012 (Cadmus Group Inc., 2012b).

4. Scenario Evaluations

The objective of this approach is to use computer models to explore hypothetical scenarios across the hydraulic fracturing water cycle. The models include models of generic engineering and geological scenarios and, where sufficient data are available, models of site-specific or region-specific characteristics. This chapter includes progress reports for the following projects:

4.1. Subsurface Migration Modeling 62
Numerical modeling of subsurface fluid migration scenarios that explore the potential for gases and fluids to move from the fractured zone to drinking water aquifers

4.2. Surface Water Modeling 75
Modeling of concentrations of selected chemicals at public water supplies downstream from wastewater treatment facilities that discharge treated hydraulic fracturing wastewater to surface waters

4.3. Water Availability Modeling 80
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

4.1. Subsurface Migration Modeling

Lawrence Berkeley National Laboratory (LBNL), in consultation with the EPA, will simulate the hypothetical subsurface migration of fluids (including gases) resulting from six possible mechanisms using computer models. The selected mechanisms address the research questions identified in Table 26.

Table 26. Secondary research questions addressed by simulating the subsurface migration of gases and fluids resulting from six possible mechanisms.

Water Cycle Stage	Applicable Research Questions
Well injection	• How effective are current well construction practices at containing gases and fluids before, during, and after fracturing? • Can subsurface migration of fluids or gases to drinking water resources occur and what local geologic or man-made features may allow this?

4.1.1. Project Introduction

Stakeholders have expressed concerns about hydraulic fracturing endangering subsurface drinking water resources by creating high permeability transport pathways that allow hydrocarbons and other fluids to escape from hydrocarbon-bearing formations (US EPA, 2010b, d, e, f, g). Experts continue to debate the extent to which subsurface pathways could cause significant adverse consequences for ground water resources (Davies, 2011; Engelder, 2012; Harrison, 1983, 1985; Jackson et al., 2011; Myers, 2012a, b; Osborn et al., 2011; Warner et al., 2012). The segment of the population that receives drinking water from private wells may be especially vulnerable to health impacts from impaired drinking water. Unlike water distributed by public water systems, water from private drinking water wells is not subject to National Primary Drinking Water Regulations, and water quality testing is at the discretion of the well owner.

Lawrence Berkeley National Laboratory, in coordination with the EPA, is using numerical simulations to investigate six possible mechanisms that could lead to upward migration of fluids, including gases, from a shale gas reservoir and the conditions under which such hypothetical scenarios may be possible. The possible mechanisms include:

- Scenario A (Figure 14): Defective or insufficient well construction coupled with excessive pressure during hydraulic fracturing operations results in damage to well integrity during the stimulation process. A migration pathway is then established through which fluids could travel through the cement or area near the wellbore into overlying aquifers. In this scenario, the overburden is not necessarily fractured.
- Scenario B1 (Figure 15): Fracturing of the overburden because inadequate design of the hydraulic fracturing operation results in fractures allowing fluid communication, either directly or indirectly, between shale gas reservoirs and aquifers above them. Indirect communication would occur if fractures intercept a permeable formation between the shale gas formation and the aquifer. Generally, the aquifer would be located at a more shallow depth than the permeable formation.
- Scenario B2 (Figure 16): Similar to Scenario B1, fracturing of the overburden allows indirect fluid communication between the shale gas reservoir and the aquifers after intercepting conventional hydrocarbon reservoirs, which may create a dual source of contamination for the aquifer.
- Scenario C (Figure 17): Sealed/dormant fractures and faults are activated by the hydraulic fracturing operation, creating pathways for upward migration of hydrocarbons and other contaminants.
- Scenario D1 (Figure 18): Fracturing of the overburden creates pathways for movement of hydrocarbons and other contaminants into offset wells (or their vicinity) in conventional reservoirs with deteriorating cement. The offset wells may intersect and communicate with aquifers, and inadequate or failing completions/cement can create pathways for contaminants to reach the ground water aquifer.
- Scenario D2 (Figure 19): Similar to Scenario D1, fracturing of the overburden results in movement of hydrocarbons and other contaminants into improperly closed offset wells (or their vicinity) with compromised casing in conventional reservoirs. The offset well could provide a low-resistance pathway connecting the shale gas reservoir with the ground water aquifer.

The research focuses on hypothetical causes of failure related to fluid pressure/flow and geomechanics (as related to operational and geological conditions and properties), and does not extend to investigations of strength of casing and tubing materials (an area that falls within the confines of mechanical engineering). Damage to the well casing due to corrosive reservoir fluids was one other scenario originally considered. Corrosion modeling requires a detailed chemical engineering analysis that is beyond the scope of this project, which focuses on geophysical and mechanical scenarios, so it is not a scenario pursued for this project. Additionally, hypothetical scenarios that would cause failure of well structural integrity (e.g., joint splits) are an issue beyond the scope of this study, as they involve material quality and integrity, issues not unique to hydraulic fracturing.

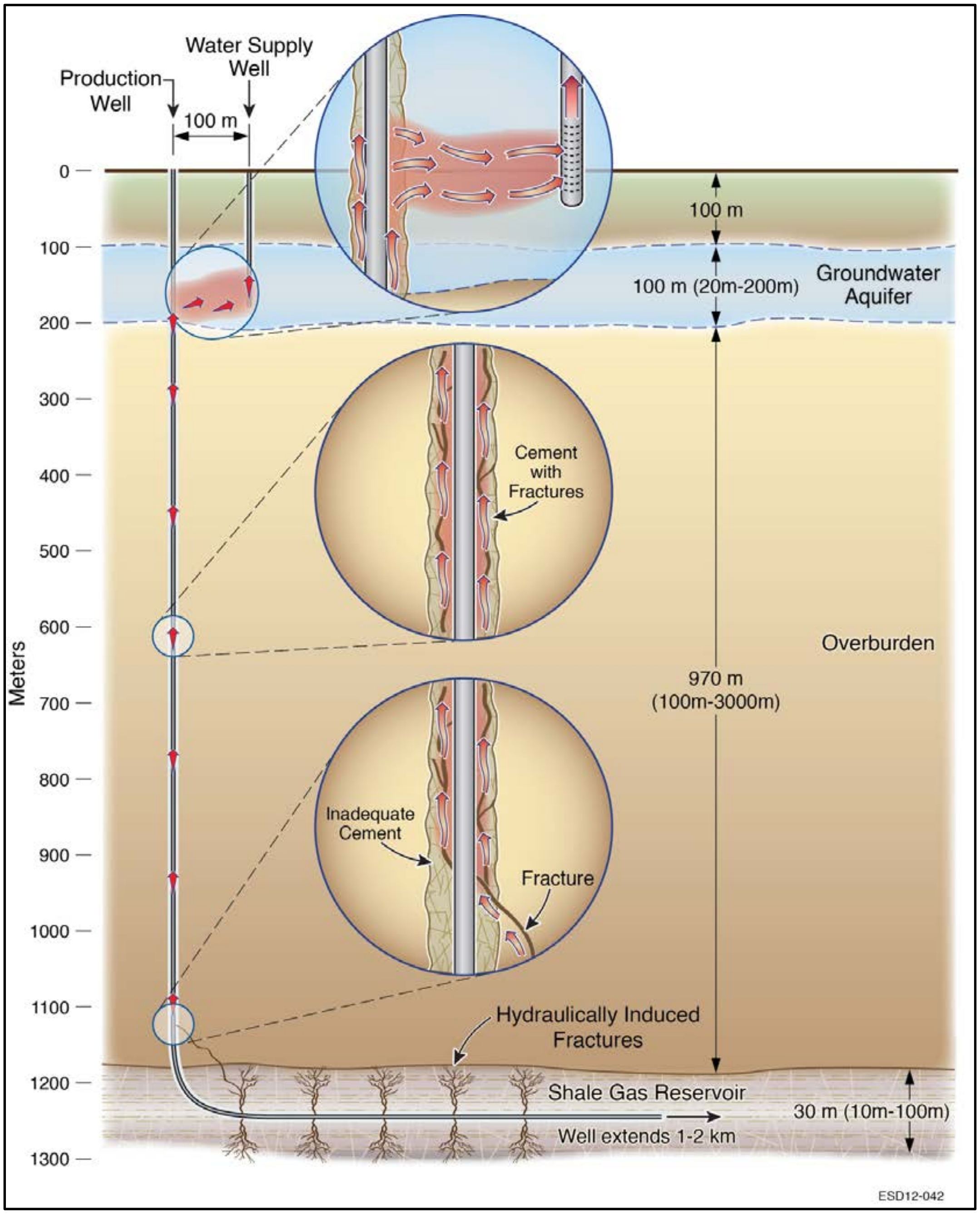

Figure 14. Scenario A of the subsurface migration modeling project. This scenario simulates a hypothetical migration pathway that occurs when a defective or insufficiently constructed well is damaged during excessive pressure from hydraulic fracturing operations. A migration pathway is established through which fluids could travel through the cement or area near the wellbore into overlying ground water aquifers.

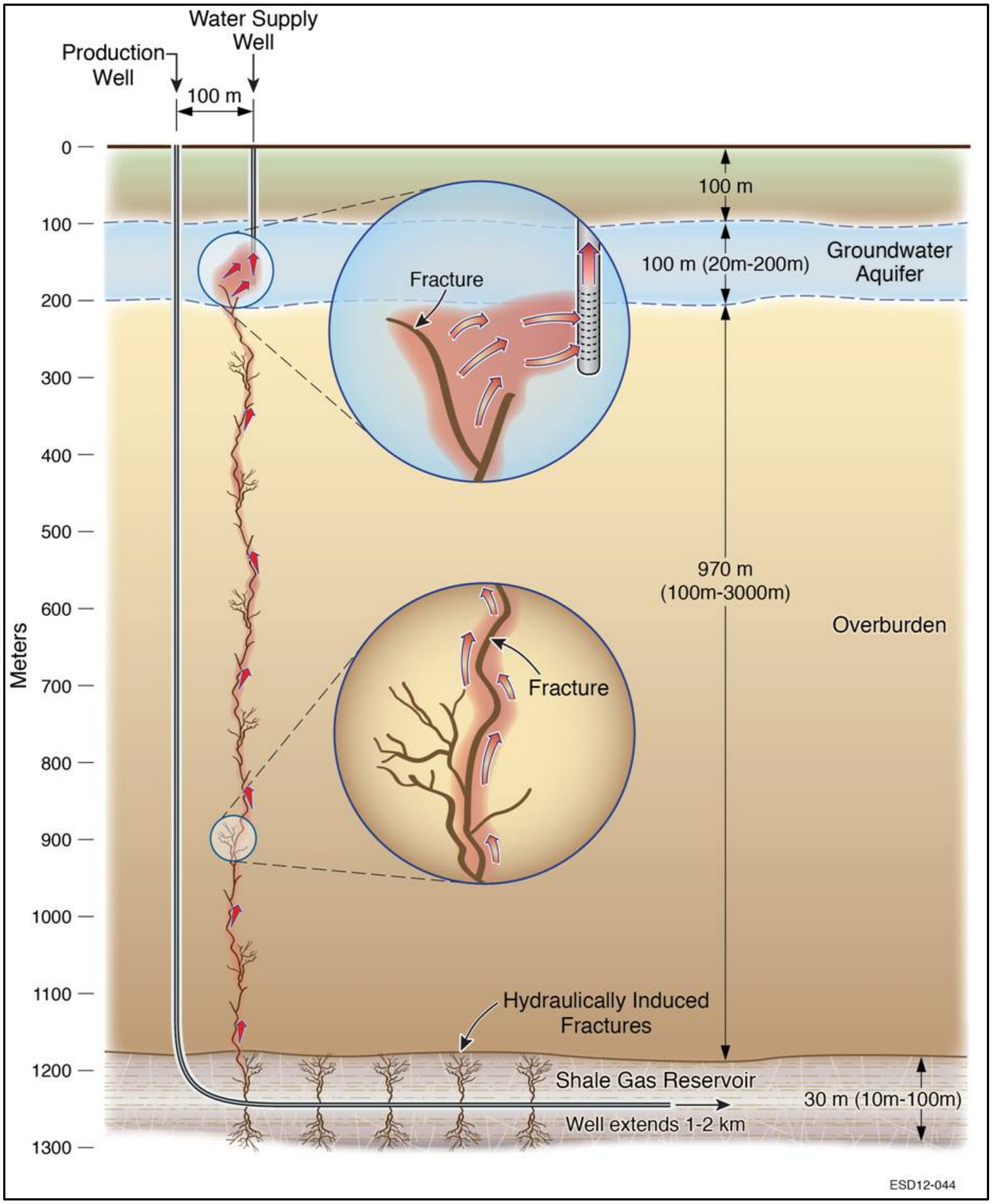

Figure 15. Scenario B1 of the subsurface migration modeling project. This hypothetical scenario simulates fluid communication, either directly or indirectly, between shale gas reservoirs and ground water aquifers as a result of the hydraulic fracturing design creating fractures in the overburden.

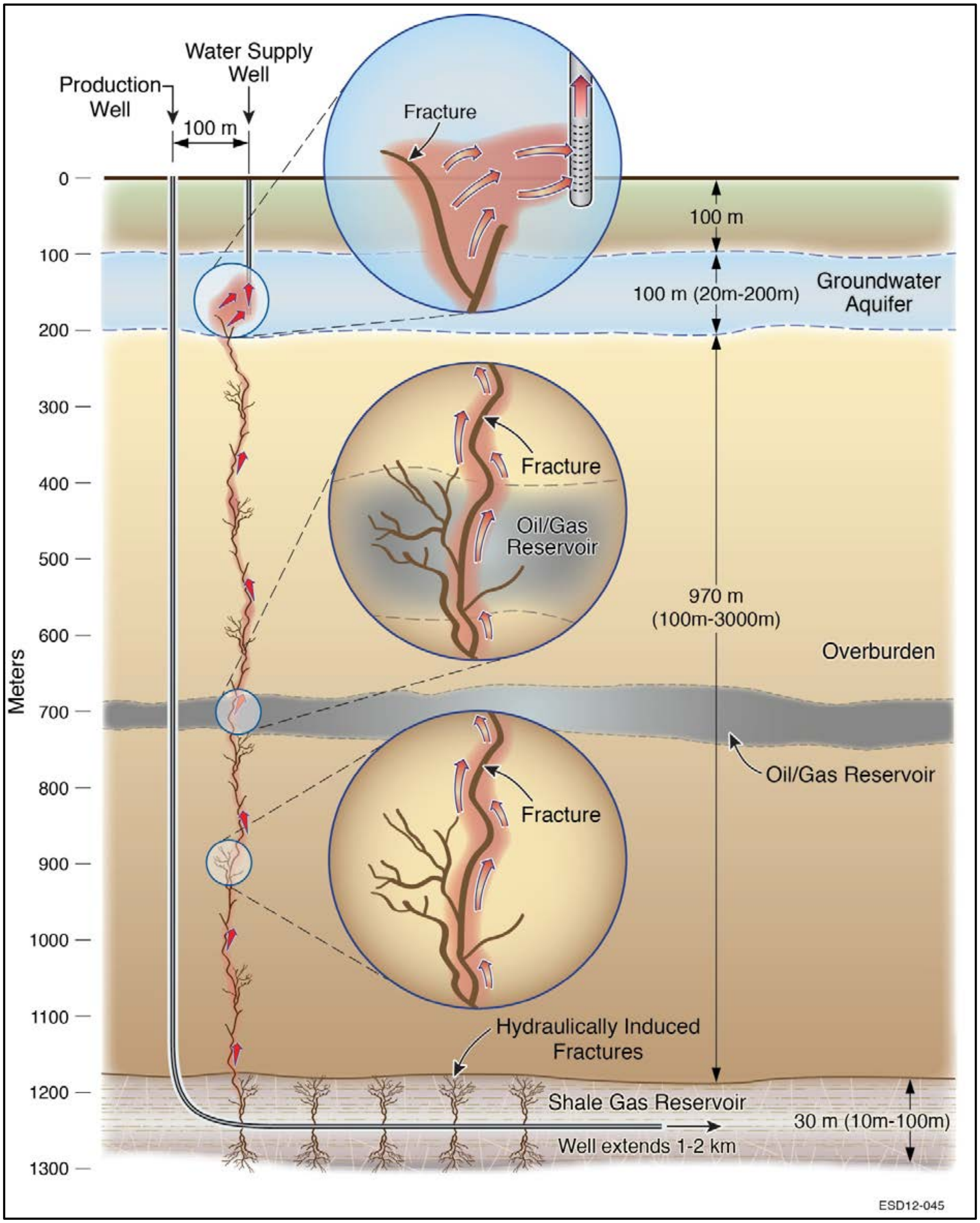

Figure 16. Scenario B2 of the subsurface migration modeling project. Similar to B1, this hypothetical scenario simulates fluid communication, either directly or indirectly, between shale gas reservoirs and ground water aquifers as a result of the hydraulic fracturing design creating fractures in the overburden. The fractures intercept a conventional oil/gas reservoir before communicating with the ground water aquifer, which may create a dual source of contamination in the aquifer.

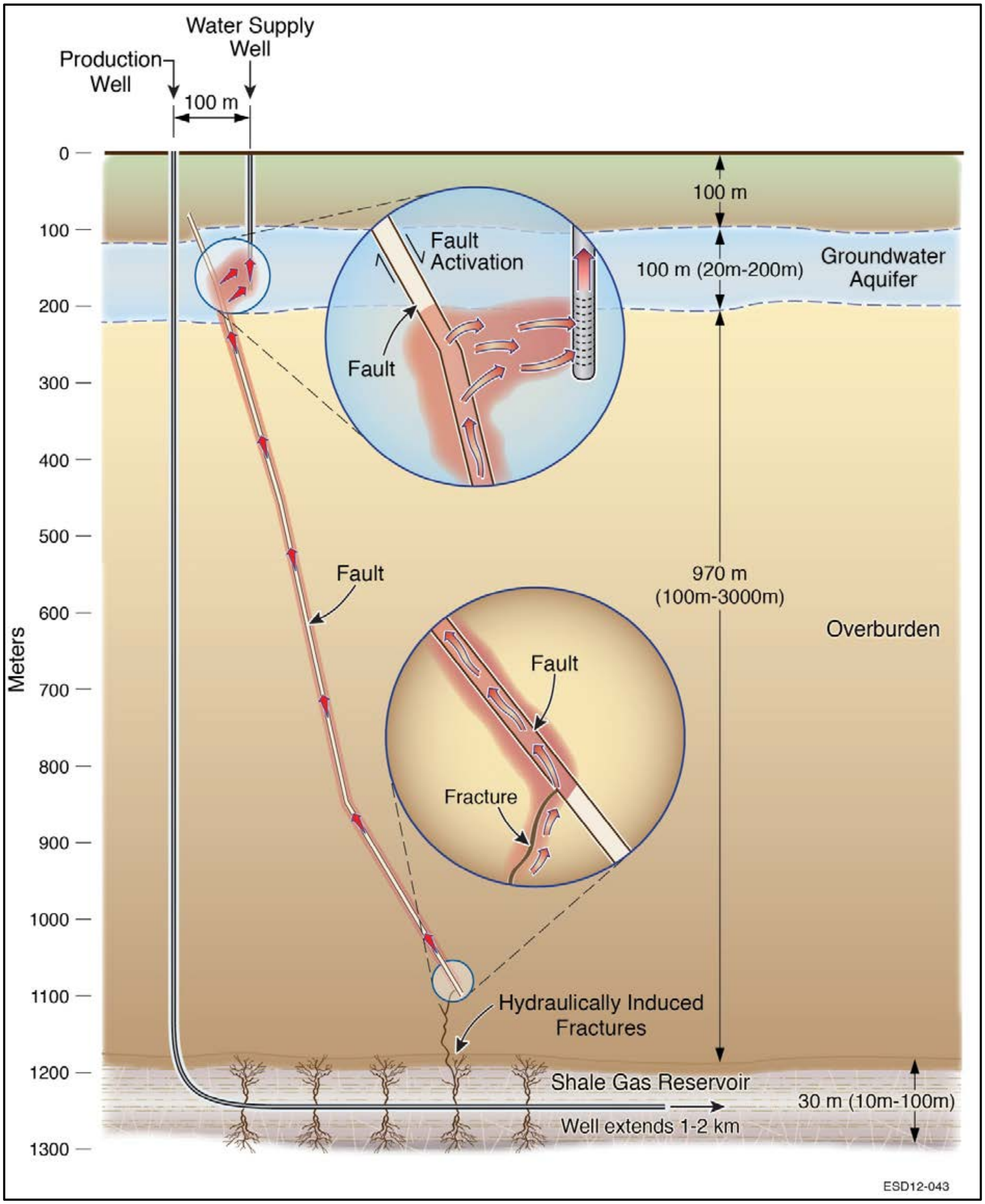

Figure 17. Scenario C of the subsurface migration modeling project. This hypothetical scenario simulates upward migration of hydrocarbons and other contaminants through sealed/dormant fractures and faults activated by the hydraulic fracturing operation.

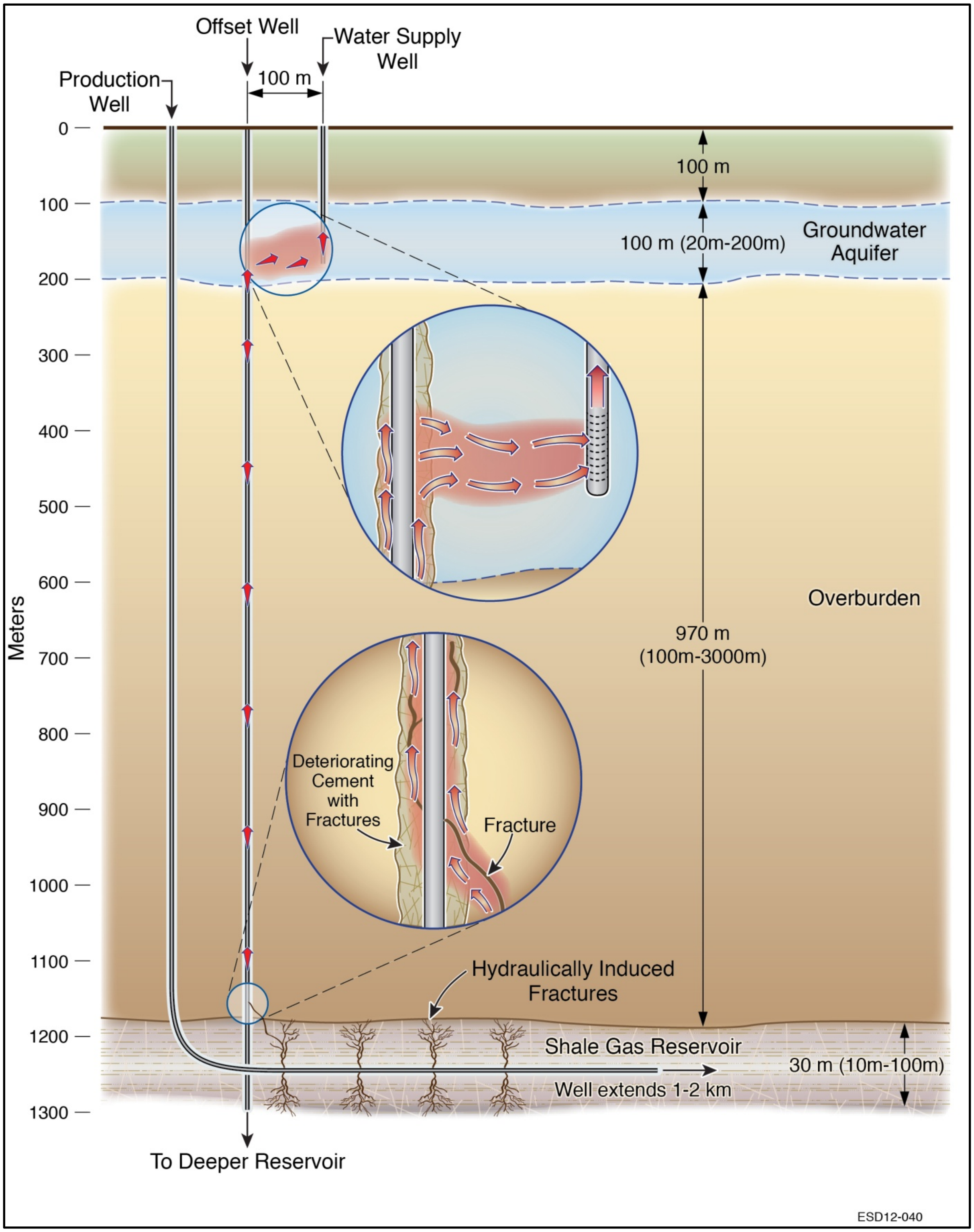

Figure 18. Scenario D1 of the subsurface migration modeling project. This hypothetical scenario simulates movement of hydrocarbons and other contaminants into offset wells in conventional oil/gas reservoirs with deteriorating cement due to fracturing of the overburden. The offset wells may intersect and communicate with aquifers, and inadequate or failing completions/cement can create pathways for contaminants to reach ground water aquifers.

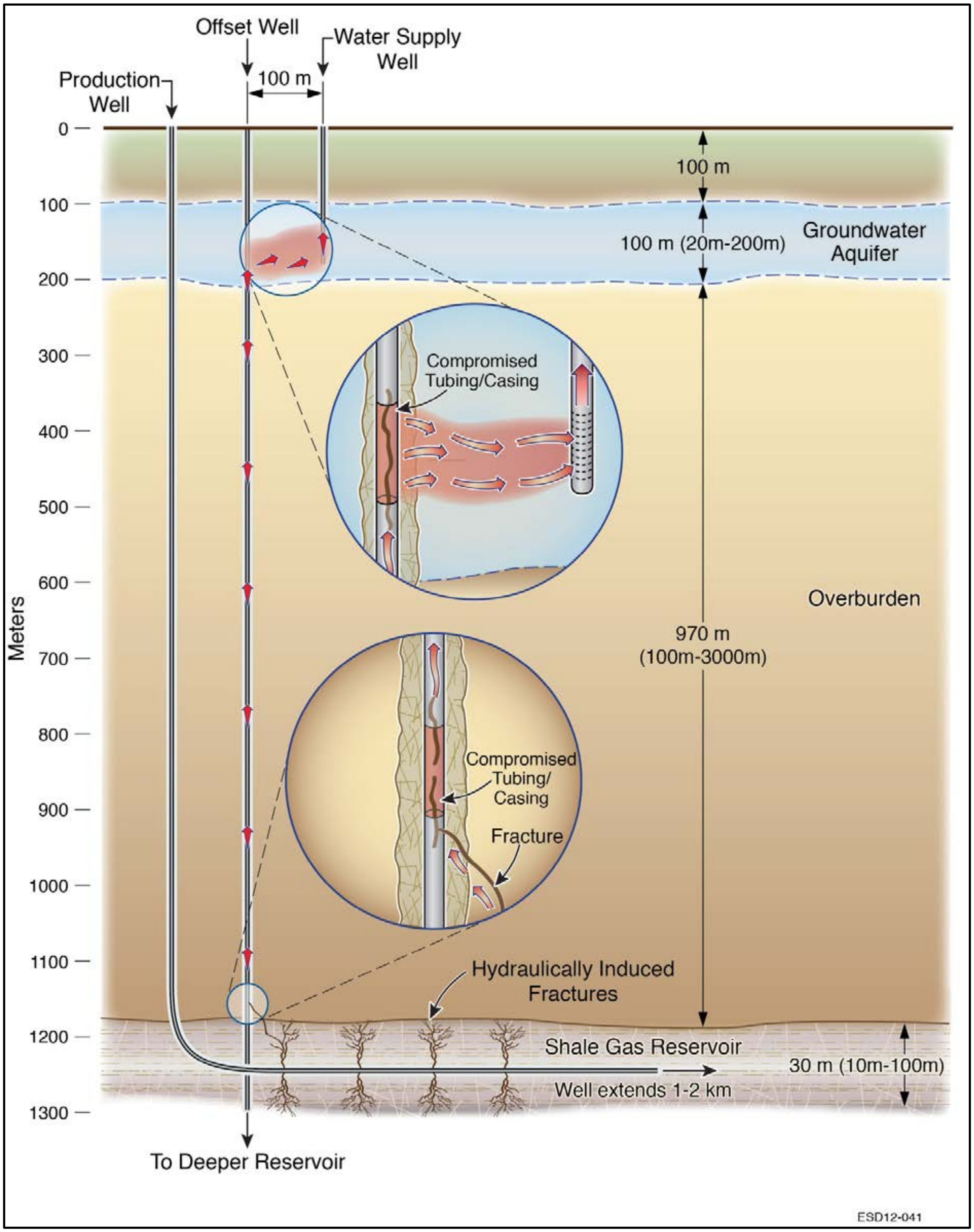

Figure 19. Scenario D2 of the subsurface migration modeling project. Similar to Scenario D1, this hypothetical scenario simulates movement of hydrocarbons and other contaminants into offset wells in conventional oil/gas reservoirs due to fracturing of the overburden. The offset wells in Scenario D2 are improperly closed with compromised casing, which provides a low-resistance pathway connecting the shale gas reservoir with the ground water aquifer.

4.1.2. Research Approach

Objectives of the subsurface migration scenario evaluation research project include:

- Determining whether the hypothetical migration mechanisms shown in Figures 14 through 19 are physically and geomechanically possible during field operations of hydraulic fracturing and, if so, identifying the range of conditions under which fluid migration is possible.
- Exploring how contaminant type, fluid pressure, and local geologic properties control hypothetical migration mechanisms and affect the possible emergence of contaminants in an aquifer.
- Conducting a thorough analysis of sensitivity to the various factors affecting contaminant transport.
- Assessing the potential impacts on drinking water resources in cases of fluid migration.

This research project does not assess the likelihood of a hypothetical scenario occurring during actual field operations.

Computational Codes. The LBNL selected computational codes able to simulate the flow and transport of gas, water, and dissolved contaminants concurrently in fractures and porous rock matrices. The numerical models used in this research project couple flow, transport, thermodynamics, and geomechanics to produce simulations to promote understanding of conditions in which fluid migration occurs.

Simulations of contaminant flow and migration began in December 2011 and identified a number of important issues that significantly affected the project approach. More specifically, the numerical simulator needed to include the following processes in order to accurately describe the hypothetical scenario conditions:

- Darcy and non-Darcy (Forchheimer or Barree and Conway) flow through the matrix and fractures of fractured media
- Inertial and turbulent effects (Klinkenberg effects)
- Real gas behavior
- Multi-phase flow (gas, aqueous, and potentially an organic phase of immiscible substances involved in the hydraulic fracturing process)
- Density-driven flow
- Mechanical dispersion, in addition to advection and molecular diffusion
- Sorption (primary and secondary) of ions introduced in hydraulic fracturing-related processes and gases onto the grains of the porous media, involving one of three possible sorption models (linear, Langmuir, or Freundlich) under equilibrium or kinetic conditions

Thermal differentials between ground water and shale gas reservoirs are substantial and may significantly impact contaminant transport processes. Thus, the simulator needed to be able to account for the following processes in order to fully describe the physics of the problem:

- Coupled flow and thermal effects, which affect fluid viscosity, density, and buoyancy and, consequently, the rate of migration.
- Effect of temperature on solubility. Lower temperatures can lead to supersaturation of dissolved gases or dissolved solids. The latter can result in halite formation stemming from salt precipitation, caused by lower temperatures and pressures as naturally occurring brines ascend toward the ground water. Halite precipitation can have a pronounced effect on both the specific fractures and the overall matrix permeability.

There is currently no single numerical model that includes all of these processes. Thus, the LBNL chose the Transport of Unsaturated Groundwater and Heat (TOUGH) family of codes[41] (Moridis et al., 2008) in combination with the existing modules listed in Table 27 to create a model that better simulates the subsurface flow and geomechanical conditions encountered in the migration scenarios.

Table 27. Modules combined with the Transport of Unsaturated Groundwater and Heat (TOUGH) (Moridis et al., 2008) family of codes to create simulations of subsurface flow and geomechanical conditions encountered in the migration scenarios designed by Lawrence Berkeley National Laboratory.

Module	Purpose
TOUGH+Rgas*	Describes the coupled flow of a real gas mixture and heat in geologic media
TOUGH+RgasH2O*	Describes the non-isothermal two-phase flow of a real gas mixture and water and the transport of heat in a gas reservoir, including tight/shale gas reservoirs
TOUGH+RGasH2OCont†	Describes physics and chemistry of flow and transport of heat, water, gases, and dissolved contaminants in porous/fractured media
ROCMECH§	Simulates geomechanical behavior of multiple porosity/permeability continuum systems and can accurately simulate the evolution and propagation of fractures in a formation following hydraulic fracturing

* (Moridis and Freeman, 2012)
† (Moridis and Webb, 2012)
§ (Kim and Moridis, 2012a, b, c, d, e)

The TOUGH+ code includes equation-of-state modules that describe the non-isothermal flow of real gas mixtures, water, and solutes through fractured porous media and accounts for all processes involved in flow through tight and shale gas reservoirs (i.e., gas-specific Knudsen diffusion, gas and solute sorption onto the media, non-Darcy flow, salt precipitation as temperature and pressure drop in the ascending reservoir, etc.) (Freeman, 2010; Freeman et al., 2011; Freeman et al., 2009a, b; Freeman et al., 2012; Moridis et al., 2010; Olorode, 2011). The LBNL paired relevant modules with TOUGH+ code: one code, TOUGH+RGasH2OCont (Moridis and Freeman, 2012), addresses the

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[41] The TOUGH codes include TOUGH2, T2VOC, TMVOC, TOUGH2-MP, TOUGHREACT, TOUGH+, AND iTOUGH2. More information on the codes can be found at http://esd.lbl.gov/research/projects/tough.

physics and chemistry of flow and transport of heat, water, gases, and dissolved contaminants in porous/fractured media; a second code, TOUGH+RgasH2O (Moridis and Webb, 2012), describes the coupled flow of a gas mixture and water and the transport of heat; a third code, TOUGH+Rgas (Moridis and Webb, 2012), is limited to the coupled flow of a real gas mixture and heat in geologic media.

A geomechanical model, ROCMECH, was also coupled with the TOUGH+ code and modules (Table 27) and describes the interdependence of flow and geomechanics including fracture growth and propagation (Kim and Moridis, 2012a, b, c, d, e). The ROCMECH[42] code is designed for the rigorous analysis of either pure geomechanical problems or, when fully coupled with the TOUGH+ multi-phase, multi-component, non-isothermal code, for the simulation of the coupled flow and geomechanical system behavior in porous and fractured media, including activation of faults and fractures. The coupled TOUGH+ ROCMECH codes allow the investigation of fracture growth during fluid injection of water (after their initial development during hydraulic fracturing) using fully dynamically coupled flow and geomechanics and were used in a series of fracture propagation studies (Kim and Moridis, 2012a, b, c, d, e). The ROCMECH code developed by the LBNL for this study includes capabilities to describe both tensile and shear failure based on the Mohr-Coulomb model, multiple porosity concepts, non-isothermal behavior, and transverse leak-off (Kim and Moridis, 2012a).

Input Data. Input data supporting the simulations are being estimated using information from the technical literature, data supplied by the EPA, and expert judgment. Input data include:

- Site stratigraphy
- Rock properties (grain density, intrinsic matrix permeability, permeability of natural fracture network, matrix and fracture porosity, fracture spacing and aperture)
- Initial formation conditions (fracture and matrix saturation, pressures)
- Gas composition
- Pore water composition
- Gas adsorption isotherm
- Thermal conductivity and specific heat of rocks
- Parameters for relative permeability
- Hydraulic fracturing pressure
- Number of hydraulic fracturing stages
- Injected volumes

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[42] ROCMECH is based on an earlier simulator called ROCMAS (Noorishad and Tsang, 1997; Rutqvist et al., 2001). The ROCMECH simulator employs the finite element method, includes several plastic models such as the Mohr-Coulomb and Drucker-Prager models, and can simulate the geomechanical behavior of multiple porosity/permeability continuum systems. Furthermore, ROCMECH can accurately simulate the process of hydraulic fracturing, i.e., the evolution and propagation of fractures in the formation following stimulation operations.

- Pressure evolution during injection
- Volumes of fracturing fluid recovered

Uncertainty in the data will be addressed by first analyzing base cases that involve reasonable estimates of the various parameters and conditions and then conducting sensitivity analyses that cover (and extend beyond) the possible range of expected values of all relevant parameters.

4.1.3. Status and Preliminary Data

The subsurface migration modeling project is proceeding along two main tracks. The first addresses the geomechanical reality of the mechanisms and seeks to determine whether it is physically possible (as determined and constrained by the laws of physics and the operational quantities and limitations involved in hydraulic fracturing operations) for the six migration mechanisms (Scenarios A to D2) to occur. The second axis focuses on contaminant transport, assuming that a subsurface migration has occurred as described in the six scenarios, and attempts to determine a timeframe for contaminants (liquid or gas phase) escaping from a shale gas reservoir to reach the ground water aquifer.

Analysis of Consequences of Geomechanical Wellbore Failure (Scenario A). A large database of relevant publications has been assembled, and several important well design parameters and hydraulic fracturing operational conditions have been identified as a foundation for the simulation. Two pathways for migration have been considered using TOUGH+RGasH2OCont: cement separation from the outer casing or a fracture pattern affecting the entire cement, from the producing formation to the point where the well intercepts the ground water formation.

A separate geomechanical study using TOUGH+RealGasH2O and ROCMECH will also assess the feasibility of either a fracture developing in weak cement around a wellbore or a cement-wellbore separation during the hydraulic fracturing process. The numerical simulation of the fracture propagation considered fracture development in the cement near the "heel" of a horizontal well during stimulation immediately after creation of the first fracture using varied geomechanical properties of gas-bearing shales. The work also involves sensitivity analyses of factors that are known to be important, as well as those that appear to have secondary effects (for completeness). Recent activities have focused mainly on such sensitivity analyses.

Analysis of the Consequences of Induced Fractures Reaching Ground Water Resources and after Intercepting Conventional Reservoirs (Scenarios B1 and B2). A high-definition geomechanical study, involving a complex fracture propagation model that incorporates realistic data and parameters (as gleaned from the literature and discussions with industry practitioners) was completed. A sensitivity analysis of the fracture propagation to the most important geomechanical properties and conditions is partially completed and will be included in the final publication.

Simulations of gas and contaminant migration from the shale gas reservoir through fractures into ground water are also in progress. The simulation domain is subdivided up to 300,000 elements[43] and up to 1.2 million equations, which requires very long execution times that can range from several days to weeks. Work continues to streamline the processing of the simulation to significantly reduce the execution time requirements.

Scoping calculations are in development to provide time estimates for the migration of gas and dissolved contaminants from the shale gas reservoir to the drinking water resource through a connecting fracture. As illustrated in Figure 15, the simulated system is composed of a 100-meter-thick aquifer (from 100 to 200 meters below the surface), a fracture extending from the bottom of the gas reservoir at 1,200 meters below surface to the base of the aquifer, which is 1,000 meters above the gas reservoir. These scoping studies indicated that the most important parameters and conditions were the permeability of the gas reservoir (matrix), the fracture permeability, the distance between the aquifer and the shale reservoir, and the pressure regimes in the aquifer and the shale. Results from this work are being analyzed and will be published when complete.

Analysis of Consequences of Activation of Native Faults and Fractures (Scenario C). The simulation conditions for the analysis of contaminant transport through native fractures and faults in response to the stimulation process have been determined, and the variations used to conduct a sensitivity analysis are being developed.

A geomechanical study using the TOUGH-FLAC[44] simulator began in March 2012 to investigate the possibility that hydraulic fracturing injections may create a pathway for transport through fault reactivation. The simulation input represents the conditions in the Marcellus Shale. Scoping calculations were developed to study the potential for injection-induced fault reactivation associated with shale gas hydraulic fracturing operations. From these scoping calculations, the LBNL simulation results suggest that the hydraulic fracturing stimulation, under conditions reported in published literature, does not appear to activate fault rupture lengths greater than 40 to 50 meters and could only give rise to microseismicity (magnitude <1), which is consistent with what has been observed in the field (NAS, 2012). Therefore, preliminary simulations suggest that the possibility of fault reactivation creating a pathway to shallow ground water resources is remote. A more detailed analysis to better resolve local conditions and mechanical response at the injection point is underway and a manuscript is in development (Rutqvist et al., 2012).

Analysis of the Consequences of Induced Fractures Intercepting Offset Unplugged Wells (Scenarios D1 and D2). A geomechanical study is in progress to assess the feasibility of a fracture extending

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[43] Elements represent the spatial properties for the geology and the wells. Conceptually, the continuous real world is represented with discrete (numerical) elements, where each element has constant properties represented. With a large number of elements, a complex geologic and engineering conceptualization may be represented.

[44] TOUGH-FLAC links the public TOUGH model with the commercial and proprietary FLAC model, which is used extensively in geotechnical applications and covers a very wide spectrum of geomechanical processes (including fault representation, plasticity and/or elasticity, anisotropy, etc.) and can describe the interdependence of flow and geomechanical properties as the pressure/stress regime changes (Cappa and Rutqvist, 2011a, b, 2012; Cappa et al., 2009; Mazzoldi et al., 2012; Rutqvist, 2012; Rutqvist et al., 2007; Rutqvist et al., 2012) .

through the shale gas reservoir into the weak/fractured cement around, or the unplugged wellbore of offset wells (Figures 18 and 19). The LBNL is investigating two mechanisms for fluid communication. In the first case, the fractures extend across the shale stratum into a nearby depleted conventional reservoir with abandoned defective wells in the overburden or underburden. The energy for the lift of contaminants in this case is most likely provided by the higher pressure of the fluids in the shale (as the abandoned reservoir pressure is expected to be low) and by buoyancy; the main contaminant reaching the ground water is expected to be gas. In the second case, fractures extend from a deeper over-pressurized saline aquifer through the entire thickness of the shale to an overburden (a depleted conventional petroleum reservoir with abandoned unsealed wells). The energy for the lift of contaminants in this case is most likely provided by the higher pressure of the fluids in the shale and in the saline aquifer in addition to buoyancy, and the contaminants reaching the ground water are expected to include gas and solutes encountered in the saline aquifer.

4.1.4. Quality Assurance Summary

The QAPP, "Analysis of Environmental Hazards Related to Hydrofracturing (Revision: 0)," was accepted by the EPA on December 7, 2011 (LBNL, 2011).

A TSA of the work being performed by the LBNL was conducted on February 29, 2012. The designated EPA QA Manager found the methods in use satisfactory and further recommendations for improving the QA process were unnecessary. Work performed and scheduled to be performed was within the scope of the project. Work is proceeding on Scenarios A through D2 as described in Section 4.1.3. Reports, when presented, will be subjected to appropriate QA review.

4.2. Surface Water Modeling

4.2.1. Relationship to the Study

The EPA is using established surface water transport theory and models to identify concentrations of selected hydraulic fracturing-relevant chemicals at public water supply intakes located downstream from wastewater treatment facilities that discharge treated hydraulic fracturing wastewater to rivers. This work is expected to provide data that will be used to answer the research question identified in Table 28.

Table 28. Secondary research question addressed by modeling surface water discharges from wastewater treatment facilities accepting hydraulic fracturing wastewater.

Water Cycle Stage	Applicable Research Questions
Wastewater treatment and waste disposal	What are the potential impacts from surface water disposal of treated hydraulic fracturing wastewater on drinking water treatment facilities?

4.2.2. Project Introduction

When an operator reduces the injection pressure applied to a well, the direction of fluid flow reverses, leading to the recovery of flowback and produced water, collectively referred to as "hydraulic fracturing wastewater."[45] The wastewater is generally stored onsite before being transported for treatment, recycling or disposal. Most hydraulic fracturing wastewater is disposed in UIC wells. In Pennsylvania, however, wastewater has been treated in wastewater treatment facilities (WWTFs), which subsequently discharge treated wastewater to surface water bodies.

The extent to which common treatment technologies used in WWTFs effectively remove chemicals found in hydraulic fracturing wastewater is currently unclear.[46] Depending in part on the concentration of chemicals in the effluent, drinking water quality and the treatment processes at public water systems (PWSs) downstream from WWTFs might be negatively affected. For example, bromide in source waters can cause elevated concentrations of brominated disinfection byproducts (DBPs) in treated drinking water (Brown et al., 2011; Plewa et al., 2008),[47] which are regulated by the National Primary Drinking Water Regulations.[48] To learn more about impacts to downstream PWSs, the Pennsylvania Department of the Environment asked 25 WWTFs that accept Marcellus wastewater to monitor effluent for parameters such as radionuclides, total dissolved solids (TDS), alkalinity, chloride, sulfate, bromide, gross alpha, radium-226 and -228, and uranium in March 2011 (PADEP, 2011). The department also asked 14 PWSs with surface water intakes downstream from WWTFs that accept Marcellus wastewater to test for radionuclides, TDS, pH, alkalinity, chloride, sulfate, and bromide (PADEP, 2011). Bromide and radionuclides are of particular concern in discharges because of their carcinogenicity and reproductive and developmental affects.

The EPA will use computer models—mass balance, empirical, and numerical—to estimate generic impacts of bromide and radium in wastewater discharges, based on the presence of these chemicals in discharge data from WWTFs in Pennsylvania, impacts to downstream PWSs' ability to meet National Primary Drinking Water Regulations for DBPs and radionuclides, and the potential human health impacts from the chemicals.[49] Uranium, also a radionuclide, was frequently not detected by analytical methods for the discharges and therefore not considered for simulations. The generic model results are designed to illustrate the general conditions under which discharges might cause impacts on downstream public water supplies. The analysis will include the effect of distance to the PWS, discharge concentration, and flow rate in the stream or river, among others. The uncertainties in these quantities will be addressed through Monte Carlo analysis, as described below.

A steady-state mass balance model provides an upper-bound impact assessment of the transport simulation and a partially transient approach simulates the temporal variation of effluent concentration and discharge. Key data collected to model the transport of potential contaminants include actual effluent data from WWTF discharges and receiving water body flow rates. Effluent data can be obtained from National Pollutant Discharge Elimination System (NPDES) monitoring

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[45] Produced water is produced from many oil and gas wells and not unique to hydraulic fracturing.

[46] See Section 5.2 for a more thorough discussion and for EPA-funded research into this question.

[47] See Section 5.3 for more information on DBPs and related research.

[48] Authorized by the Safe Drinking Water Act.

[49] Discharge data for four WWTFs in Pennsylvania that accepted oil and gas wastewater during 2011 are available on the EPA's website at http://www.epa.gov/region3/marcellus_shale/.

data reported to states by the dischargers.[50] NPDES information also documents the design of the industrial treatment plants, which can give insights into the capabilities of these and similarly designed treatment plants. The US Geological Survey (USGS) provides limited water quality and flow rate data from monitoring stations within the watersheds of the receiving water bodies. The surface water modeling results will directly address the applicable secondary research question (Table 28) by evaluating the possible impacts from a permitted release of treated effluent on both a downstream drinking water intake and in a watershed where there may be multiple sources and receptors.[51]

4.2.3. Research Approach

Multiple approaches generate results on impacts: steady-state mass balance; transient empirical modeling; and a transient, hybrid empirical-numerical model developed by the EPA. The results of the mass balance model simulate possible impacts during a large volume, high concentration discharge without natural attenuation of contaminants. The empirical model and a hybrid empirical-numerical model estimate impacts in a more realistic setting with variable chemical concentrations, discharge volumes, and flow rates of the receiving surface water. The numerical model confirms the results of the empirical and hybrid models. The numerical modeling is based on an approach developed for this study from existing methods (Hairer et al., 1991; Leonard, 2002; Schiesser, 1991; Wallis, 2007). Application of these three types of models provides a panoramic view of possible impacts and enhances confidence in the study results.

Mass Balance Approach Estimates Impacts from an Upper-Bound Discharge Scenario. A simple, steady-state mass balance model simulates drinking water impacts from upper-bound discharge cases. This model assumes that the total mass of the chemical of interest is conserved during surface water transport and that the chemical concentration does not decrease due to reaction, decay, or uptake. The model estimates potential impacts to downstream PWSs using the maximum effluent concentration, maximum WWTF discharge volume, minimum flow rate in the receiving stream, and the distance to the downstream PWS intake. The EPA constructed generic discharge scenarios for rivers with varying flow regimes to determine the potential for adverse impacts at drinking water intakes. Because the parameters describing transport are uncertain, Monte Carlo techniques will be used to generate probabilistic outputs of the model.

Empirical Model Estimates Impacts with Varying Discharge Volumes over Time. The upper-bound case simulated in the steady-state mass balance model may be too conservative (by providing larger concentration estimates) to accurately represent downstream concentrations of chemicals since effluent concentrations, treatment plant discharge volumes, and flow rates change over time. Therefore, the EPA will also use an empirical transport model originally developed by the USGS (Jobson, 1996) to simulate impacts from varying monthly discharge volumes over time. The

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[50] Information on WWTF discharges in Pennsylvania can be found at https://www.paoilandgasreporting.state.pa.us/publicreports/Modules/Welcome/Welcome.aspx.

[51] Impacted watersheds may also have other sources of compounds of interest, possibly acid mine drainage and coal-fired utility boilers. This is discussed in more detail in Section 5.1, which also outlines work being done by the EPA to assess the contribution of hydraulic fracturing wastewater to contamination in surface water bodies.

empirical approach is based on tracer studies performed around the United States since the early 1970s (e.g., Nordin and Sabol (1974)). The empirical equations address two major difficulties in applying models to chemical transport scenarios: the inability to estimate travel times from cross-sectional data and the reduction of concentration due to turbulent diffusion. The empirical equation approach gives an estimate of travel time and peak concentration so that the model does not need to be calibrated to tracer data.

Hybrid Empirical-Numerical Model Estimates Impacts for River Networks. The original empirical approach was suited for a single river segment, or reach, of spatially uniform properties. The hybrid empirical-numerical model being developed by the EPA to expand the capabilities of the just-described Jobson technique will easily account for multiple reaches that can form branching river networks. Similar to all statistical relationships, the empirical equations do not always match tracer data exactly; therefore, the EPA is including the ability to perform Monte Carlo techniques in the software being developed. The EPA will confirm the accuracy of the hybrid model with tracer data that fall within the range of Jobson's original set of inputs (taken from Nordin and Sabol (1974)) as well as later data from the Yellowstone River that provide a real-world test of this approach (McCarthy, 2009).

The numerical portion of the hybrid model provides a direct and automatic comparison with the empirical equations. The method is based on a finite difference solution to the transport equation using recent developments in modeling to improve accuracy (Hairer et al., 1991; Leonard, 2002; Schiesser, 1991; Wallis, 2007). By including this numerical method, a hybrid empirical-numerical approach can be achieved. The empirical travel times from Jobson (1996) can be used to parameterize velocity in the numerical method. Dispersion coefficients can be derived from empirical data or a method developed by Deng et al. (2002). Using these approaches provides improved accuracy in the simulation results. The EPA will prepare a user's guide to the model and make both the computer model and user's guide widely available for duplicating the results prepared for this project and for more general use.

For the generic simulations described above, effluent concentrations and discharge volumes will be modeled directly as variable inputs based on the effluent data evaluation (as discussed next in Section 4.2.4), while flow conditions will be modeled as low, medium, and high flow. Because the parameters describing transport are uncertain, statistical measures and Monte Carlo techniques will be used to generate probabilistic outputs from the model. To provide further assurance of the accuracy of the EPA hybrid model results, the Water Quality Simulation Package has been used to simulate tracer data and confirm the results (Ambrose et al., 1983; Ambrose and Wool, 2009; DiToro et al., 1981).

4.2.4. Status and Preliminary Data

The models described above are being used to determine potential impacts of treated wastewater discharges on downstream PWSs. Enough data have been identified to perform generic simulations for the steady-state mass balance simulations and hybrid empirical-numerical models with variable effluent concentration and plant discharge. For two WWTFs in Pennsylvania, USGS flow data have been compiled for segments of the rivers that reach downstream to drinking water intakes (50 to 100 miles downstream) for the two locations. These data will be used to generate realistic model inputs to assess, in a generic sense, the potential impacts of discharges from realistic treatment plants.

The EPA-developed hybrid empirical-numerical model has been favorably compared against a tracer experiment used by Jobson (1996) in developing the original empirical formulas. Calibration or other parameter adjustment was unnecessary for the hybrid model to produce accurate results. The EPA plans to compare the hybrid model to five more of the tracer experiments to cover the range of flow conditions used by Jobson (1996). Additionally, data from the more recent Yellowstone River experiment (McCarthy, 2009) are being prepared for testing the hybrid model. Similar comparisons of empirical to tracer experiments were performed by Reed and Stuckey (2002) for streams in the Susquehanna River Basin. The EPA Water Quality Simulation Package numerical model was set up to simulate the same tracer experiment performed for the hybrid model. Additional calibration is planned to refine the results from the Water Quality Simulation Package. After completing the evaluation of the hybrid model, the WWTF simulations will be completed.

4.2.5. Next Steps

A description of the EPA-developed empirical-numerical model and application of the empirical-numerical and mass balance models to tracer experiments is being developed by EPA scientists and are expected to be submitted for publication in a peer-reviewed journal. The results from testing of the models and the analysis of the WWTF effluent data will be included in another peer-reviewed journal article.

4.2.6. Quality Assurance Summary

The initial QAPP for “Surface Water Transport of Hydraulic Fracturing-Derived Waste Water” was approved by the designated EPA QA Manager on September 8, 2011 (US EPA, 2012s). The QAPP was subsequently revised and approved on February 22, 2012.

A TSA was conducted on March 1, 2012. The designated EPA QA Manager found the methods in use satisfactory and further recommendations for improving the QA process were unnecessary. An audit of data quality (ADQ) will be performed to verify that the quality requirements specified in the approved QAPP were met.

4.3. Water Availability Modeling

The EPA selected humid and semi-arid river basins as study areas for identifying potential impacts to drinking water resources from large volume water withdrawals (1 to 9 million gallons per well for the selected river basins) associated with hydraulic fracturing operations. This work is expected to address the research questions listed in Table 29.

Table 29. Research questions addressed by modeling water withdrawals and availability in selected river basins.

Water Cycle Stage	Applicable Research Questions
Water acquisition	• How much water is used in hydraulic fracturing operations, and what are the sources of this water? • How might water withdrawals affect short- and long-term water availability in an area with hydraulic fracturing? • What are the possible impacts of water withdrawals for hydraulic fracturing operations on local water quality?

4.3.1. Project Introduction

The volume of water needed in the hydraulic fracturing process for stimulation of unconventional oil and gas wells depends on the type of formation (e.g., coalbed, shale, or tight sands), the well construction (e.g., depth, length, vertical or directional drilling), and fracturing operations (e.g., fracturing fluid properties and fracture job design). Water requirements for hydraulic fracturing of CBM range from 50,000 to 250,000 gallons per well (Holditch, 1993; Jeu et al., 1988; Palmer et al., 1991; Palmer et al., 1993), although much larger volumes of water are produced during the lifetime of a well in order to lower the water table and expose the coal seam (ALL Consulting, 2003; S.S. Papadopulos & Associates Inc., 2007a, b). The water usage for hydraulic fracturing in shale gas plays is significantly larger than CBM reservoirs—2 to 4 million gallons of water are typically needed per well (API, 2010; GWPC and ALL Consulting, 2009; Satterfield et al., 2008). The volume of water needed for well drilling is understood to be much less, from 60,000 gallons in the Fayetteville Shale to 1 million gallons in the Haynesville Shale (GWPC and ALL Consulting, 2009). Water-based mud systems used for drilling vertical or horizontal wells generally require that fresh water (non-potable, potable, or treated) be used as makeup fluid, although wells can also be drilled using compressed air and oil-based fluids.

Water needed for hydraulic fracturing may come from multiple sources with varying quality. Sources may include raw surface and ground water, treated water from public water supplies, and water recycled from other purposes such as flowback and produced water from previous oil and gas operations or even acid mine drainage. The quality of water needed is dependent on the other chemicals in the fracturing fluid formulations, availability of water source, and the chemical and physical properties of the formation. The goal of this project is to investigate the water needs and sources to support hydraulic fracturing operations at the river basin and county spatial scales and to place this demand in the watershed context in terms of annual, seasonal, and monthly water availability.

The EPA recognizes the unique circumstances of the geography and geology of every unconventional oil and gas resource and has chosen two study sites to initially explore and identify the potential differences related to water acquisition. The study areas includes two river basins: the Susquehanna River Basin (SRB), located in the eastern United States (humid climate) and overlying the Marcellus Shale gas reservoir (Figure 20), and the Upper Colorado River Basin (UCRB), located in the western United States (semi-arid climate) and overlying the Piceance structural basin and tight gas reservoir (Figure 21). The EPA is calibrating and testing watershed models for the study; the SRB and UCRB watershed models were previously calibrated and tested in the EPA investigation of future climate change impacts on watershed hydrology (the "20 watersheds study") (Johnson et al., 2011).

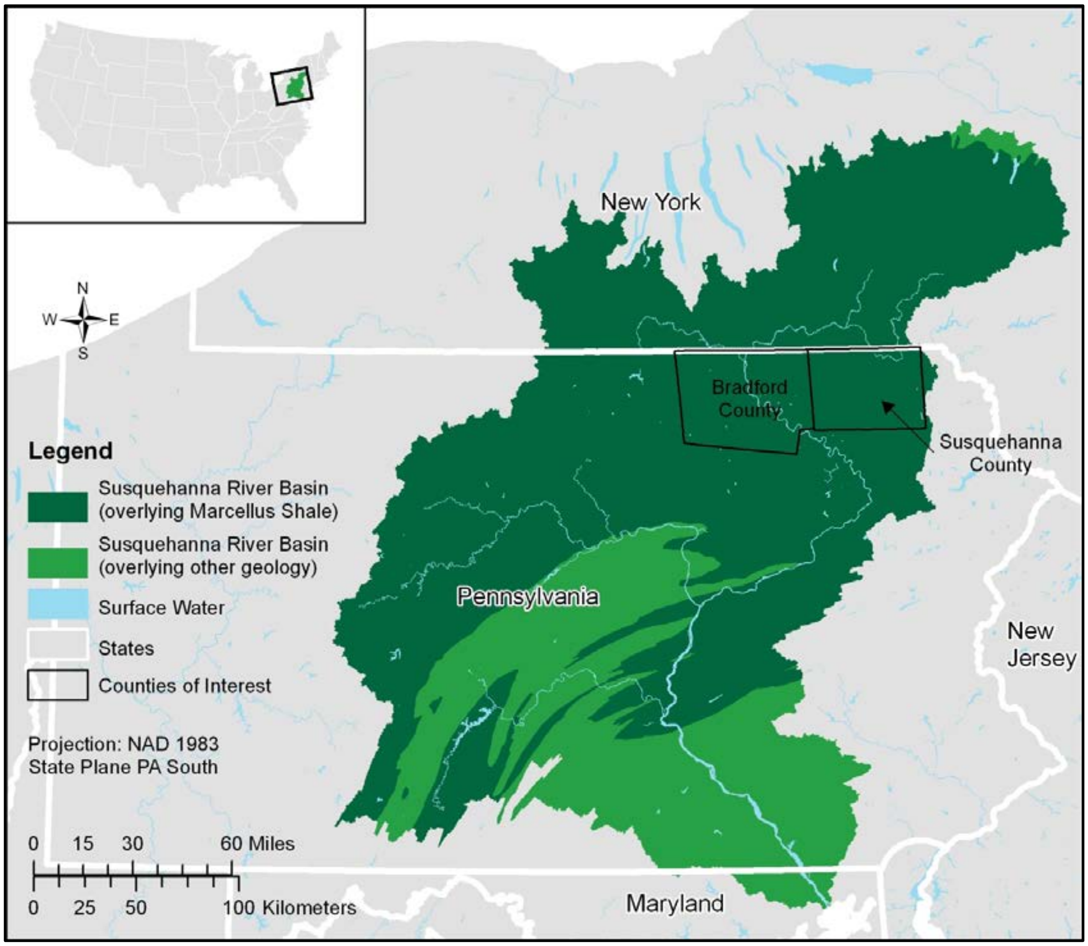

Figure 20. The Susquehanna River Basin, overlying a portion of the Marcellus Shale, is one of two study areas chosen for water availability modeling. Water acquisition for hydraulic fracturing will focus on Bradford and Susquehanna Counties in Pennsylvania. (GIS data obtained from ESRI, 2010a; US EIA, 2011e; US EPA, 2007.)

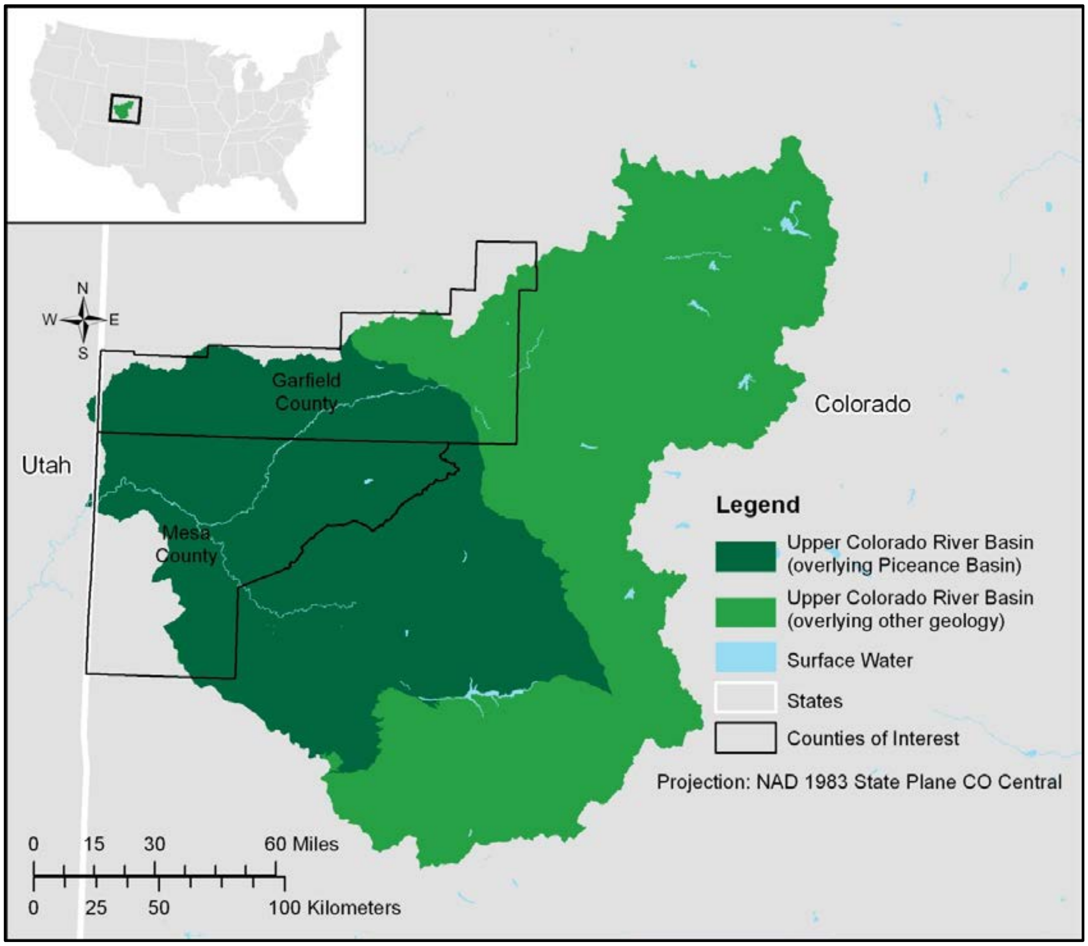

Figure 21. The Upper Colorado River Basin, overlying a portion of the Piceance Basin, is one of two river basins chosen for water availability modeling. Water acquisition for hydraulic fracturing will focus on Garfield and Mesa Counties in Colorado. (GIS data obtained from ESRI, 2010a; US EIA, 2011e; US EPA, 2007.)

In both study areas, the river watershed and its subsurface basin include the river flows and reservoir and aquifer storages based on the hydrologic cycle, geography, geology, and water uses. The EPA's goal is to explore future hypothetical scenarios of hydraulic fracturing use in the eastern and western study areas based on current understanding of hydraulic fracturing water acquisition and watershed hydrology. The EPA intends to characterize the significance, or insignificance, of hydraulic fracturing water use on future drinking water resources for the two study areas. The research will involve detailed representation of water acquisition supporting hydraulic fracturing in the Bradford County and Susquehanna County area in Pennsylvania and in the Garfield County and Mesa County areas of Colorado. These areas have concentrated hydraulic fracturing activity, as discussed below.

4.3.1.1. Susquehanna River Basin

Geography, Hydrology, and Climate. The SRB has over 32,000 miles of waterways, drains 27,510 square miles, and covers half of Pennsylvania and portions of New York and Maryland (Figure 20) (SRBC, 2006). On average, the SRB contributes 18 million gallons of water every minute (25,920 million gallons per day, or MGD) to the Chesapeake Bay (SRBC, 2006). The humid climate of the region experiences long-term average precipitation of 37 to 43 inches per year (McGonigal, 2005).

Oil and Gas Resources and Activity. Large portions of the SRB watershed are underlain by the Marcellus Shale formation, which is rich in natural gas. Estimates of recoverable and undiscovered natural gas from this formation range from 42 to 144 trillion cubic feet (Coleman et al., 2011) and production well development estimates for the next two decades range as high as 60,000 total wells drilled by 2030 (Johnson et al., 2010). The Pennsylvania Department of Environmental Protection reports that the number of drilled wells in the Marcellus Shale has been increasing rapidly. In 2007, only 27 Marcellus Shale wells were drilled in the state; in 2010 the number of wells drilled was 1,386. Data extracted from FracFocus[52] indicate that the total vertical depth of wells in Bradford and Susquehanna Counties is between 5,000 and 8,500 feet (mean of 6,360 feet) below ground surface, which implies that this depth range is the target production zone for the Marcellus Shale.

Water Use. The SRB supports a population of over 4.2 million people. Table 30 lists the estimated water use for the SRB and Bradford and Susquehanna Counties. The Susquehanna River Basin Commission estimates consumptive water use in five major categories, with PWSs consuming the greatest volume of water per day (325 MGD) followed by thermoelectric energy production (190 MGD) (Richenderfer, 2011). The greatest water withdrawals per day in Bradford and Susquehanna Counties are for drinking water (8.25 MGD for combined public and domestic use) and self-supplied industrial uses (4.59 MGD).

Table 30. Water withdrawals for use in the Susquehanna River Basin (Richenderfer, 2011) and Bradford and Susquehanna Counties, Pennsylvania (Kenny et al., 2009).

Use	Water Withdrawals (million gallons per day)	
	Susquehanna River Basin	Bradford and Susquehanna Counties, Pennsylvania
Public supply	325	4.59
Self-supplied domestic	Not reported	3.66
Irrigation (crop)	Not reported	0.110
Irrigation (golf courses)	Not reported	0.060
Self-supplied industrial	22.0	4.59
Livestock	Not reported	3.41
Thermoelectric	190 (energy production, non-gas)	0.00
Mining	10.0	0.10
Other	50.0 (recreation)	Not reported

Figure 22 displays the geographic distribution of PWSs in the SRB.[53]

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[52] See Section 3.5 for additional information on the FracFocus data extraction and analysis research project.

[53] The location and type of drinking water supply is significant when represented in watershed hydrology models. The extraction of surface water is removed from the watershed model subbasin from its main river reach. The extraction of ground water is removed from the model subbasin from its ground water storage.

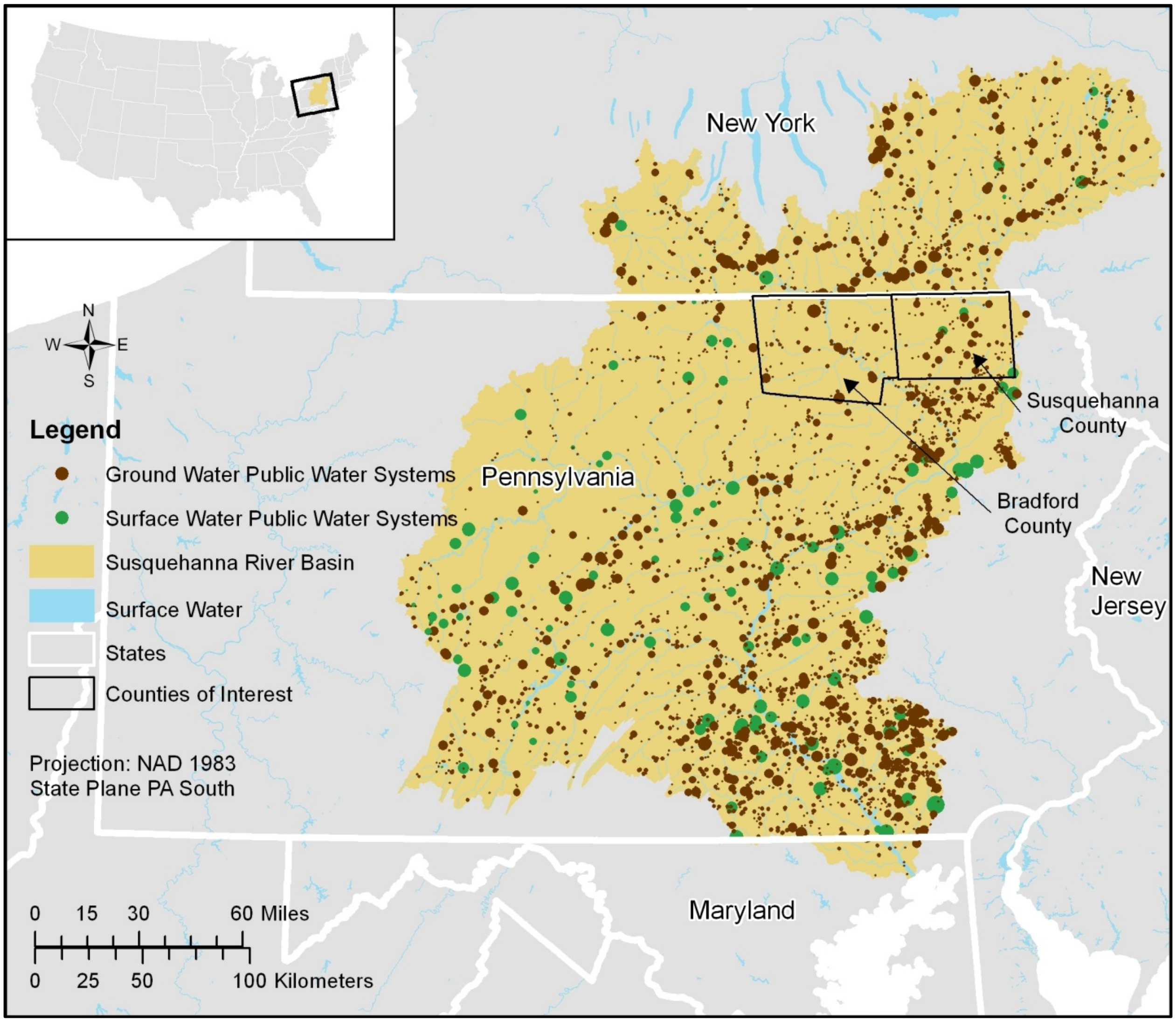

Figure 22. Public water systems in the Susquehanna River Basin (US EPA, 2011j). The legend symbol size for public water systems is proportional to the number of people served by the systems. For example, the smallest circle represents water systems serving 25 to 100 people and the largest circle represents systems serving over 100,000 people.

The Susquehanna River Basin Commission reports that the oil and gas industry consumed over 1.6 billion gallons of water for well drilling and hydraulic fracturing in the entire SRB from July 1, 2008, to February 14, 2011. If averaged over the entire time, this is roughly 1.7 MGD. This amount of water was used for approximately 1,800 gas production wells with about 550 wells hydraulically fractured by the end of 2010 (Richenderfer, 2011). The majority (65%) of the water came from direct surface water withdrawals, with smaller fractions from PWSs (35%) and ground water (very small). The average total volume of fluid used per well was 4.2 million gallons, with about 10% of the volume as treated flowback and 90% fresh water (Richenderfer, 2011). The average recovery of fluids was reported to be 8% to 12% of the injected volume within the first 30 days (Richenderfer, 2011).

Water use reported in FracFocus for Bradford and Susquehanna Counties ranges between 2 and 9 million gallons per well (median of 4.7 million gallons per well; (GWPC, 2012a)), consistent with data reported by the Susquehanna River Basin Commission.[54] In this part of the SRB, the wells are almost exclusively horizontal and producing from the Marcellus Shale. The operators are blending treated produced water into hydraulic fracturing fluids (Rossenfoss, 2011).

4.3.1.2. Upper Colorado River Basin

Geography, Hydrology, and Climate. The UCRB drains an area of 17,800 square miles and is characterized by high mountains in the east and plateaus and valleys in the west. The average discharge of the Colorado River near the Colorado-Utah state line is about 2.8 million gallons per minute (about 4,000 MGD) (Coleman et al., 2011). Precipitation ranges from 40 inches per year or more in the eastern part of the basin to less than 10 inches per year in the western part of the basin (Spahr et al., 2000).

Oil and Gas Resources and Activity. The UCRB has a long history of oil, gas, and coal exploration. The Piceance Basin is a source of unconventional natural gas and oil shale. The basin was originally exploited for its coal resources, and the associated CBM production peaked around 1992 (S.S. Papadopulos & Associates Inc., 2007a). The Upper Cretaceous Williams Fork Formation, a thick section of shale, sandstone, and coal, has been recognized as a significant source of gas since 2004 (Kuuskraa and Ammer, 2004). The wells producing gas from the Williams Fork are either vertically or directionally ("S"-shaped wells) drilled rather than horizontal. While the deeper Mancos Shale is considered a major resource for shale gas (Brathwaite, 2009), it must be exploited with horizontal drilling methods, and the economics are such that only prospecting wells are being drilled at this time (personal communication, Jonathan Shireman, Shaw Environmental & Infrastructure, May 1, 2012). Estimated reserves in coalbeds and unconventional tight gas reservoirs are nearly 84 trillion cubic feet (Tyler and McMurry, 1995).

Gas production activities occur in the following counties within the UCRB: Delta, Eagle, Garfield, Grand, Gunnison, Hinsdale, Mesa, Montrose, Ouray, Pitkin, Routt, Saguache, and Summit (COGCC, 2012b). Table 31 indicates that the greatest drilling activity has been in Garfield and Mesa Counties (Figure 21), where well completions increased steadily from 2000 (212 wells) to 2008 (2,725 wells), then dropped slightly to 1,160 wells in 2010 (COGCC, 2012b). The total vertical depth of wells in Garfield County and Mesa County as reported in FracFocus implies that the location of the target production zone(s) lies between 6,000 and 13,000 feet (mean of 8,000 feet) below ground surface.

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[54] More information on FracFocus is available in Section 3.5.

Table 31. Well completions for select counties in Colorado within the Upper Colorado River Basin watershed (COGCC, 2012b).

County	Annual Well Completions from 2000 to 2010										
	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
Delta				8	5	8	3	2			4
Garfield	207	244	287	507	679	892	1269	1689	2255	1050	1139
Gunnison			2	3	2	1	11	8	2	4	2
Mesa	5	21	26	18	53	203	336	501	470	43	21
Montrose		4		2	2			3	4		1
Routt	10	21				8	5	2		4	1

Water Use. The UCRB supports a population of over 275,000 people. Table 32 lists the estimated water use for the UCRB and Garfield and Mesa Counties in Colorado. According to the USGS, the total water use in 2005 in the UCRB and Garfield and Mesa Counties was dominated by irrigation (1702 and 1200 MGD, respectively), followed by public and domestic water supply (60.4 and 29.6 MGD), and thermoelectric energy production (44 MGD) (Ivahnenko and Flynn, 2010; Kenny et al., 2009).

Table 32. Water withdrawals for use in the Upper Colorado River Basin (Ivahnenko and Flynn, 2010) and Garfield and Mesa Counties in Colorado (Kenny et al., 2009).

Use	Water Withdrawals (million gallons per day)	
	Upper Colorado River Basin	Garfield and Mesa Counties, Colorado
Public supply	58.6	29.2
Self-supplied domestic	1.81	1.35
Irrigation (crop)	1702	1200
Irrigation (golf courses)	8.00	3.50
Self-supplied industrial	2.71	1.05
Livestock	0.870	0.840
Thermoelectric	43.9 (non-consumptive)	43.9 (non-consumptive)
Mining	0.390	0.280
Other	Not reported	1.88 (aquaculture)

Figure 23 displays the distribution of public water systems in the basin. Interbasin water transfers, mining, urbanization, and agriculture are the principal human activities that potentially impact water quantity in the UCRB.

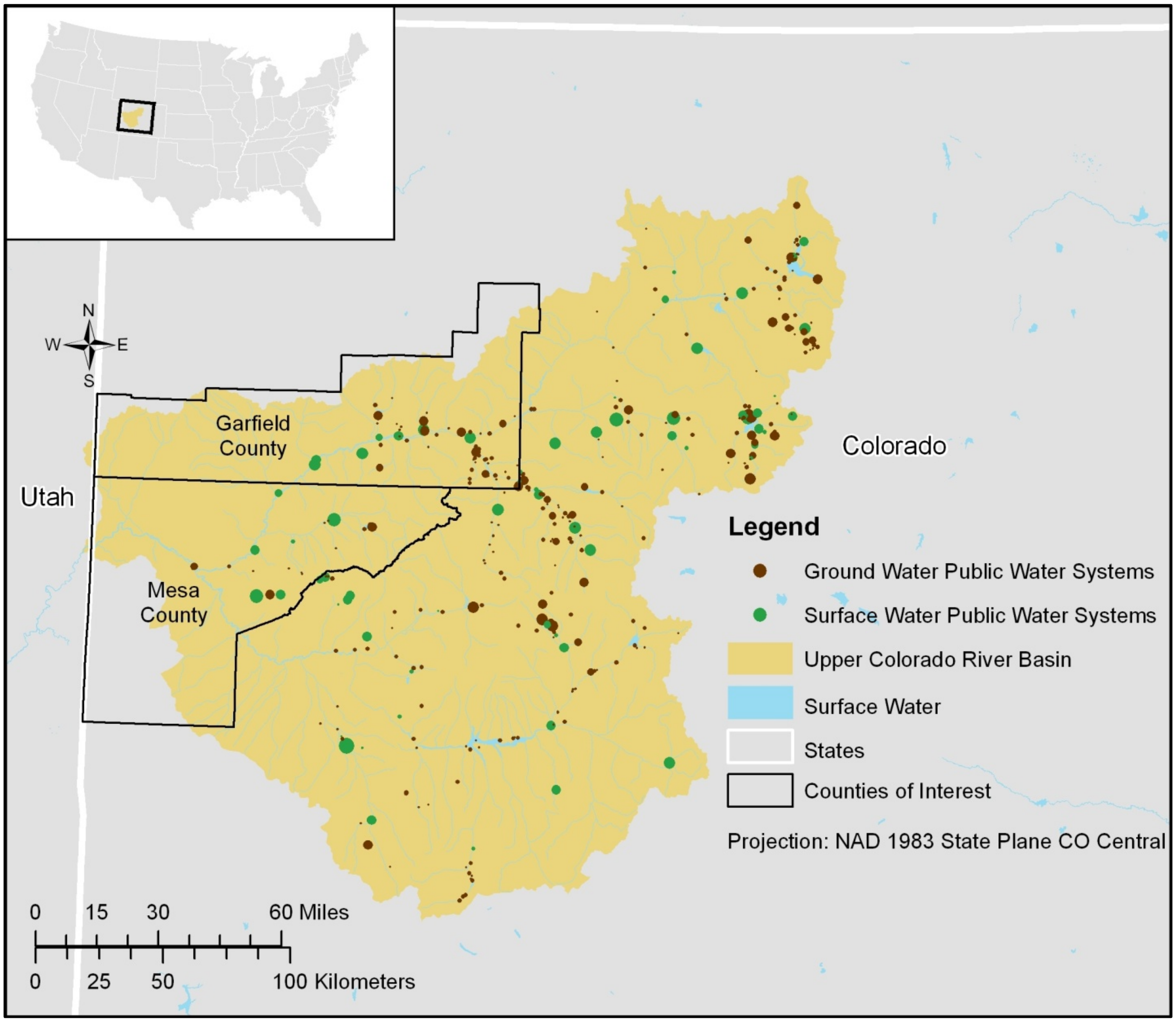

Figure 23. Public water systems in the Upper Colorado River Basin (US EPA, 2011j). The legend symbol size for public water systems is proportional to the number of people served by the systems. For example, the smallest circle represents water systems serving 25 to 100 people and the largest circle represents systems serving over 70,000 people.

The State of Colorado estimates that total annual statewide water demand for hydraulic fracturing associated with oil and gas wells increased from 4.5 billion gallons in 2010 to almost 4.9 billion gallons in 2011 (12.3 MGD in 2010 to almost 13.4 MGD in 2011), which parallels the increasing number of wells spudded, as shown in Table 33 (COGCC, 2012a). The amount of water demand was determined using the number of wells spudded (horizontal and vertical) multiplied by an average amount of water required for hydraulic fracturing per well type based on data reported in 2011. COGCC (2012a) estimates the average water use per well at about 1.6 million gallons in 2010 and 2011.

Table 33. Estimated total annual water demand for oil and gas wells in Colorado that were hydraulically fractured in 2010 and 2011 (COGCC, 2012a). Data for vertical and horizontal wells are not differentiated in the estimates and well spud dates.

Category	Year	
	2010	2011
Wells spudded	2,753	2,975
Estimated annual water demand (million gallons)	4,531	4,857
Estimated water use per well (million gallons)	1.65	1.63

Data extracted from FracFocus for Garfield and Mesa Counties shows water use per well between 1 and 9 million gallons (median 1.3 million gallons), which is consistent with the Colorado Oil and Gas Compact Commission data (COGCC, 2012a; GWPC, 2012a). In this part of the Piceance Basin (Figure 21), the majority of wells are vertically drilled and producing gas from the Williams Fork tight sandstones. Based on conversations with Berry Petroleum, Williams Production, Encana Oil and Gas, and the Colorado Field Office of the US Bureau of Land Management, the water used to fracture wells in this area is entirely recycled formation water that is recovered during production operations. Fresh water is used only for drilling mud, cementing the well casing, hydrostatic testing, and dust abatement and is estimated to be about 251,000 gallons per well (US FWS, 2008).

4.3.2. Research Approach

Watershed Models. In order to assess the impact of hydraulic fracturing water withdrawals on drinking water availability at watershed and county spatial scales as well as annual, seasonal, monthly, and daily time scales, the EPA is developing separate hydrologic watershed models for the SRB and UCRB. The models are based in part on the calibrated and verified watershed models (hereafter called the "foundation" models) of the EPA Global Change Research Program (Johnson et al., 2011), namely the Hydrologic Simulation Program FORTRAN (HSPF)[55] and the Soil and Water Assessment Tool (SWAT).[56] Both HSPF and SWAT are physically based, semi-distributed watershed models that compute changes in water storage and fluxes within drainage areas and water bodies over time. Each model can simulate the effect of water withdrawals or flow regulation on modeled stream or river flows. Key inputs for the models include meteorological data, land use data, and time series data representing water withdrawals. The models give comparable performance at the scale of investigation (Johnson et al., 2011).

Modeling of the SRB will be completed using the calibrated and tested HSPF. Since its initial development nearly 20 years ago, HSPF has been applied around the world; it is jointly sponsored by the EPA and the USGS, and has extensive documentation and references (Donigian Jr., 2005; Donigian Jr. et al., 2011). The choice of HSPF in the SRB, a subwatershed within the larger

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[55] More information on the HSPF model including self-executable file, is available at http://www.epa.gov/ceampubl/swater/hspf/.

[56] More information on the SWAT model including self-executable file, is available at http://swat.tamu.edu/software/swat-model/.

Chesapeake Bay watershed, allows benchmarking to the peer-reviewed and community-accepted Chesapeake Bay Program watershed model.[57]

Modeling of the UCRB will be completed using the calibrated and tested SWAT. The SWAT is a continuation of over 30 years of modeling efforts conducted by the US Department of Agriculture's Agricultural Research Service and has extensive peer review (Gassman et al., 2007). SWAT is an appropriate choice in the less data-rich UCRB, where hydrological response units can be parameterized based on publicly available GIS maps of land use, topography, and soils.

The SRB and UCRB models will build on the "foundation" models and be updated to represent baseline and current watershed conditions. The baseline model will add reservoirs and major consumptive water uses for watershed conditions of the year 2000 for the SRB and 2005 for the UCRB. The baseline year predates the significant expansion of hydraulic fracturing in the basin (2007 for SRB, 2008 for UCRB) and corresponds with the USGS' water use reports (every five years since 1950) and the National Land Cover Dataset (Homer et al., 2007). The baseline models will represent the USGS's major water use categories, including the consumptive component of both PWS and domestic water use, and the other major water use categories (irrigation, livestock, industrial, mining, thermoelectric power). The snapshot of each watershed in the year 2010 will be the current model representation in both basins. The current models will include all water use categories from the baseline model plus hydraulic fracturing water withdrawals and refine the representation of PWS and hydraulic fracturing in county-scale focus areas—Garfield/Mesa Counties in Colorado and Bradford/Susquehanna Counties in Pennsylvania.

The foundation, baseline, and current watershed models will be exposed to the historical meteorology (precipitation, temperature) from National Weather Service gauges located within each watershed. The calibration and validation of the foundation, baseline, and current models will be checked by comparing goodness-of-fit statistics and through expert judgment of comparisons of observed and modeled stream discharges.

Key characteristics of model configuration include:

- Land use will be based on the 2001 National Land Cover Dataset (Homer et al., 2007). Land use data are used for segmenting the basin land area into multiple hydrologic response units, each with unique rainfall/runoff response properties. For the SWAT model, soil and slope data will also be used for defining unique hydrologic response units.
- Each basin will be segmented into multiple subwatersheds at the 10-digit hydrologic unit scale.[58]

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[57] More information on the Chesapeake Bay Program watershed model is available at http://www.chesapeakebay.net/about/programs/modeling/53/.

[58] Hydrologic units refer to the Watershed Boundary Dataset developed through a coordinated effort by the USGS, the US Department of Agriculture, and the EPA. The intent of defining hydrologic units for the Watershed Boundary Dataset is to establish a baseline drainage boundary framework, accounting for all land and surface areas. Several levels of watershed are defined based on size. A 10-digit hydrologic unit is a level 5 watershed of average size 227 square miles (USDA, 2012).

- Observed meteorological data for water years 1972 to 2004 for SRB and 1973 to 2003 for UCRB will be applied to assess water availability over a range of weather conditions.
- The effect of reservoirs on downstream flows will be simulated using reservoir dimensions/operation data from circa 2000 from the Chesapeake Bay Program watershed model (Phase 5.3; (US EPA, 2010a)).
- Point source dischargers with NPDES-permitted flow rates of at least 1 MGD will be represented as sources of water on the appropriate stream reaches.
- Surface water withdrawals will be simulated for three unique water use categories: hydraulic fracturing water use, PWSs, and other. For the "other" category, the magnitude of withdrawals from modeled stream reaches will be based on water use estimates developed by the USGS (year 2000 for SRB; year 2005 for UCRB).[59]

Modeling Future Scenarios. The modeling effort will also simulate a snapshot of heightened annual hydraulic fracturing relative to the baseline and current condition models at levels that could feasibly occur over the next 30 years, based on recent drilling trends and future projections of natural gas production (US EIA, 2012; US EPA, 2012w). Because projections of future conditions are inherently uncertain, three separate scenarios will be simulated: business-as-usual, energy plus, and green technology. The scenarios assume distinct levels of natural gas drilling and hydraulic fracturing freshwater use and, therefore, apply distinct hydraulic fracturing water withdrawal time series to modeled stream reaches. Further, significant population growth is projected in Garfield/Mesa Counties, Colorado, over the next 30 years (US EPA, 2010c), where natural gas extraction in the UCRB has recently been concentrated. Therefore, the UCRB future scenarios also consider a potential increase in PWS surface withdrawals in the basin. The balance between surface water availability and demand depicted in each scenario's annual snapshot of water use will be assessed across a range of weather conditions (i.e., drought, dry, wet, and very wet years based on the historical record). A description of each scenario, and the methods used for scenario development, are provided below and in Tables 34 and 35.

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[59] The USGS water use estimates can be found at http://water.usgs.gov/watuse/.

Table 34. Data and assumptions for future watershed availability and use scenarios modeled for the Susquehanna River Basin. Current practices for water acquisition and disposal are tracked by the Susquehanna River Basin Commission (SRBC).

Model Assumptions	Future Scenarios		
	Business as Usual	Energy Plus	Green Technology
Hydraulic fracturing well deployment	Current well inventory and future deployment schedules and play-level development projections*	Maximum projected development of gas reserves*	Current well inventory and future deployment schedules and play-level development projections*
Hydraulic fracturing water management practices	Current practices for water acquisition, production and disposal tracked by SRBC†	Current practices for water acquisition, production and disposal tracked by SRBC†	Increased recycling of produced water for hydraulic fracturing†

* US EPA, 2012w; USGS, 2011c
† SRBC, 2012

Table 35. Data and assumptions for future watershed availability and use scenarios modeled for the Upper Colorado River Basin.

Model Assumptions	Future Scenarios		
	Business as Usual	Energy Plus*	Green Technology*
Hydraulic fracturing well deployment	Current well inventory and future deployment schedules and play-level development projections†	Maximum projected development of gas reserves†	Maximum projected development of gas reserves†
Hydraulic fracturing water management practices	Current practices for water acquisition, production and disposal estimated for UCRB§	Current practices for water acquisition, production and disposal estimated for UCRB§	Increased recycling of produced water for drilling§

* Reflects 2040 population increase (US EPA, 2010c) and corresponding change in PWS demand.
† US EIA, 2011b, 2012; US EPA, 2012w; USGS, 2003
§ US FWS, 2008

Future drilling patterns in the SRB and UCRB are assessed from National Energy Modeling System (NEMS) regional projections of the number of wells drilled annually from 2011to 2040 in shale gas (SRB) and tight gas (UCRB) plays (US EIA, 2012; US EPA, 2012w). Based on analysis of NEMS well projections and undiscovered resources in the Marcellus Shale (Coleman et al., 2011), peak annual drilling in the SRB could exceed the recent high in 2011 by as much as 50%. In the UCRB, analysis of NEMS well projections and undiscovered tight gas resources in the Piceance Basin (USGS, 2003) suggest that the 2008 peak level of drilling in the basin could be repeated in the late 2030s, when a growing population would exert a higher demand for freshwater. The future scenarios will incorporate these projections, with high-end estimates of the number of wells drilled/fractured applied in the energy plus scenario.

The volume of surface water required for drilling and hydraulic fracturing varies according to local geology, well characteristics, and the amount of recycled water available for injection. In the SRB, 2008 to 2011 water use data (SRBC, 2012) show that, on average, 13% of total water injected for hydraulic fracturing is composed of recycled produced water or wastewater. Per well surface water use in the SRB business as usual and energy plus scenarios will therefore be established as 87% of the 4 million gallons of water used for hydraulic fracturing, or 3.5 million gallons. The SRB green technology scenario reflects a condition of increased water recycling, where the 90th percentile of current recycled water amount (29%) becomes the average. Per well surface water use in the SRB green technology scenario will therefore be established as 71% of the 4 million gallons of water used for hydraulic fracturing, or 2.8 million gallons.

In the UCRB, 100% recycled water use is typical for hydraulic fracturing of tight sandstones (personal communication, Jonathan Shireman, Shaw Environmental & Infrastructure, May 7, 2012). Surface water is acquired for well drilling and cementing (0.18 million gallons), dust abatement (0.03 million gallons), and hydrostatic testing (0.04 million gallons) only (US FWS, 2008). Per well surface water use in the UCRB business as usual and energy plus scenarios will therefore be 0.25 million gallons. For the UCRB green technology scenario, surface water will be assumed to be acquired for well drilling and cementing only (0.18 million gallons per well).

Following the development of water withdrawal datasets for each scenario, model output will be reviewed to assess the impacts of water acquisition for hydraulic fracturing on drinking water supplies by evaluating annual and long-term streamflow and water demand, and identifying short-term periods (daily to monthly) in which water demand exceeds streamflow. Since many public water supplies originate from ground water sources, simulated ground water recharge will also be computed. Results will be compared among the three scenarios to identify noteworthy differences and their implications for future management of hydraulic fracturing-related water withdrawals.

4.3.3. Status and Preliminary Data

Existing water use information for hydraulic fracturing has been collected from the Susquehanna River Basin Commission and the Colorado Oil and Gas Compact Commission by Shaw Environmental Technologies. The data underwent a QA review before submission to the modeling teams of The Cadmus Group, Inc. The models are being calibrated and validated. The future scenarios are being designed, with model simulations to follow. Work is underway and will be published in peer-reviewed journals when completed.

4.3.4. Quality Assurance Summary

The QAPP, "Modeling the Impact of Hydraulic Fracturing on Water Resources Based on Water Acquisition Scenarios (Version 1.0)," contracted through The Cadmus Group, Inc., was accepted on February 8, 2012 (Cadmus Group Inc., 2012a). A technical directive/contract modification dated April 25, 2012, modifies the scope of the project but not the procedures. Additionally, there is a pending QAPP revision that adapts the scope to the contract modification.

A TSA of The Cadmus Group, Inc., contract was performed by the designated EPA QA Manager on June 14, 2012. The methods in use were found to be satisfactory and further recommendations for improving the QA process were unnecessary. Work performed and scheduled to be performed was within the scope of the project.

The interim progress report “Development and Evaluation of Baseline and Current Conditions for the Susquehanna River Basin,” received on June 19, 2012, was found to be concise but detailed enough to meet the QA requirements, as expressed in the QAPP, its revision, and the contract modification/technical directive. The same was true for the interim progress report “Impact of Water Use and Hydro-Fracking on the Hydrology of the Upper Colorado River Basin,” submitted on July 2, 2012.

5. Laboratory Studies

The laboratory studies are targeted research projects designed to improve understanding of the ultimate fate and transport of selected chemicals, which may be components of hydraulic fracturing fluids or naturally occurring substances released from the subsurface during hydraulic fracturing. This chapter includes progress reports for the following projects:

5.1. Source Apportionment Studies

5.1.1. Relationship to the Study

The EPA is combining data collected from samples of wastewater treatment facility discharges and receiving waters with existing modeling programs to identify the proportion of hydraulic fracturing wastewater that may be contributing to contamination at downstream public water system intakes. This work has been designed to help inform the answer to the research question listed in Table 36.

Table 36. Secondary research questions addressed by the source apportionment research project.

Water Cycle Stage	Applicable Research Questions
Wastewater treatment and waste disposal	What are the potential impacts from surface water disposal of treated hydraulic fracturing wastewater on drinking water treatment facilities?

5.1.2. Project Introduction

The large national increase in hydraulic fracturing activity has generated large volumes of hydraulic fracturing wastewater for treatment and disposal or recycling. In some cases, states have allowed hydraulic fracturing wastewater to be treated by WWTFs with subsequent discharge to rivers. Most WWTFs are designed to filter and flocculate solids, as well as consume biodegradable organic species associated with human and some commercial waste. Very few facilities are designed to manage the organic and inorganic chemical compounds contained in hydraulic fracturing wastewater.

Public water supply intakes may be located in river systems downstream from WWTFs and a variety of other industrial and urban discharges, and it is critical to evaluate sources of contamination at those drinking water intakes. Elevated bromide and chloride concentrations are of particular concern in drinking water sources due to the propensity of bromides to react with organic compounds to produce THMs and other DBPs during drinking water treatment processes (Plewa and Wagner, 2009). High TDS levels—including bromide and chloride—have been detected in the Monongahela River in 2008 and the Youghiogheny River in 2010 (Lee, 2011; Ziemkiewicz, 2011). The source and effects of these elevated concentrations remains unclear.

This project's overall goal is to establish an approach whereby surface water samples may be evaluated to determine the extent to which hydraulic fracturing wastewaters (treated or untreated) may be present, and to distinguish whether any elevated bromide and chloride in those samples may be due to hydraulic fracturing or other activities. To accomplish this goal, the EPA is: (1) quantifying the inorganic chemical composition of discharges in two Pennsylvania river systems from WWTFs that accept and treat flowback and produced water, coal-fired utility boilers, acid mine drainage, stormwater runoff of roadway deicing material, and other industrial sources; (2) investigating the impacts of the discharges by simultaneously collecting multiple upstream and downstream samples to evaluate transport and dispersion of inorganic species; and (3) estimating the impact of these discharges on downstream bromide and chloride levels at PWS intakes using mathematical models.

5.1.3. Research Approach

The "Quality Assurance Project Plan for Hydraulic Fracturing Wastewater Source Apportionment" provides a detailed description of the research approach (US EPA, 2012q). Briefly, water samples are being collected at five locations on two river systems; each river has an existing WWTF that is currently accepting hydraulic fracturing wastewater for treatment. Source profiles for significant sources such as hydraulic fracturing wastewater, WWTF effluent, coal-fired utility boiler discharge, acid mine drainage, and stormwater runoff from roadway deicing will be developed from samples collected from these sources during the study. Computer models will then be used to compare data from these river systems to chemical and isotopic composition profiles obtained from potential sources.

Three two-week intensive sampling events were conducted to assess river conditions under different flow regimes: spring, summer, and fall 2012. As shown in Table 37, the amount of water in the river has historically been highest in the spring, resulting in the dilution of pollutants, and the summer and fall seasons typically have decreased stream flow, which may result in elevated concentrations due to less dilution (USGS, 2011a, b). USGS gauging stations near the WWTFs will be used to measure the flow rate during the three sampling periods.

Table 37. Historical average of monthly mean river flow and range of monthly means from 2006 through 2011 for two rivers in Pennsylvania where the EPA collects samples for source apportionment research (USGS, 2011a, b).

Month	Average of Monthly Mean River Flow from 2006 Through 2011 (cubic feet per second)		Range of Monthly Means from 2006 Through 2011 (cubic feet per second)	
	Allegheny River	Blacklick Creek	Allegheny River	Blacklick Creek
May	12,100	357	7,330–28,010	220.2–479.7
July	5,740	134	2,164–10,840	65.8–198.2
September	4,940	174	2,873–13,560	48.8–520.0

During each sampling event, automatic water samplers (Teledyne Isco, model 6712) at each site collect two samples daily—morning and afternoon—based on the PWS and WWTF operations schedule. The samples are stored in the sampler for one to four days, depending on the site visit schedule. Each river is sampled in five locations, as shown in Table 38. The first sampling device downstream of the WWTF is far enough downstream to allow for adequate mixing of the WWTF effluent and river water. The second downstream sampling device is between the first downstream sampling location and the closest PWS intake. The locations of the samplers downstream of the WWTF also take into account the presence of other significant sources, such as coal-fired utility boiler and acid mine drainage discharges, and allow for the evaluation of their impacts.

Table 38. Distance between sampling sites and wastewater treatment facilities on two rivers where the EPA collects samples for source apportionment research.

Site	Distance Between Sampling Sites (kilometers)	
	Allegheny River	Blacklick Creek
Site 1 (upstream)	-1.6	-1.2
Site 2 (wastewater treatment facility)	0	0
Site 3 (downstream)	12.2	2.7
Site 4 (downstream)	44.1	43.1
Site 5 (public water system intake)	52.3	88.6

5.1.3.1. Sample Analyses

The EPA will analyze the river samples and effluent samples according to existing EPA methods for the suite of elements and ions listed in Table 39. Inorganic ions (anions and cations) are being determined by ion chromatography. Inorganic elements are being determined using a combination of inductively coupled plasma optical emission spectroscopy for high-concentration elements and high-resolution magnetic sector field inductively coupled plasma mass spectrometry for low concentration elements. Additionally, the characteristic strontium (Sr) ratios ($^{87}Sr/^{86}Sr$; 0.7101–0.7121) in Marcellus Shale brines are extremely sensitive tracers, and elevated concentrations of readily water soluble strontium are present in the hydraulic fracturing wastewaters (Chapman et al., 2012). Isotope analyses for $^{87}Sr/^{86}Sr$ are being conducted on a subset (~20%) of samples by thermal ionization mass spectrometry to corroborate source apportionment modeling results.

Table 39. Inorganic analyses and respective instrumentation planned for source apportionment research. The EPA will analyze samples from two rivers and effluent discharged from wastewater treatment facilities located on each river. Instruments used for analysis include high-resolution magnetic sector field inductively coupled plasma mass spectrometry (HR-ICP-MS), ion chromatography (IC), inductively coupled plasma optical emission spectroscopy (ICP-OES), and thermal ionization mass spectroscopy (TIMS).

Element	Instrument Used
Ag*	HR-ICP-MS
Al*	ICP-OES
As*	HR-ICP-MS
B*	ICP-OES
Ba*	ICP-OES
Be*	HR-ICP-MS
Bi	HR-ICP-MS
Ca*	ICP-OES
Cd*	HR-ICP-MS
Ce	HR-ICP-MS
Co*	HR-ICP-MS
Cr*	HR-ICP-MS
Cs*	HR-ICP-MS
Cu*	ICP-OES, HR-ICP-MS
Fe*	ICP-OES, HR-ICP-MS
Gd	HR-ICP-MS
Ge	HR-ICP-MS
K*	ICP-OES
La	HR-ICP-MS
Li*	ICP-OES
Mg*	ICP-OES
Mn*	ICP-OES, HR-ICP-MS
Mo*	HR-ICP-MS
Na*	ICP-OES
Nd	HR-ICP-MS
Ni*	HR-ICP-MS
P*	ICP-OES
Pb*	HR-ICP-MS
Pd	HR-ICP-MS
Pt	HR-ICP-MS
Rb	HR-ICP-MS
S*	ICP-OES
Sb*	HR-ICP-MS
Sc	HR-ICP-MS
Se*	HR-ICP-MS
Si	ICP-OES
Sm	HR-ICP-MS
Sn	HR-ICP-MS
Sr*	HR-ICP-MS
Tb	HR-ICP-MS
Th	HR-ICP-MS
Ti*	ICP-OES
Tl*	HR-ICP-MS
U	HR-ICP-MS
V*	HR-ICP-MS
W	HR-ICP-MS
Y	HR-ICP-MS
Zn*	ICP-OES
Isotope Ratio	**Instrument Used**
^{87}Sr/^{86}Sr*	TIMS
Ion	**Instrument Used**
Ca^{2+} *	IC
K^{+} *	IC
Li^{+} *	IC
Mg^{2+} *	IC
NH_4^{+}	IC
Na^{+} *	IC
Br^{-} *	IC
Cl^{-} *	IC
F^{-} *	IC
NO_2^{-}	IC
NO_3^{2-}	IC
PO_4^{3-}	IC
SO_4^{2-} *	IC

* Chemicals detected in flowback and produced water. See Table A-3 in Appendix A.

Although the majority of the species that are being quantified in this study have been identified in flowback or produced water,[60] the species relationships and relative quantities of the species in

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[60] See Table A-3 in Appendix A.

other sources (i.e., coal-fired utility boiler and acid mine drainage discharges) will differ (Chapman et al., 2012). This will allow the models described below to distinguish among the contributions from each source type.

5.1.3.2. Source Apportionment Modeling

The EPA is using the data gathered through the analyses described above to support source apportionment modeling. This source apportionment effort will use peer-reviewed receptor models to identify and quantify the relative contribution of different contaminant source types to environmental samples.[61] In this case, river samples collected near PWS intakes are being evaluated to discern the contributing sources (e.g., hydraulic fracturing wastewater or acid mine drainage) of bromide and chloride to those stream waters. Receptor models require a comprehensive analysis of environmental samples to provide a sufficient number of constituents to identify and separate the impacts of different source types. Analysis of major ions and inorganic trace elements (Table 39) will accomplish the needs for robust receptor modeling. Contaminant sources may be distinguished by unique ranges of chemical species and their concentrations, and the models provide quantitative estimates of the source type contributions along with robust uncertainty estimates.

EPA-implemented models and commercial off-the-shelf software are being used to analyze the data from this particular study (e.g., Unmix, Positive Matrix Factorization, chemical mass balance). These models have previously been used to evaluate a wide range of environmental data for air, soil, and sediments (Cao et al., 2011; Pancras et al., 2011; Soonthornnonda and Christensen, 2008), and are now being used for emerging issues, such as potential impacts to drinking water from hydraulic fracturing.

5.1.4. Status and Preliminary Data

The EPA completed the two-week spring, summer, and fall intensive sampling periods beginning on May 16, July 20, and September 19, 2012, respectively. The EPA collected 206, 198, and 209 samples during the spring, summer, and fall intensives, consisting of WWTF-treated discharge, river samples, raw hydraulic fracturing wastewater, and acid mine drainage. The data quality objectives (US EPA, 2012q) of 80% valid sample collection were met for both the spring (>85%) and summer (>96%) measurement intensives. Preparation work for the extraction and filtration of spring intensive samples for inductively coupled plasma optical emission spectroscopy and high-resolution magnetic sector field inductively coupled plasma mass spectrometry is ongoing.

Table 40 shows the median discharge concentrations of chloride, bromide, sulfate, sodium, and conductivity in effluent from the two monitored WWTFs (prior to discharge and dilution in the rivers) during the spring sampling period; Table 40 also shows the conductivity of the effluent. Median chloride and sodium concentrations at Discharge A (Allegheny River) were almost 50% less than concentrations found at Discharge B (Blacklick Creek). High levels of sodium chloride (>20,000 milligrams per liter) are present in the discharge from both facilities (A and B). Bromide concentrations are roughly 35% lower at Discharge A than Discharge B.

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[61] The receptor model, Positive Matrix Factorization, was peer-reviewed in 2007 (version 1.1) and 2011 (version 4.2), and Unmix (version 5.0) underwent peer review in 2007.

Table 40. Median concentrations of selected chemicals and conductivity of effluent treated and discharged from two wastewater treatment facilities that accept oil and gas wastewater. Discharge A is located on the Allegheny River and Discharge B is located on Blacklick Creek, both in Pennsylvania. The EPA collected samples beginning on May 16, 2012.

Measurement	Median Concentration (milligrams per liter)	
	Discharge A	Discharge B
Chloride	49,875	97,963
Bromide	506	779
Sulfate	679	976
Sodium	20,756	38,394
Conductivity (millisiemens per centimeter)	110	168

The differences in the discharge concentrations are due to a combination of the treatment processes and unique regional chemical characteristics of oil and gas wastewater being treated at each of the facilities. Additionally, the discharge from the WWTFs is diluted into surface waters with very different median flows, with the USGS provisional median flows for the river sampling events reported as 15,158 and 2,531 cubic feet per second for the Allegheny River in spring (May 16–30, 2012) and summer (July 20–August 3, 2012), respectively (USGS, 2012a); and 642 and 35 cubic feet per second for Blacklick Creek in spring (May 17–31, 2012) and summer (July 21–August 4, 2012), respectively (USGS, 2012b). The relative impact of these seasonal dilution scenarios from the WWTF discharges will be determined with the measured chemical species.

5.1.5. Next Steps

Analysis of field and source samples will continue in order to obtain the necessary data for source apportionment modeling. Once sample analyses are completed, data will be used as input to the receptor models described above to identify and quantify the sources of chloride and bromide at PWS intakes.

5.1.6. Quality Assurance Summary

The "QAPP for Hydraulic Fracturing Wastewater Source Apportionment" was approved on April 17, 2012 (US EPA, 2012q). A TSA of the field sampling was conducted on May 3, 2012, by the designated EPA QA Manager. There were two findings and two observations. The agreed-upon corrective actions were reported in writing to the researchers and management on May 17, 2012, and have been implemented by the research team.

One finding identified the need to verbally "call back" measurement numbers between the sampler and scribe to confirm values when collecting short-term river measurements. The researchers instituted the verbal confirmation immediately in the field as suggested by the auditor. The second finding highlighted the need to accurately track the sample cooler temperature. A corrective action was implemented to improve the monitoring/recording of sample shipping cooler temperatures by ordering new National Institute of Standards and Technology traceable logging temperature loggers and keeping the loggers with the samples throughout the day in order to record accurate data of the temperatures at which the samples are stored and shipped. The new loggers were received and used in the field on May 8, 2012.

During the audit, it was observed that the custody seals may not have offered a level of security necessary for the project. The field team had already identified this potential problem and had ordered different tamper-resistant seals before the field trip. The new seals (NIK Public Safety Tamperguard brand evidence tape) have been in use since they were received on May 10, 2012. The second observation during the audit was the need to document the reasoning of changes performed to standard operating procedures. The researchers have documented all the changes performed as well as the logic and reasoning of the changes in the field laboratory notebooks. Most modifications to the procedures were related to procedural adjustments made as a result of the field site characteristics, which were slightly different from the field site characteristics used to field-test the procedures in North Carolina. The documents also included updates to points of contact, references, and added text for clarification (e.g., river velocity measurements). Revisions reflecting these changes have been made to the QAPP and four SOPs based on the spring intensive field experience and the TSA. The revised version of the QAPP and four SOPs were approved on June 29, 2012. These updates do not impact the original data quality objectives.

The researchers are following the QA procedures described in the QAPP and the standard operating procedures. In accordance to the QAPP, a TSA was performed on July 16 and 17, 2012, to evaluate laboratory operations. The designated EPA QA Manager reviewed the ion chromatography and high-resolution magnetic sector field inductively coupled plasma mass spectrometer analyses, data processing, storage, sample receiving and chain of custody procedures. The audit identified two observations and one best practice. One of the observations highlighted the need for a process that would ensure proper transcription of the data from the ion chromatography instrument to the report file. To reduce uncertainty and potential transcription errors, the analyst developed a process to export the data produced by the instrument in a text file instead of copying and pasting the data to a separate file. Another observation was the need to include performance evaluation samples in the analytical set. The performance evaluation samples will be analyzed in addition to the other quality controls already in place, which include blanks, duplicates, standard reference materials, and continuing calibration verification. The performance evaluation audit is being scheduled as specified in the QAPP. The blind performance evaluation samples will be analyzed with the regular samples and the data reported back to the QA Manager of the organization providing the blind performance evaluation samples. The best practice identified by the auditor was the tracking system, which uses a scanner and bar codes to track sampling bottles through the whole process: preparation, deployment to/from the field, sample analysis, and data reporting. The quality control (QC) procedures described in the QAPP have been followed in all instances. Besides the two TSAs performed and the performance evaluation audit, an ADQ is being coordinated by the designated EPA QA Manager. The source apportionment modeling will be described in a separate modeling QAPP. A TSA will be scheduled in 2013 for the modeling component of the study.

5.2. Wastewater Treatability Studies

5.2.1. Relationship to the Study

The EPA is conducting laboratory experiments to assess the efficacy of conventional wastewater treatment processes on selected chemicals found in hydraulic fracturing wastewater to provide data to inform the research question posed in Table 41. The results of the water treatability experiments also complement the surface water modeling research project (see Section 4.2).

Table 41. Secondary research questions addressed by the wastewater treatability laboratory studies.

Water Cycle Stage	Applicable Research Questions
Wastewater treatment and waste disposal	How effective are conventional POTWs and commercial treatment systems in removing organic and inorganic contaminants of concern in hydraulic fracturing wastewater?

5.2.2. Introduction

Hydraulic fracturing wastewater, including flowback and produced water, is generally disposed of through underground injection in Class II UIC wells or treatment by a WWTF followed by surface water discharge. A generalized diagram for the onsite flow of water is given in Figure 24. A US Department of Energy report provides a state-by-state description of costs, regulations, and treatment/disposal practices for hydraulic fracturing wastes, including wastewater (Puder and Veil, 2006).

Wastewater may be treated at a WWTF, such as a POTW or centralized waste treatment facility (CWT). This project focuses on the efficacy of treatment processes at POTWs and CWTs, since discharge of treated wastewater to surface waters provides an opportunity for chemicals found in the effluent to be transported to downstream PWS intakes. This project will also explore treatment processes used for reuse of hydraulic fracturing wastewater.

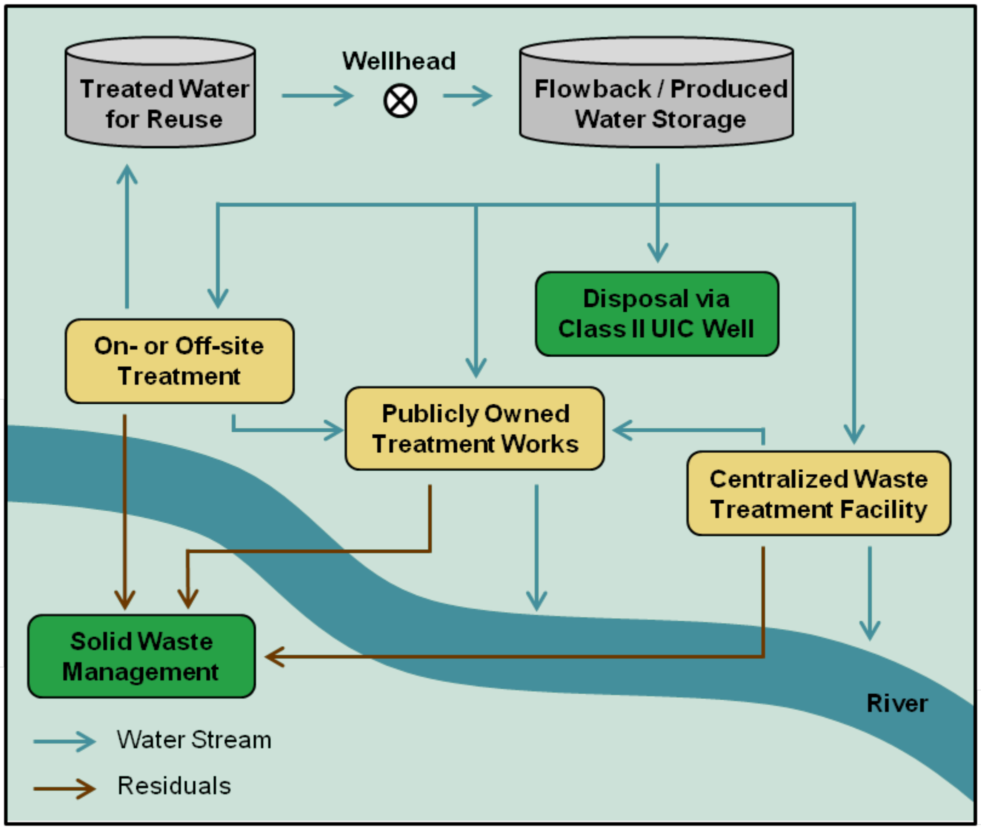

Figure 24. Hydraulic fracturing wastewater flow in unconventional oil and gas extraction. Flowback and produced water (collectively referred to as "hydraulic fracturing wastewater") is typically stored onsite prior to disposal or treatment. Hydraulic fracturing wastewater may be disposed of through Class II underground injection control (UIC) wells or through surface water discharge following treatment at wastewater treatment facilities, such as publicly owned treatment works or centralized waste treatment facilities. Wastewater may be treated on- or offsite prior to reuse in hydraulic fracturing fluids.

5.2.2.1. Publicly Owned Treatment Works Treatment Processes

Conventional POTW treatment processes are categorized into four groups: primary, secondary, tertiary, and advanced treatment. A generalized flow diagram is presented in Figure 25.

Primary treatment processes remove larger solids and wastewater constituents that either settle or float. These processes include screens, weirs, grit removal, and/or sedimentation and flotation (e.g., primary clarification). Secondary treatment processes typically remove biodegradable organics by using microbial processes (e.g., "bioreactor" in Figure 25) in fixed media (e.g., trickling filters) or in the water column (e.g., aeration basins). There is typically another settling stage in the secondary treatment process where suspended solids generated in the aeration basin are removed through settling ("secondary clarifier" in Figure 25). In some systems, tertiary or advanced treatment ("filter and UV disinfection" in Figure 25) may be applied as a polishing step to achieve a particular end use water quality (e.g., for reuse in irrigation).The POTW then discharges the treated effluent to surface water, if recycling or reuse is not intended. Solid residuals formed as byproducts of the treatment processes may contain metals, organics, and radionuclides that were removed from the water. Residuals are typically de-watered and disposed of via landfill, land application, or incineration.

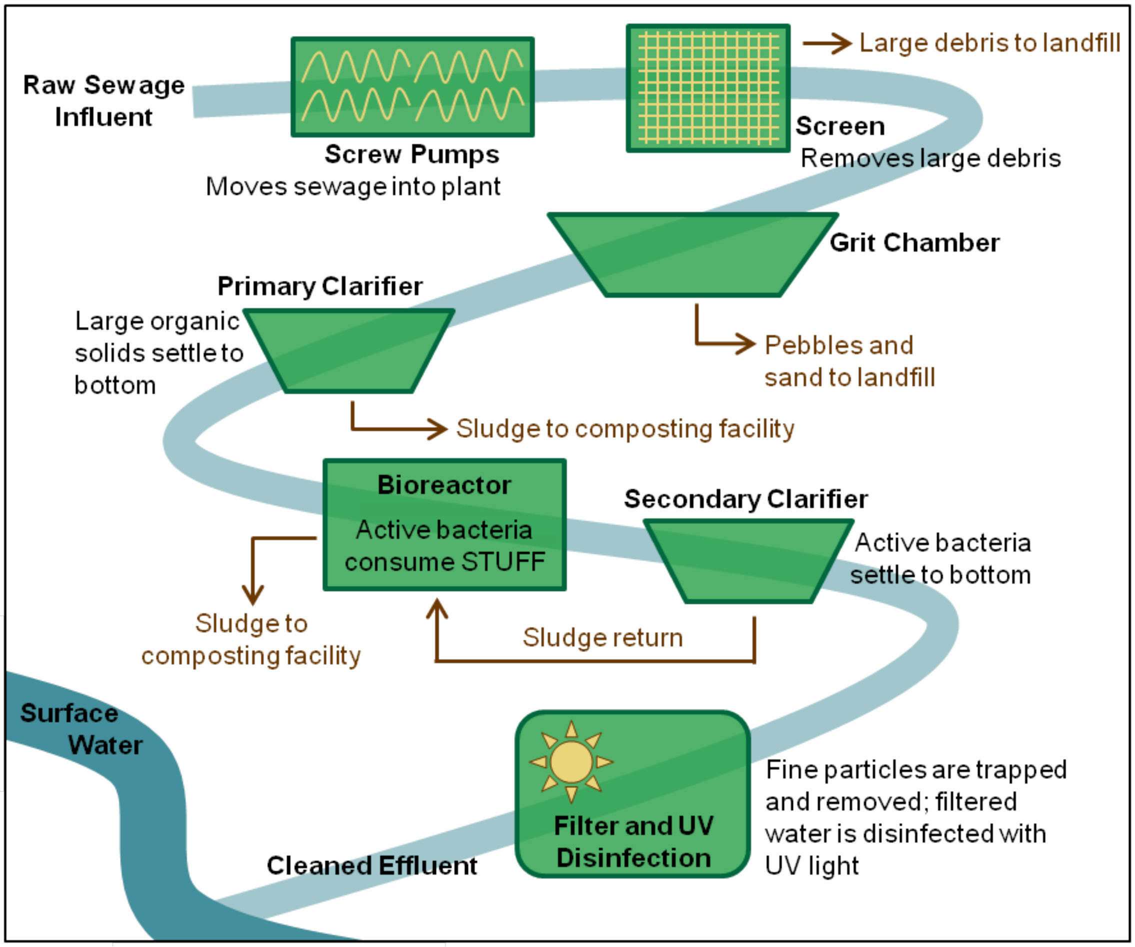

Figure 25. Generalized flow diagram for conventional publicly owned works treatment processes. See the text for descriptions of primary, secondary, tertiary, and advanced treatment processes.

The exact number of POTWs currently accepting hydraulic fracturing wastewater is not known. In Pennsylvania, where gas production from the Marcellus Shale is occurring, approximately 15 POTWs were accepting hydraulic fracturing wastewater until approximately May 2011. In April 2011, the Pennsylvania Department of Environmental Protection announced a request for Marcellus Shale natural gas drillers to voluntarily cease delivering their wastewater to the 15 POTWs. The state also promulgated regulations in November 2011 that established monthly average limits (500 milligrams per liter TDS, 250 milligrams per liter chloride, 10 milligrams per liter total barium, and 10 milligrams per liter total strontium) for new and expanded TDS discharges (PADEP, 2011). These limits do not apply to the 15 facilities identified in the voluntary request or other grandfathered treatment plants.

5.2.2.2. Commercial Waste Treatment Facility Processes

Commercial processes for treating hydraulic fracturing wastewater include crystallization (zero-liquid discharge), thermal distillation/evaporation, electrodialysis, reverse osmosis, ion exchange, and coagulation/flocculation followed by settling and/or filtration. Some treatment processes are better able to treat high-TDS waters, which is a common property of hydraulic fracturing wastewater. Thermal processes are energy-intensive, but are effective at treating high-TDS waters and may be able to treat hydraulic fracturing wastewater with zero liquid discharge, leaving only a residual salt. Electrodialysis and reverse osmosis may be feasible for treating lower-TDS wastewaters. These technologies are not able to treat high-TDS waters (>45,000 milligrams per liter) and may require pre-treatment (e.g., coagulation and filtration) to minimize membrane fouling.

Centralized waste treatment facilities can be used for pre-treatment prior to a POTW or, under an approved NPDES permit, can discharge directly to surface water (Figure 24). Commercial waste treatment processes will also result in some residual material that will require management and disposal.

5.2.2.3. Reuse

Gas producers are accelerating efforts to reuse and recycle hydraulic fracturing wastewater in some regions in order to decrease costs associated with procuring fresh water supplies, wastewater transportation, and offsite treatment and disposal. The EPA requested information on current wastewater management practices in the Marcellus Shale region from six oil and gas operators in May 2011.[62] Responses to the request for information indicated that reuse treatment technologies are similar, if not the same, to those used by WWTFs. Reuse technologies included direct reuse, onsite treatment (e.g., bag filtration, weir/settling tanks, third-party mobile treatment systems) and offsite treatment. Offsite treatment, in most instances, consisted of some form of stabilization, primary clarification, precipitation process, and secondary clarification and/or filtration. Specific details for offsite treatment methods were lacking as they are considered proprietary.

Innovation in coupling various treatment processes may help reduce wastewater volumes and fresh water consumed in hydraulic fracturing operations. A challenge facing reuse technology development is treating water onsite to an acceptable quality for reuse in subsequent hydraulic fracturing operations. Key water quality parameters to control include TDS, calcium, and hardness, all of which play a major role in scale formation in wells.

Recycling and reuse reduce the immediate need for treatment and disposal and water acquisition needs. There will likely be a need to treat and properly dispose of the final concentrated volumes of wastewater and residuals produced from treatment processes from a given area of operation, however.

5.2.3. Research Approach

The EPA is examining the fate and transport of chemicals through conventional POTW treatment processes and commercial chemical coagulation/settling processes. The objective of this work is to identify the partitioning of selected chemicals between solid and aqueous phases and to assess the biodegradation of organic constituents. In addition, microbial community health will be monitored in the reactors to identify the point where biological processes begin to fail. Contaminants that can pass through treatment processes and impact downstream PWS intakes will be identified.

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[62] Documents received pursuant to the request for information are available at http://www.epa.gov/region3/marcellus_shale/.

Fate and Transport of Selected Contaminants in Wastewater Treatment Processes. The EPA will initially analyze the fate and transport of selected hydraulic fracturing–related contaminants in wastewater treatment processes, including conventional processes (primary clarifier, aeration basin, secondary clarifier), commercial processes (chemical precipitation/filtration and evaporation/distillation), and water reuse processes (pretreatment and filtration). The initial phase of this work will involve bench-scale fate and transport studies in a primary clarifier followed by 10 liter chemostat reactors seeded with microbial organisms from POTW aeration basins. In bench-scale work relevant to CWTs, similar fate and transport studies will be performed in chemical coagulation, settling, and filtration processes.

A list of contaminants (Table 42) for initial treatability studies have been identified and are based on the list of hydraulic fracturing-related chemicals identified for initial analytical method development (Table 45 in Section 5.4). Table 42 may change as future information on toxicity and occurrence is gathered. In addition to monitoring the fate of the contaminants listed in Table 42 in treatment settings, impacts on conventional wastewater treatment efficiency will be monitored by examining changes in chemical oxygen demand, biological oxygen demand, and levels of nitrate, ammonia, phosphorus, oxygen, TDS, and total organic carbon in the aeration basin.

Table 42. Chemicals identified for initial studies on the adequacy of treatment of hydraulic fracturing wastewaters by conventional publicly owned treatment works, commercial treatment systems, and water reuse systems. Chemicals were identified from the list of chemicals needing analytical method development (Table 45).

Target Chemical	CASRN	Target Chemical	CASRN
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	Isopropanol*	67-63-0
Acrylamide	79-06-1	Magnesium*	7439-95-4
Arsenic*	7440-38-2	Manganese*	7439-96-5
Barium*	7440-39-3	Methanol*	67-56-1
Benzene*	71-43-2	Napthalene*	91-20-3
Benzyl chloride	100-44-7	Nonylphenol	68152-92-1
Boron*	7440-42-8	Nonylphenol ethoxylate	68412-54-4
Bromide*	24959-67-9	Octylphenol	1806-26-4
t-Butyl alcohol	75-65-0	Octylphenol ethoxylate	26636-32-8
Chromium*	7440-47-3	Potassium*	7440-09-7
Diethanolamine	111-42-2	Radium*	7440-14-4
Ethoxylated alcohols, C10–C14	66455-15-0	Sodium*	7440-23-5
Ethylbenzene*	100-41-4	Strontium*	7440-24-6
Ethylene glycol*	107-21-1	Thiourea	62-56-6
Formaldehyde	82115-62-6	Toluene*	108-88-3
Glutaraldehyde	111-30-8	Uranium	7440-61-1
Iron*	7439-89-6	Xylene*	1330-20-7

* Chemicals reported to be in flowback and produced water. See Table A-3 in Appendix A.

Characterization of Contaminants in Hydraulic Fracturing Wastewater Treatment Residuals. The EPA will examine the concentrations and chemical speciation of inorganic contaminants in treatment residuals. Residuals generated from the research described above will be analyzed for inorganic contaminant concentrations via EPA Method 3051A (Microwave Assisted Digestion) and inductively coupled argon plasma-optical emission spectrometry. Samples will also undergo analysis via X-ray absorption spectroscopy in order to assess oxidation state and chemical speciation of target contaminants. Organic contaminants will be analyzed via liquid or gas chromatography-mass spectrometry after accelerated solvent extraction of the solids.

5.2.4. Status and Preliminary Data

This research is currently in the planning stage.

5.2.5. Next Steps

Initial studies will focus on establishing thresholds of TDS tolerance in chemostat bioreactors. Once the basic salt thresholds have been established, selected chemicals from the 26R forms will be added to the salt stock solutions. Salt concentrations will be kept below the thresholds where effects on the biological processes were observed. Potentially biodegradable pollutants (e.g., organics) will be measured, and the EPA will attempt to identify breakdown products.

Constituents that are not biodegradable (e.g., elements and anions) will be tracked through the treatment process by analyzing system effluent using the appropriate EPA Methods and by analyzing residuals from the primary clarifier and the bioreactors. The results of these bench-scale studies will be applied to a pilot-scale system that would target compounds identified in bench-scale studies as being the most problematic due to their lack of degradation or removal in the treatment process.

For studies on commercial treatment systems using chemical addition/settling, the EPA plans to conduct jar tests that employ coagulants/flocculants at appropriate contact and settling times. The jar tests will be conducted at the bench-scale using actual hydraulic fracturing wastewater samples. The EPA will also attempt to mimic evaporative/distillation processes by using thermal treatment on actual hydraulic fracturing wastewater samples. Both the jar test samples and residuals from thermal treatment will be analyzed for the chemicals listed in Table 42. Elements in the residuals will also be characterized via X-ray diffraction and X-ray absorption microscopy.

5.2.6. Quality Assurance Summary

The initial QAPP, "Fate, Transport and Characterization of Contaminants in Hydraulic Fracturing Water in Wastewater Treatment Processes," was submitted on December 20, 2011, and approved in August 2012 (US EPA, 2012q).

Because project activities are still in an early stage, no TSA has been performed. A TSA will be performed once the project advances to the data collection stage.

As results are reported and raw data are provided from the laboratories, ADQs will be performed to verify that the quality requirements specified in the approved QAPP were met. Data will be qualified if necessary, based on these ADQs. The results of the ADQs will be reported with the summary of results in the final report.

5.3. Brominated Disinfection Byproduct Precursor Studies

The EPA is assessing the ability of hydraulic fracturing wastewater to contribute to DBP formation in drinking water treatment facilities, with a particular focus on the formation of brominated DBPs. This work will inform the following research question listed in Table 43 and is complemented by the analytical method development for DBPs (see Section 5.4).

Table 43. Secondary research questions potentially answered by studying brominated DBP formation from treated hydraulic fracturing wastewater.

Water Cycle Stage	Applicable Research Questions
Wastewater treatment and waste disposal	What are the potential impacts from surface water disposal of treated hydraulic fracturing wastewater on drinking water treatment facilities?

5.3.1. Introduction

Wastewaters from hydraulic fracturing processes typically contain high concentrations of TDS, including significant concentrations of chloride and bromide. These halogens are difficult to remove from wastewater; if discharged from treatment works, they can elevate chloride and bromide concentrations in drinking water sources. Upon chlorination at a drinking water treatment facility, chloride and bromide can react with naturally occurring organic matter (NOM) in the water and lead to the formation of DBPs. Because of their carcinogenicity and reproductive and developmental affects, the maximum contaminant levels (MCLs) of the DBPs bromate, chlorite, haloacetic acids, and total THMs in finished drinking water are regulated by the National Primary Drinking Water Regulations.[63] Table 44 summarizes the DBPs regulated and their corresponding MCLs.

Increased bromide concentrations in drinking water resources can lead to greater total THM concentrations on a mass basis and may make it difficult for some PWSs to meet the regulatory limits of total THM listing in Table 44 in finished drinking water. As a first step, this project is examining the formation of brominated THMs, including bromoform ($CHBr_3$), dibromochloromethane ($CHClBr_2$), and bromodichloromethane ($CHCl_2Br$), during drinking water treatment processes. The formation of haloacetic acids (HAAs) and nitrosamines during drinking water treatment processes is also being investigated.[64]

Reactions of brominated biocides used in hydraulic fracturing operations with typical drinking water disinfectants associated with chlorination or chloramination are also being explored.[65] Brominated biocides are often used in fracturing fluids to minimize biofilm growth. The objective of this work is to assess the contribution, if any, to brominated DBP formation and identify degradation pathways for brominated biocides.

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[63] Authorized by the Safe Drinking Water Act.

[64] Nitrosamines are byproducts of drinking water disinfection, typically chloramination, and currently unregulated by the EPA. Data collected from the second Unregulated Contaminant Monitoring Rule indicate that nitrosamines are frequently being found in PWSs. Nitrosamines are potentially carcinogenic.

[65] Chlorination and chloramination are common disinfection processes used for drinking water.

Table 44. Disinfection byproducts regulated by the National Primary Drinking Water Regulations.

Disinfection Byproduct	Maximum Contaminant Level Goal* (milligrams per liter)	Maximum Contaminant Level[†] (milligrams per liter)
Total Trihalomethanes		
Bromodichloromethane	Zero	0.080 as an annual average (sum of the concentrations of all four trihalomethanes)
Bromoform	Zero	
Dibromochloromethane	0.060	
Chloroform	0.070	
Haloacetic Acids		
Dichloroacetic acid	Zero	0.060 as an annual average (sum of the concentrations of all five haloacetic acids)
Trichloroacetic acid	0.020	
Monochloroacetic acid	0.070	
Bromoacetic acid	Regulated with this group but has no MCL goal	
Dibromoacetic acid	Regulated with this group but has no MCL goal	
Bromate	Zero	0.010 as an annual average
Chlorite	0.80	1.0

* A maximum contaminant level goal is the non-enforceable concentration of a contaminant in drinking water below which there is no known or expected risk to health; they are established under the Safe Drinking Water Act.

[†] A maximum contaminant level (MCL) is an enforceable standard corresponding to the highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCL goals as feasible using the best available treatment technology and taking cost into consideration. MCLs are set under the Safe Drinking Water Act and apply only to water delivered by public water supplies (water supplies that serve 15 or more service connections or regularly serves an average of 25 or more people daily at least 60 days out of the year) (40 CFR 141.2).

It is important to note that hydraulic fracturing wastewater can potentially contain other contaminants in significant concentrations that could affect human health. The EPA identified the impacts of elevated bromide and chloride levels in surface water from hydraulic fracturing wastewater discharge as a priority for protection of public water supplies. This project will ultimately provide PWSs with information on the potential for brominated DBP formation in surface waters receiving discharges from WWTFs.

5.3.2. Research Approach

This research will (1) analyze and characterize hydraulic fracturing wastewater for presence of halides, (2) evaluate the effects of high TDS upon chlorination of surface water receiving discharges of treated hydraulic fracturing wastewater, and (3) examine the reactions of brominated biocides subjected to chlorination during drinking water treatment. Selected analytes for characterizing hydraulic fracturing wastewater include nitrosamines and the halide anions chloride, bromide, and iodide—ions that are the likeliest to form DBPs (Richardson, 2003), including THMs and HAAs.

Hydraulic fracturing wastewater samples have been obtained from several sources in Pennsylvania. The quantification of background concentrations of halides in the samples follows EPA Method 300.1 (rev. 1) and the modified version of the method using mass spectrometry detection for bromide and bromate (discussed in Section 5.4). The samples are also being analyzed for the presence of DBPs, including THMs (EPA Method 551.1), HAAs (EPA Method 552.1), and N-nitrosamines (EPA Method 521), as well as elemental composition, anion concentration, TDS, and total organic carbon.

Three treatments are being applied to high-TDS wastewater samples: (1) samples will be blended with deionized water at rates that mimic discharge into varying flow rates of receiving water in order to account for dilution effects; (2) samples will be blended with deionized water with NOM additions at concentration ranges typically found in surface waters; and (3) samples will be blended with actual surface water samples from rivers that receive treated hydraulic fracturing wastewater discharges. All samples will be subjected to formation potential experiments in the presence of typical drinking water disinfectants associated with chlorination or chloramination. Formation potential measures will be obtained separately for THMs, HAAs, and nitrosamines. Disinfection byproduct formation in surface water samples will be compared with DBP formation in deionized water as well as deionized water fortified with several NOM isolates from different water sources in order to examine the effects of different NOM on DBP formation.[66]

The brominated biocides 2,2-dibromo-3-nitropropionamide and 2-bromo-2-nitrol-1,3-propanediol, employed in hydraulic fracturing processes, are being subjected to chlorination conditions encountered during drinking water treatment. These experiments should provide insight on the potential formation of brominated THMs from brominated biocides. Effects of chlorination on the brominated biocides are also being monitored.

5.3.3. Status and Preliminary Data

Work has begun on total THM formation studies to identify potential problems with analysis (EPA Method 551.1) due to the high TDS levels typical in hydraulic fracturing wastewater. Wastewater influent and effluent samples were obtained from researchers involved in the source apportionment studies (Section 5.1) at two CWTs in Pennsylvania that are currently accepting hydraulic fracturing wastewater for treatment via chemical addition and settling. For this preliminary research, samples were diluted 1:100 with deionized water and equilibrated with sodium hypochlorite until a 2 milligrams per liter concentration of sodium hypochlorite was achieved (a typical disinfectant concentration for finished water from a PWS). The samples are being analyzed for pH, metals, TDS, total suspended solids, total organic content, and selected anions.

Efforts to identify and quantify the parent brominated biocides using liquid chromatography/mass spectrometry methods have been unsuccessful to date, possibly due to poor ionization of the brominated molecules. The biocide samples subject to chlorination have been prepared for analysis of THMs.

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[66] The concentration, chemical composition, and reactivity of NOM varies by geographic location due to factors such as presence and type of vegetation, physical and chemical properties of the surrounding soil and water, biological activity, and human activity among many others.

5.3.4. Next Steps

When the preliminary work on potential analytical effects from high TDS on total THM recovery is complete, a series of experiments to assess the potential formation of DBPs during chlorination will be run on the following samples:

- Deionized water
- Deionized water, varying concentrations of NOM
- Deionized water plus TDS
- Deionized water plus TDS and NOM
- Hydraulic fracturing wastewater

This series of samples will allow THM formation comparisons between hydraulic fracturing wastewater samples and less complex matrices. Dilutions will be made on the samples based on effluent discharge rates for existing WWTFs and receiving water flow rates. The samples will undergo chlorination and be sub-sampled over time (e.g., 0 to 120 minutes). Chloride to bromide ratios will be set at 50:1, 100:1, and 150:1 to encompass the range of conditions that may be found in surface waters impacted by varying concentrations of chloride and bromide. The sub-samples will be analyzed for individual THMs and formation kinetics will be determined. The EPA anticipates obtaining data for the formation of HAAs and nitrosamines, though THMs are the priority at this time.

5.3.5. Quality Assurance Summary

The initial QAPP, "Formation of Disinfection By-Products from Hydraulic Fracturing Fluids," was submitted on June 28, 2011, and approved on October 5, 2011 (US EPA, 2011h). On June 7, 2012, an addendum was submitted and approved on June 28, 2012; this provided more details on modifications to EPA Method 300.1 for optimizing bromide/bromate recoveries in high-salt matrices. There are no deviations from existing QAPPs to report at this time.

A TSA was performed on March 15, 2012, for this research project. Five findings were observed, related to improved communication, project documentation, sample storage, and QA/QC checks. Recommended corrective actions were accepted to address the findings. Since the TSA was performed before data generation activities, no impact on future reported results is expected. It is anticipated that a second TSA will be performed as the project progresses.

As raw data are provided from the laboratories and results are reported, ADQs will be performed to verify that the quality requirements specified in the approved QAPP have been met. Data will be qualified if necessary based on these ADQs. Audits of data quality are scheduled for the first quarter of 2013 (none have been performed yet). The results of these ADQs will be reported with the summary of results in the final report.

5.4. Analytical Method Development

5.4.1. Relationship to the Study

Sample analysis is an integral part of the EPA's *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (US EPA, 2011e) and is clearly specified in research plans being carried out for the study's retrospective case studies, prospective case studies, and laboratory studies. The EPA requires robust analytical methods to accurately and precisely determine the composition of hydraulic fracturing-related chemicals in ground and surface water, flowback and produced water, and treated wastewater.

5.4.2. Project Introduction

Analytical methods enable accurate and precise measurement of the presence and quantities of different chemicals in various matrices. Since the quantification of the presence or absence of hydraulic fracturing-related chemicals will likely have substantial implications for the conclusions of the study, it is important that robust analytical methods exist for chemicals of interest.

In many cases, standard EPA methods that have been designed for a specific matrix or set of matrices can be used for this study. Standard EPA methods are peer-reviewed and officially promulgated methods that are used under different EPA regulatory programs. For example, EPA Method 551.1 is being used to detect THMs as part of the Br-DBP research project (see Section 5.3) and EPA Method 8015D is being used to detect diesel range organics in ground and surface water samples collected as part of the retrospective case studies (see Chapter 7).

In other cases, standard EPA methods are nonexistent for a chemical of interest. In these situations, methods published in the peer-reviewed literature or developed by consensus standard organizations (e.g., the American Society for Testing and Materials, or ASTM) are used. However, these methods are rarely developed for or tested within matrices associated with the hydraulic fracturing process. In rare, but existing cases, where no documented methods exist, researchers generally develop their own methods for determining the concentrations of certain chemicals of interest. For these latter two situations, the analytical methods chosen must undergo rigorous testing, verification, and potential validation to ensure that the data generated they generate are of known and high quality. The EPA has identified selected chemicals found in hydraulic fracturing fluids and wastewater for the development and verification of analytical methods.

5.4.3. Research Approach

5.4.3.1. Chemical Selection

Hydraulic fracturing-related chemicals include chemicals used in the injected fracturing fluid, chemicals found in flowback and produced water, and chemicals resulting from the treatment of hydraulic fracturing wastewater (e.g., chlorination or bromination at wastewater treatment facilities). Some of these chemicals are present due to the mobilization of naturally occurring chemicals within the geologic formations or through the degradation or reaction of the injected chemicals in the different environments (i.e., subsurface, surface and wastewater). The EPA has identified over 1,000 chemicals that are reported to be used in fracturing fluids or found in hydraulic fracturing wastewaters (see Appendix A); these range from the inert and innocuous, such as sand and water, to reactive and toxic chemicals, like alkylphenols and radionuclides.

To help choose chemicals for analytical method testing, a group of EPA researchers and analytical laboratory chemists discussed the factors most important to their research needs and to the overall study. The following criteria were developed to identify a subset of the chemicals listed in Appendix A for initial analytical method testing activities:

- Frequency of occurrence[67] in hydraulic fracturing fluids and wastewater
- Toxicity[68]
- Mobility in the environment (expected fate and transport)
- Availability of instrumentation/detection systems for the chemical

Table 45 lists the chemicals selected for analytical method testing and development. It includes 14 different classes of chemicals, 51 specifically identified elements or compounds, six groups of compounds (e.g., ethoxylated alcohols and light petroleum distillates), and two related physical properties (gross α and gross β analyses associated with radionuclides). The EPA will continually review Table 45 and add new chemicals as needed.

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[67] Occurrence information was gathered from the US House of Representatives report *Chemicals Used in Hydraulic Fracturing* (2011) (USHR, 2011)and Colborn et al. (2011). Chemicals with high frequencies were considered for inclusion. However, some high-frequency chemicals were ultimately not included in the EPA's priority list of chemicals of interest. For example, while silica or silicon dioxide is often near the top of lists in terms of frequency of occurrence, this likely refers to the sand that is used as a proppant during the hydraulic fracturing process. Additionally, certain chemicals, such as hydrogen chloride or sulfuric acid, no longer exist as the initial compounds once dissolved in water and often react with other compounds. As a result, these chemicals, and others, were not added to the list.

[68] Colborn et al. (2011) provided toxicity information compiled from MSDS from industry and government agencies and compared the chemicals in their list with toxic chemical databases, such as TOXNET and the Hazardous Substances Database.

Table 45. Chemicals identified for analytical method testing activities. Selection criteria for the chemicals included, but were not limited to, frequency of occurrence in fracturing fluids and wastewater, toxicity, environmental mobility, and availability of detection systems for the chemical.

Chemical Class	Chemical Name(s)	CASRN	Purpose in Hydraulic Fracturing	Reason Selected
Alcohols	Propargyl alcohol	107-19-7	Corrosion inhibitor	Toxicity, frequency of use
	Methanol	67-56-1		
	Isopropanol	67-63-0		
	t-Butyl alcohol	75-65-0	Byproduct of t-butyl hydroperoxide	
Aldehydes	Glutaraldehyde	111-30-8	Biocide	Toxicity, frequency of use
	Formaldehyde	50-00-0	Biocide	
Alkylphenols	Octylphenol	27193-28-8	Surfactant	Toxicity, frequency of use
	Nonylphenol	84852-15-3		
Alkylphenol ethoxylates	Octylphenol ethoxylate	9036-19-5	Surfactant	Frequency of use
	Nonylphenol ethoxylate	26027-38-3		
Amides	Thiourea	62-56-6	Corrosion inhibitor	Toxicity
	Acrylamide	79-06-1	Friction reducer	Toxicity, frequency of use, requested by EPA researchers
	2,2-Dibromo-3-nitrilopropionamide	10222-01-2	Biocide	
Amines (alcohol)	Diethanolamine	111-42-2	Foaming agent	Frequency of use
Aromatic hydrocarbons	BTEX, naphthalene, benzyl chloride, light petroleum hydrocarbons		Gelling agents, solvents	Toxicity, frequency of use, requested by EPA researchers
Carbohydrates	Polysaccharides		Byproduct	Requested by EPA researchers
Disinfection byproducts	Trihalomethanes, haloacetic acids, N-nitrosamines*		Byproduct	Toxicity
Ethoxylated alcohols	Ethoxylated alcohols, C8–10 and C12–18	68954-94-9	Surfactant	Frequency of use

Table continued on next page

Table continued from previous page

Chemical Class	Chemical Name(s)	CASRN	Purpose in Hydraulic Fracturing	Reason Selected
Glycols	Ethylene glycol	107-21-1	Crosslinker, breaker, scale inhibitor	Frequency of use
	Diethylene glycol	111-46-6		
	Triethylene glycol	112-27-6		
	Tetraethylene glycol	112-60-7		
	2-Methoxyethanol†	109-86-4	Foaming agent	
	2-Butoxyethanol†	111-76-2		
Halogens	Chloride	16887-00-6	Brine carrier fluid, breaker	Frequency of use
Inorganics	Barium	7440-39-3	Mobilized during hydraulic fracturing	Toxicity, frequency of use of potassium and sodium salts, mobilization of naturally occurring ions
	Strontium	7440-24-6	Mobilized during hydraulic fracturing	
	Boron	7440-42-8	Crosslinker	
	Sodium	7440-23-5	Brine carrier fluid, breaker	
	Potassium	7440-09-7	Brine carrier fluid	
Radionuclides	Gross α		Mobilized during hydraulic fracturing	Toxicity, mobilization of naturally occurring ions
	Gross β			
	Radium	13982-63-3		
	Uranium	7440-61-1		
	Thorium	7440-29-1		

* See Section 5.3.

† These compounds are chemically similar to glycols and are analyzed using the same methods.

5.4.3.2. *Analytical Method Testing and Development*

Method Development. The EPA's process for analytical method development is shown in Figure 26. In the first step, an existing base method is identified for the specific chemical(s) of interest in a given matrix. Base methods may include promulgated, standard methods or, if no standard methods are available, methods existing in peer-reviewed literature or developed through a consensus standard organization.

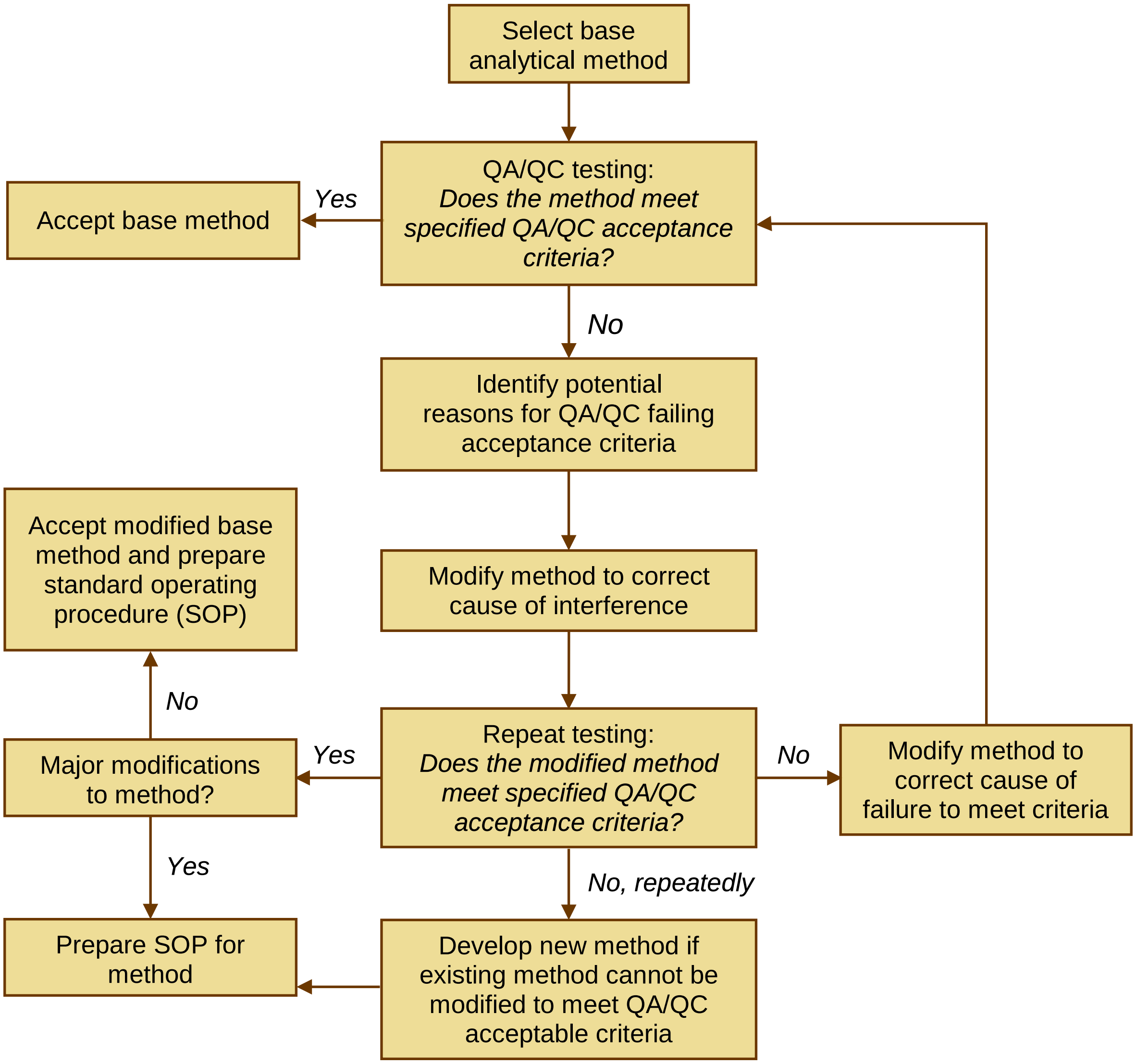

Figure 26. Flow diagram of the EPA's process leading to the development of modified or new analytical methods.

Analytical methods may exist for specific chemicals or for a general class of chemicals (e.g., alcohols). Table 46 lists the base methods identified for the 14 chemical classes shown in Table 45.

Table 46. Existing standard methods for analysis of selected hydraulic fracturing-related chemicals listed in Table 45. The EPA will analyze samples using existing methods to determine if the procedure meets the quality assurance criteria for the current study.

Chemical Class	Standard Method*
Alcohols	SW-846 Methods 5030 and 8260C
Aldehydes	SW-846 Method 8315
Alkylphenols	No standard method
Alkylphenol ethoxylates	No standard method
Amides	SW-846 Methods 8032A
Amines (alcohols)	No standard method
Aromatic hydrocarbons	SW-846 Methods 5030 and 8260C
Carbohydrates	No standard method
Disinfection byproducts	DWA Methods 521, 551, and 552
Ethoxylated alcohols	ASTM D7485-09
Glycols	Region 3 Draft Standard Operating Procedure
Halogens	SW-846 Method 9056A
Inorganic elements	SW-846 Methods 3015A and 6020A
Radionuclides	SW-846 Method 9310

* DWA methods can be found at http://water.epa.gov/scitech/methods/cwa/index.cfm. SW-846 Methods can be found at http://www.epa.gov/epawaste/hazard/testmethods/sw846/online/index.htm.

Once a candidate base method is selected,[69] an initial QA/QC round of testing is conducted. Testing occurs first with spiked laboratory water samples to familiarize the analyst with the method procedure, eliminate any potential matrix interferences, and determine various QA/QC control parameters, such as sensitivity, bias, precision, spike recovery, and analytical carry-over potential (sample cross-contamination). The results from the initial QA/QC testing are examined to determine if they meet the acceptance criteria specified in the QAPP (US EPA, 2011g) and thus are sufficient to meet the needs of the research study. Some of the key QA/QC samples examined include:

- Standard and certified reference materials (where available) for bias
- Matrix and surrogate spikes for bias (when reference materials are not available) and matrix interferences
- Replicates for precision
- Blanks for analytical carry-over

If an acceptance criterion for any of the QA/QC samples is not met, the sample is typically re-run to ensure that the result is not a random event. If an acceptance criterion is repeatedly not met, a

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[69] Additional information on selecting a base method can be found in the QAPP, "Quality Assurance Project Plan for the Chemical Characterization of Select Constituents Relevant to Hydraulic Fracturing," found at http://www.epa.gov/hfstudy/qapps.html.

systematic problem is indicated, and method modification is undertaken to help reduce or eliminate the problem.

The method modification process can take many forms, depending on the specific circumstances, and may include changing sample preparation and cleanup techniques, solvents, filters, gas flow rates, temperature regimes, injector volumes, chromatographic columns, analytical detectors, etc. Once the method modification process is complete, the analysis is repeated as described above using spiked laboratory water samples. If the new QA/QC sample results meet the acceptance criterion, the method modification is deemed to have been successful for that matrix and an updated SOP is prepared. Additional testing in more complex water matrices will continue, if appropriate.

If testing and modification of the identified base method fails to accurately and precisely quantify the chemical of interest and/or fails to have the sensitivity required by the research program, the EPA may undertake new method development activities.

Method Verification. Method verification determines the robustness of successfully tested and modified analytical methods. This involves the preparation of multiple blind spiked samples (i.e., samples whose concentrations are only known to the sample preparer) by an independent chemist (i.e., one not associated with developing the method under testing and verification) and the submission of the samples to at least three other analytical laboratories participating in the verification process. Results from the method verification process can lead to either the acceptance of the method or re-evaluation and further testing of the method (US EPA, 1995).

Method Validation. The final possible step in analytical method testing and development is method validation. Method validation involves large, multi-laboratory, round robin studies and is generally conducted by the EPA program offices responsible for the publication and promulgation of standard EPA methods.

5.4.4. Status, Preliminary Data, and Next Steps

Method development, testing, and verification are being conducted according to the procedures outlined in two QAPPs: "Quality Assurance Project Plan for the Chemical Characterization of Select Constituents Relevant to Hydraulic Fracturing" (US EPA, 2011g) and "Quality Assurance Project Plan for the Inter-Laboratory Verification and Validation of Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, 2-Butoxyethanol and 2-Methoxyethanol in Ground and Surface Waters by Liquid Chromatography/Tandem Mass Spectrometry" (US EPA, 2012r).

5.4.4.1. Glycols and Related Compounds

Glycols (diethylene glycol, triethylene glycol, and tetraethylene glycol) and the chemically related compounds 2-butoxyethanol and 2-methoxyethanol are frequently used in hydraulic fracturing fluids and not naturally found in ground water. Thus, they may serve as reliable indicators of contamination of ground water from hydraulic fracturing activities. EPA Method 8015b is the gas chromatography-flame ionization detector method typically used to analyze for glycols; however, the sensitivity is not sufficient for the low-level analysis required for this project. Therefore, the EPA's Region 3 Environmental Science Center developed a method for the determination and quantification of these compounds using liquid chromatography-tandem mass spectrometry. The method is based on ASTM D7731-11e1 and EPA SW-846 Method 8321. The EPA is currently verifying this method to determine its efficacy in identifying and quantifying these compounds in drinking water and other water matrices associated with the hydraulic fracturing process.

5.4.4.2. Acrylamide

Acrylamide is often used as a friction reducer in injected hydraulic fracturing fluids (GWPC, 2012b). EPA SW-846 Methods 8316 and 8032A are both suitable methods for the analysis of acrylamide. Method 8316 involves analysis by high-performance liquid chromatography with ultraviolet detector at 195 nanometers, with a detection level of 10 micrograms per liter. This short wavelength, however, is not very selective for acrylamide (i.e., interferences are likely), and the sensitivity is not adequate for measurements in water. Method 8032A involves the bromination of acrylamide, followed by gas chromatography-mass spectrometry analysis. This method is much more selective for acrylamide, and detection limits are much lower (0.03 micrograms per liter). However, in complex matrices (e.g., hydraulic fracturing wastewater), the accuracy and precision of acrylamide analysis may be limited by poor extraction efficiency and matrix interference.

To avoid reactions with other compounds present in environmental matrices and to lower the detection limit, the EPA is developing a new analytical method for the determination of acrylamide at very low levels in water containing a variety of additives. The method currently under development involves solid phase extraction with activated carbon followed by quantitation by liquid chromatography-tandem mass spectrometry using an ion exclusion column. The EPA has begun the multi-laboratory verification of the method.

5.4.4.3. Ethoxylated Alcohols

Surfactants are often added to hydraulic fracturing fluids to decrease liquid surface tension and improve fluid passage through pipes. Most of the surfactants used are alcohols or some derivative of an ethoxylated compound, typically ethoxylated alcohols. Many ethoxylated alcohols and ethoxylated alkylphenols biodegrade in the environment, but often the degradation byproducts are toxic (e.g., nonylphenol, a degradation product of nonylphenol ethoxylate, is an endocrine disrupting compound) (Talmage, 1994). No standard method currently exists for the determination of ethoxylated alcohols; therefore, the EPA is developing a quantitative method for ethoxylated alcohols. ASTM Method D 7458-09 and USGS Method Number O1433-01 were used as starting points for this method development effort; both of these methods involve solid-phase extraction followed by liquid chromatography-tandem mass spectrometry quantitation. These methods both allow the analysis of nonylphenol diethoxylate and alkylphenols, but there are currently no standard methods for the analysis of the full range of nonylphenol ethoxylate oligomers (EO_3–EO_{20}) or alcohol ethoxylate oligomers ($C_{12–15}EO_x$, where $x = 2–20$). This method SOP is being prepared and will be followed by method verification.

5.4.4.4. Disinfection Byproducts

Flowback and produced water can contain high levels of TDS, which may include bromide and chloride (US EPA, 2012d). In some cases, treatment of flowback and produced water occurs at WWTFs, which may be unable to effectively remove bromide and chloride from hydraulic fracturing wastewater before discharge. The presence of bromide ions in source waters undergoing chlorination disinfection may lead to the formation of brominated DBPs—including bromate, THMs, and HAAs—upon reaction with natural organic material (Richardson, 2003). Brominated DBPs are considerably more toxic than corresponding chlorinated DBPs (Plewa et al., 2004; Richardson et al., 2007) and have higher molecular weight. Therefore, on an equal molar basis, brominated DBPs will have a greater concentration by weight than chlorinated DBPs, hence leading to a greater likelihood of exceeding the total THM and HAA MCLs that are stipulated in weight concentrations (0.080 and 0.060 milligrams per liter, respectively). Accordingly, it is important to assess and quantify the effects of flowback and produced water on DBP generation (see Section 5.3).

Analytical methods for the measurement of bromide and bromate in elevated TDS matrices are currently being developed. EPA Method 300.1 is being modified to use a mass spectrometer rather that an electroconductivity detector, which is unable to detect bromide and bromate in the presence high anion concentrations (SO_4^{2-}, NO_2^-, NO_3^-, F^-, Cl^-). The mass spectrometer allows selected ion monitoring specifically for the two natural stable isotopes of bromine (^{79}Br and ^{81}Br), with minimal interference from other anions in the high-salt matrix. Interference of the bromide and bromate response in the mass spectrometer are being assessed by comparing instrument responses to solutions of bromide and bromate in deionized water with selected anions over a range of ratios typically encountered in hydraulic fracturing wastewater samples (US EPA, 2012d). Interference concentration thresholds are being established, and a suitable sample dilution method is being developed for the quantification of bromide and bromate in actual hydraulic fracturing wastewater samples. Method detection limits and lowest concentration minimum reporting levels are being calculated for bromide and bromate in high-salt matrices according to EPA protocols (US EPA, 2010h).

5.4.4.5. *Radionuclides*

Gross α and β analyses measure the radioactivity associated with gross α and gross β particles that are released during the natural decay of radioactive elements, such as uranium, thorium, and radium. Gross α and β analyses are typically used to screen hydraulic fracturing wastewater in order to assess gross levels of radioactivity. This information can be used to identify waters needing radionuclide-specific characterization. The TDS and organic content characteristic of hydraulic fracturing wastewater, however, interferes with currently accepted methods for gross α and β analyses. The QAPP for testing and developing gross α and β analytical methods is in development, and, after it is approved, work will begin.

5.4.4.6. *Inorganic Chemicals*

In addition to the potential mobilization of naturally occurring radioactive elements, hydraulic fracturing may also release other elements from the fractured shales, tight sands, and coalbeds, notably heavy metals such as barium and strontium. Inorganic compounds may also be added to hydraulic fracturing fluids to perform various functions (e.g., cross-linkers using borate salts, brine carrier fluids using potassium chloride, and pH-adjusting agents using sodium carbonates) (US EPA, 2011e). Due to the injection or release of naturally occurring metals in unknown quantities, it is essential that analytical methods for the determination of inorganic elements in waters associated with hydraulic fracturing be robust and free from interferences that may mask true concentrations.

The EPA SW-846 Method 6010, employing inductively coupled plasma-optical emission spectrometry, will be used as a base method for major elements while SW-846 Method 6020 based on inductively coupled plasma-mass spectrometry will be used as a base method for trace elements.[70] These methods will be tested and potentially modified for detection of major and trace elements in hydraulic fracturing wastewater.

5.4.5. Quality Assurance Summary

Three QAPPs have been prepared for the analytical method testing research program. The first QAPP, "Quality Assurance Project Plan for the Chemical Characterization of Select Constituents Relevant to Hydraulic Fracturing" (US EPA, 2011g), is the broad general QAPP for the methods development research project. The QAPP was approved on September 1, 2011. In order to maintain high QA standards and practices throughout the project, a surveillance audit was performed on November 15, 2011. The purpose of the surveillance audit was to examine the processes associated with the in-house extraction of ethoxylated alcohols. Three recommendations were identified and have been accepted.

The second QAPP, "Formation of Disinfection By-Products from Hydraulic Fracturing Fluid Constituents Quality Assurance Project Plan," (US EPA, 2011h), provides details on modifications to EPA Method 300.1 for optimizing bromide/bromate recoveries in high-salt matrices. The QAPP was approved on October 5, 2011, and the addendum for bromide/bromate analytic method development was approved on June 28, 2012. There are no deviations from existing QAPPs to report at this time. A surveillance audit was performed in March 2011 before the analytical method addendum (June 28, 2012); therefore, the analytical method development for bromide/bromate has not yet been audited.

The third QAPP, "Quality Assurance Project Plan for the Inter-Laboratory Verification and Validation of Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, 2-Butoxyethanol and 2-Methoxyethanol in Ground and Surface Waters by Liquid Chromatography/Tandem Mass Spectrometry" (US EPA, 2012r), was prepared specifically for the verification of the EPA Region 3 SOP. The QAPP was approved on April 4, 2012. Since then, two surveillance audits and two internal TSAs have been performed, specifically looking at procedures related to glycol standard preparation and analysis. The two surveillance audits resulted in one case of potentially mislabeled samples during stock solution preparation. The potential mislabeling was already identified and documented by the researchers involved and corrective action taken. The designated EPA QA Manager found the methods in use satisfactory and further recommendations for improving the QA process were unnecessary. The internal TSAs also yielded no acts, errors, or omissions that would have a significant adverse impact on the quality of the final product.

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[70] Major and trace elements are identified in the retrospective case study QAPPs found at http://www.epa.gov/hfstudy/qapps.html.

6. Toxicity Assessment

Throughout the hydraulic fracturing water lifecycle, routes exist through which fracturing fluids and/or naturally occurring substances could be introduced into drinking water resources. To support future risk assessments, the EPA is gathering existing data regarding toxicity and potential human health effects associated with the chemicals reported to be in fracturing fluids and found in wastewater. At this time, the EPA has not made any judgment about the extent of exposure to these chemicals when used in hydraulic fracturing fluids or found in hydraulic fracturing wastewater, or their potential impacts on drinking water resources.

6.1. Relationship to the Hydraulic Fracturing Study

The EPA is compiling existing information on chemical, physical, and toxicological properties of hydraulic fracturing-related chemicals, which include chemicals reported to be used in injected hydraulic fracturing fluids and chemicals detected in flowback and produced water. There are currently over 1,000 chemicals. This work focuses particularly on compiling and evaluating existing toxicological properties and will inform answers to the research questions listed in Table 47.

Table 47. Secondary research questions addressed by compiling existing information on hydraulic fracturing-related chemicals.

Water Cycle Stage	Applicable Research Questions
Chemical mixing	What are the chemical, physical, and toxicological properties of hydraulic fracturing chemical additives?
Flowback and produced water	What are the chemical, physical, and toxicological properties of hydraulic fracturing wastewater constituents?

6.2. Project Introduction

Given the potential for accidental human exposure due to spills, improper wastewater treatment, and potential seepage, it is important to understand the known and potential hazards posed by the diversity of chemicals needed during hydraulic fracturing. The US House of Representatives' Committee on Energy and Commerce Minority Staff released a report (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 SDWA (see Table 11 in Section 3.1) (USHR, 2011). However, the report did not characterize the inherent chemical properties and potential toxicity of many of the reported compounds. The identification of inherent chemical properties will facilitate the development of models to predict environmental fate, transport, and the toxicological properties of chemicals. Through this level of understanding, scientists can design or identify more sustainable alternative chemicals that minimize or even avoid many fate, transport, and toxicity issues, while maintaining or improving commercial use.

The EPA must understand (1) potential hazards inherent to the chemicals being used in or released by hydraulic fracturing and returning to the surface in flowback and produced water, (2) dose-response characteristics, and (3) potential exposure levels in order to assess the potential impacts to human health from ingestion of drinking water that might contain the chemicals. The information from the toxicity assessment project provides a foundation for future risk assessments.

While the EPA currently does not have plans to conduct a formal risk assessment on this topic, the information may aid others who are investigating the risk of exposure.

6.3. Research Approach

Once the EPA identifies chemicals reported to be used in hydraulic fracturing fluids or found in flowback and produced water, physicochemical properties and chemical structures are assigned using various chemical software packages. Toxicological properties are then identified from authoritative sources or are estimated based on chemical structure.

Identification of Chemicals. The EPA, to date, has identified nine sources, listed in Table 48, that contain authoritative information on chemicals in used in hydraulic fracturing fluids or found in hydraulic fracturing wastewater. The sources have been used to compile two lists: chemicals reported to be used in hydraulic fracturing fluids and chemicals detected in hydraulic fracturing wastewater. Chemicals will be added to the two lists as new data become available.

Table 48. References used to develop a consolidated list of chemicals reportedly used in hydraulic fracturing fluids and/or found in flowback and produced water.

Description / Content	Reference
Chemicals reportedly used by 14 hydraulic fracturing service companies from 2005 to 2009	USHR, 2011
Products and chemicals used during natural gas operations with some potential health effects	Colborn et al., 2011
Chemicals used or proposed for use in hydraulic fracturing and chemicals found in flowback	NYSDEC, 2011
Chemicals reportedly used by nine hydraulic fracturing service companies from 2005 to 2010	US EPA, 2011b
MSDSs provided to the EPA during on-site visits	Material Safety Data Sheets
Table 4-1: Characteristics of undiluted chemicals found in hydraulic fracturing fluids (based on MSDSs)	US EPA, 2004b
Chemicals used in Pennsylvania for hydraulic fracturing activities (compiled from MSDSs)	PADEP, 2010
Chemical records entered in FracFocus for individual wells from January 1, 2011, through February 27, 2012	GWPC, 2012b
Chemicals detected in flowback from 19 hydraulically fractured shale gas wells in Pennsylvania and West Virginia	Hayes, 2009
Chemicals reportedly detected in flowback and produced water from 81 wells	US EPA, 2011k

While compiling the list of chemicals used in fracturing fluids, the EPA identified instances where various chemical names were reported for a single CASRN. Chemical name and structure annotation QC methods were applied to the reported chemicals in order to standardize the chemical names; this process is described in “Chemical Information Quality Review Procedures” for the Distributed Structure-Searchable Toxicity (DSSTox) Database Network.[71] The chemical QC methods included ensuring correct chemical names and CASRNs, and eliminating duplicates where appropriate. Chemical structures from the DSSTox database were assigned where possible.

Physicochemical Properties. Physicochemical properties of chemicals in the hydraulic fracturing fluid chemical list were generated from the two-dimensional (2-D) chemical structures from the EPA's DSSTox Database Network in structure-data file format. Properties were calculated using LeadScope chemoinformatic software (Leadscope Inc., 2012), Estimation Programs Interface Suite for Microsoft Windows (US EPA, 2012a), and QikProp (Schrodinger, 2012).[72] 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 ChemFolder (ACD Labs, 2008). All Leadscope general chemical descriptors (Parent Molecular Weight, AlogP, Hydrogen Bond Acceptors**,** Hydrogen Bond Donors, Lipinski Score, Molecular Weight, Parent Atom Acount, Polar Surface Area, and Rotatable Bonds) were calculated by default. For EPISuite properties, both the desalted and non-desalted 2-D files were run using Batch Mode 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 (Chemical Computing Group). All computed physicochemical properties are added into the structure-data file prior to assigning toxicological properties.

Toxicological Properties. Known and predicted toxicity reference values are being combined into a single toxicity reference value resource for hydraulic fracturing-related chemicals. The EPA's list of hydraulic fracturing-related chemicals was cross-referenced against the following nine sources to obtain authoritative toxicity reference values:

- US EPA Integrated Risk Information System (IRIS)
- US EPA Provisional Peer-Reviewed Toxicity Value (PPRTV) database
- US EPA Health Effects Assessment Summary Tables
- Agency for Toxic Substances and Disease Registry Minimum Risk Levels
- State of California Toxicity Criteria Database
- State of Alabama Risk-Based Corrective Action document
- State of Florida Cleanup Target Levels
- State of Hawaii Maximum Contaminant List
- State of Texas Effects Screening Levels List

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[71] For more information on DSSTox, see http://www.epa.gov/ncct/dsstox/ChemicalInfQAProcedures.html.

[72] The QikProp, EPI Suite, and LeadScope chemoinformatics programs calculate complementary properties with some overlap due to the process being performed in batch mode with all default properties included.

Authoritative toxicity reference values have been identified for over 100 of the more than 1,000 chemicals reported as being present in injected water or present in produced water. These include the benzene, toluene, ethylbenzene, and xylene (BTEX) chemicals, and over 70 others with toxicity reference values in the IRIS and PPRTV databases.

For the remaining chemicals that lack authoritative toxicity reference values, the structure-data file (generated for assigning physicochemical properties) can be used with the quantitative structure toxicity relationship software Toxicity Prediction by Komputer Assisted Technology, or TOPKAT (Accelrys Discovery Studio, 2012) to identify toxicity values. Rat chronic lowest observed adverse effect levels (LOAELs) were estimated using the LOAEL module for TOPKAT. The LOAEL module compares LOAEL values from open literature, National Cancer Institute/National Toxicology Program technical reports, and EPA databases to estimated rat oral LD_{50} values, and then compares the octanol-water partition coefficient from the chemical structure data file to the range in the training set.

The estimated LOAEL values will be compared to the authoritative toxicity reference values (for the chemicals with these authoritative values) to provide an estimate of how similar these values are. It is important to note that there may be significant deviation between the estimated LOAEL and the authoritative toxicity reference value for any given chemical due to the use of uncertainty factors in calculating the reference value, the fact that the reference values are not based on a rat chronic assay, and whether the reference values are calculated using the benchmark dose, a no observed adverse effect level, or a LOAEL. However, there is evidence that the estimated LOAEL is generally within 100 times the concentration of the actual rat chronic LOAEL (Rupp et al., 2010).

6.4. Status and Preliminary Data

Chemicals used in fracturing fluids or found in flowback and produced water, reported by the sources listed in Table 48, were consolidated and annotated, resulting in lists containing 1,027 unique chemical substances, of which 751 could be assigned a chemical structure and all but 5 assigned CASRNs. Physicochemical properties have been obtained for 318 of the 751 chemicals with structures. Physicochemical properties for the remainder of the chemicals with structures are currently being calculated. There were an additional 409 substances that were too poorly defined in the original lists to be unambiguously designated as unique substances, assigned CASRNs or chemical structures. The chemical lists are provided in Appendix A. The EPA has completed the first phase of development for the toxicity reference value database described above.

6.5. Next Steps

The EPA is currently identifying any additional state-based reference value data sources that can be useful; these additional sources, if any, will be brought into the database as they are identified.

6.6. Quality Assurance Summary

There are two QAPPs associated with this project. The first "Health and Toxicity Theme Hydraulic Fracturing Study Immediate Office National Center for Environmental Assessment," was approved February 2012 and describes the development of the toxicity reference value master spreadsheet (US EPA, 2012k). The second QAPP, "Health and Toxicity (HT) Hydraulic Fracturing (HF) National Center for Computational Toxicology," was approved February 2012 and describes the planning and quality processes for the generation of the chemical lists and the calculation of physicochemical properties for the chemicals for which chemical structures can be assigned (US EPA, 2012i).

7. Case Studies

7.1. Introduction to Case Studies

Case studies are widely used to conduct in-depth investigations of complex topics and provide a systematic framework for investigating relationships among relevant factors. In conjunction with other elements of the research program, they help determine whether hydraulic fracturing can impact drinking water resources and, if so, the extent and possible causes of any impacts. Case studies may also provide opportunities to assess the fate and transport of fluids and contaminants in different regions and geologic settings. Results from the case studies are expected to help answer the secondary research questions listed in Table 49.

Table 49. Secondary research questions addressed by conducting case studies.

Water Cycle Stage	Applicable Secondary Research Questions
Chemical mixing	• If spills occur, how might hydraulic fracturing chemical additives contaminate drinking water resources?
Well injection	• How effective are current well construction practices at containing gases and fluids before, during, and after hydraulic fracturing? • Can subsurface migration of fluids or gases to drinking water resources occur, and what local geologic or man-made features might allow this?
Flowback and produced water	• If spills occur, how might hydraulic fracturing wastewaters contaminate drinking water resources?

Two types of case studies are being conducted as part of this study. Retrospective case studies focus on investigating reported instances of drinking water resource contamination in areas where hydraulic fracturing events have already occurred. Prospective case studies involve sites where hydraulic fracturing will be implemented after the research begins, which allows sampling and characterization of the site before, during, and after drilling, injection of the fracturing fluid, flowback, and production. The EPA continues to work with industry partners to design and develop prospective case studies. Because prospective case studies remain in their early stages, the progress report focuses on the progress of retrospective case studies only.

To select the retrospective case study sites, the EPA invited stakeholders from across the country to participate in the identification of locations for potential case studies through informational public meetings and the submission of electronic or written comments. Following thousands of comments, over 40 locations were nominated for inclusion in the study.[73] These locations were prioritized and chosen based on a rigorous set of criteria, including proximity of population and drinking water supplies, evidence of impaired water quality, health and environmental concerns, and knowledge gaps that could be filled by a case study at each potential location. Sites were prioritized based on geographic and geologic diversity, population at risk, geologic and hydrologic features, characteristics of water resources, and land use (US EPA, 2011e). Five retrospective case study locations were ultimately chosen for inclusion in this study and are shown in Figure 27.

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[73] A list of the sites submitted for consideration can be found in the Study Plan.

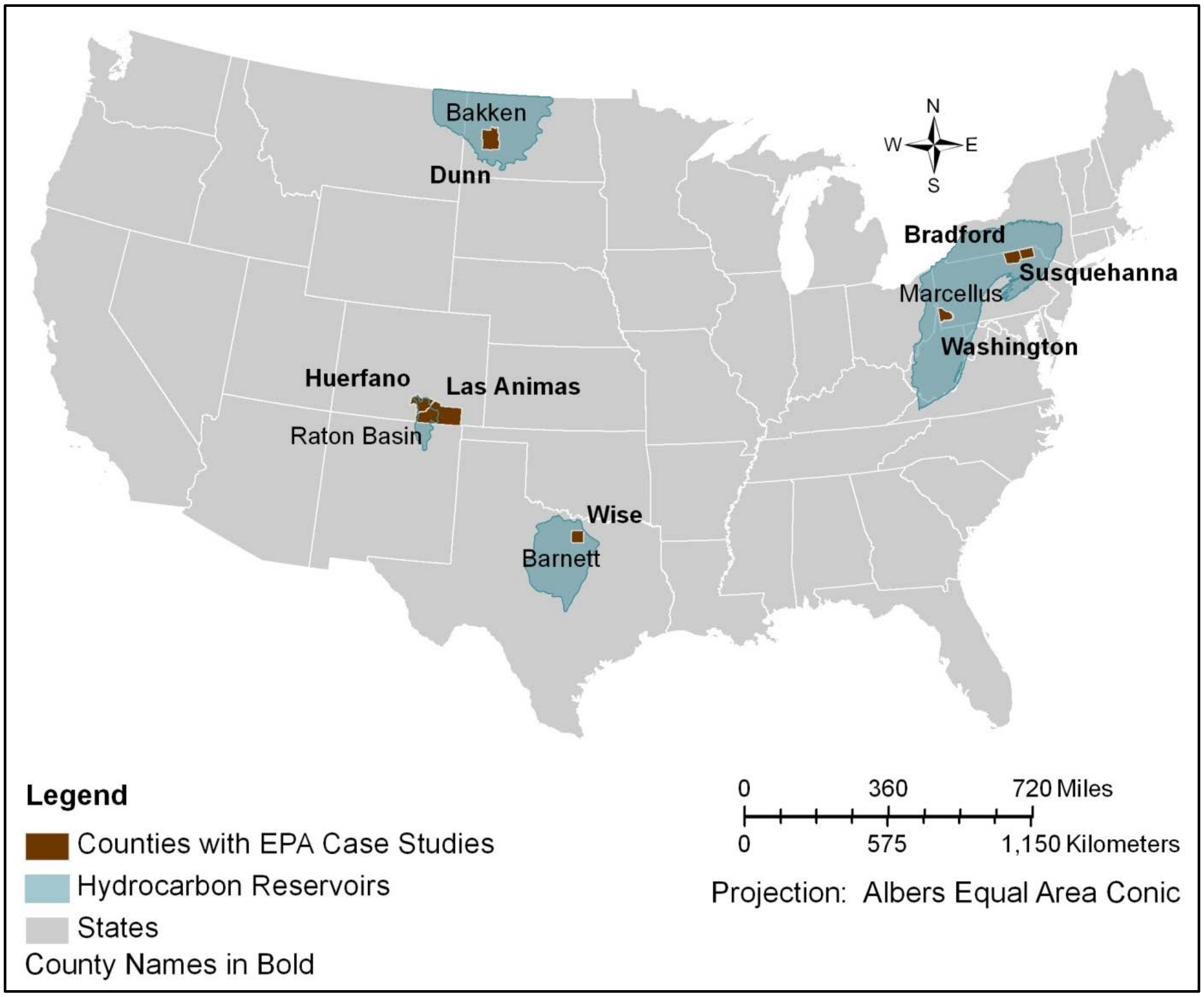

Figure 27. Locations of the five retrospective case studies chosen for inclusion in the EPA's Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources. The locations were nominated by stakeholders and selected based on criteria described in the text. (ESRI, 2010a, b; US EIA, 2011d, e)

7.1.1. General Research Approach

Although each retrospective case study differs in the geologic and hydrologic characteristics, as well as the hydraulic fracturing techniques used and the oil and gas exploration and production history of the area, the methods used to assess potential drinking water impacts are applicable to all of the study sites. By coordinating the case study methods and analyses, it will be possible to compare the results of each study. Table 50 describes the general research approach being used for the retrospective case studies.[74] The tiered scheme uses the results of earlier tiers to refine sampling activities in later tiers. This approach is both useful and appropriate when the impacts to drinking water resources and the potential sources of the impacts are unknown. For example, it allows the sampling to verify key findings and adjust to the improved understanding of the site.

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[74] The Dunn County, North Dakota, retrospective case study does not use this tiered sampling plan because it is designed to examine the impacts of a well blowout during hydraulic fracturing. Since the potential source of contamination is known, the tiered sampling plan is not necessary.

Table 50. General approach for conducting retrospective case studies. The tiered approach uses the results of earlier tiers to refine sampling activities in later tiers.

Tier	Goal	Critical Path
1	Verify potential issue	• Evaluate existing data and information from operators, private citizens, state and local agencies, and tribes (if any) • Conduct site visits • Interview stakeholders and interested parties
2	Determine approach for detailed investigations	• Conduct initial sampling of water wells, taps, surface water, and soils • 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)
3	Conduct detailed investigations to detect and evaluate potential sources of contamination	• Conduct additional sampling of soils, aquifer, surface water, and wastewater pits/tanks (if 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
4	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

Each retrospective case study has developed a QAPP that describes the detailed plan for the research at that location. The QAPP integrates the technical and quality aspects of the case study in order to provide a guide for obtaining the type and quality of environmental data required for the research. Before each new tier of sampling begins, the QAPPs are revised to account for any changes.

Ground water samples have been collected at all retrospective case study locations. The samples come from a variety of available sources, such as existing monitoring wells, domestic and municipal water wells, and springs. Surface water, if present, has also been sampled. During sample collection, the following water quality parameters were monitored and recorded:

- Temperature
- pH
- TDS
- Specific conductivity
- Alkalinity
- Turbidity
- Dissolved oxygen

- Oxidation/reduction potential
- Ferrous iron
- Hydrogen sulfide

Each water sample has been analyzed for a suite of chemicals; groups of analytes and examples of specific chemicals of interest are listed in Table 51. These chemicals include major anions, components of hydraulic fracturing fluids (i.e., glycols), and potentially mobilized natural occurring substances (i.e., metals);[75] these chemicals are thought to be present frequently in hydraulic fracturing fluids or wastewater. As indicated in Table 51, stable isotope analyses are also being conducted. Stable isotope compositions can be important indicators of what is naturally occurring in the environment being studied. If an element has multiple stable isotopes, one is usually the most common form in that environment. Due to different processes that may occur in or around the environment, other stable isotopes of the element may be found. The different isotopes can make it easier to determine the source of, or distinguish between, sources of contamination.

Table 51. Analyte groupings and examples of chemicals measured in water samples collected at the retrospective case study locations.

Analyte Groups	Examples
Anions	Bromide, chloride, sulfate
Carbon group	Dissolved organic carbon,* dissolved inorganic carbon†
Dissolved gases	Methane, ethane, propane
Extractable petroleum hydrocarbons	Gasoline range organics,§ diesel range organics‡
Glycols	Diethylene glycol, triethylene glycol, tetraethylene glycol
Isotopes	Isotopes of oxygen and hydrogen in water, carbon and hydrogen in methane, strontium
Low molecular weight acids	Formate, acetate, butyrate
Measures of radioactivity	Radium, gross α, gross β
Metals	Arsenic, manganese, iron
Semivolatile organic compounds	Benzoic acid; 1,2,4-trichlorobenzene; 4-nitrophenol
Surfactants	Octylphenol ethoxylate, nonylphenol
Volatile organic compounds	Benzene, toluene, styrene

* Dissolved organic carbon is a result of the decomposition of organic material in aquatic systems.
† Dissolved inorganic carbon is the sum of the carbonate species (e.g., carbonate, bicarbonate) dissolved in water.
§ Gasoline range organics include hydrocarbon molecules containing 5–12 carbon atoms.
‡ Diesel range organics include hydrocarbon molecules containing 15–18 carbon atoms.

The samples taken for the case studies were analyzed by the EPA Region 8 Laboratory and the EPA Robert S. Kerr Environmental Research Center. A laboratory TSA was conducted at the EPA Region 8 Laboratory on July 26, 2011; no findings were identified. In addition, a laboratory TSA was conducted for the onsite analytical support at the Robert S. Kerr Environmental Research Center on July 28, 2011, which included Shaw Environmental and the EPA General Parameter Lab; no findings

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[75] A complete list of chemicals and corresponding analytical methods is available in the QAPPs for each case study. See http://www.epa.gov/hfstudy/qapps.html.

were identified. The laboratory TSAs were conducted on these laboratories during the first retrospective case study sampling event to identify any problems early and allow for corrective actions, if needed. Additional TSAs will be performed if determined to be necessary based on quality concerns.

This chapter includes progress reports for the following retrospective case studies:

7.2. Las Animas and Huerfano Counties, Colorado

7.2.1. Project Introduction

Las Animas and Huerfano Counties, Colorado, are located on the eastern edge of the Rocky Mountains and have a combined population of about 22,000 people and a population density of about 4 people per square mile (USCB, 2010c, d). As shown in Figure 28, the coal-bearing region of the Raton Basin occupies an area of 1,100 square miles within these two counties. The development of CBM resources in the Raton and Vermejo Formations within the Raton Basin has increased due to advances in hydraulic fracturing technology (Keighin, 1995; Watts, 2006b).

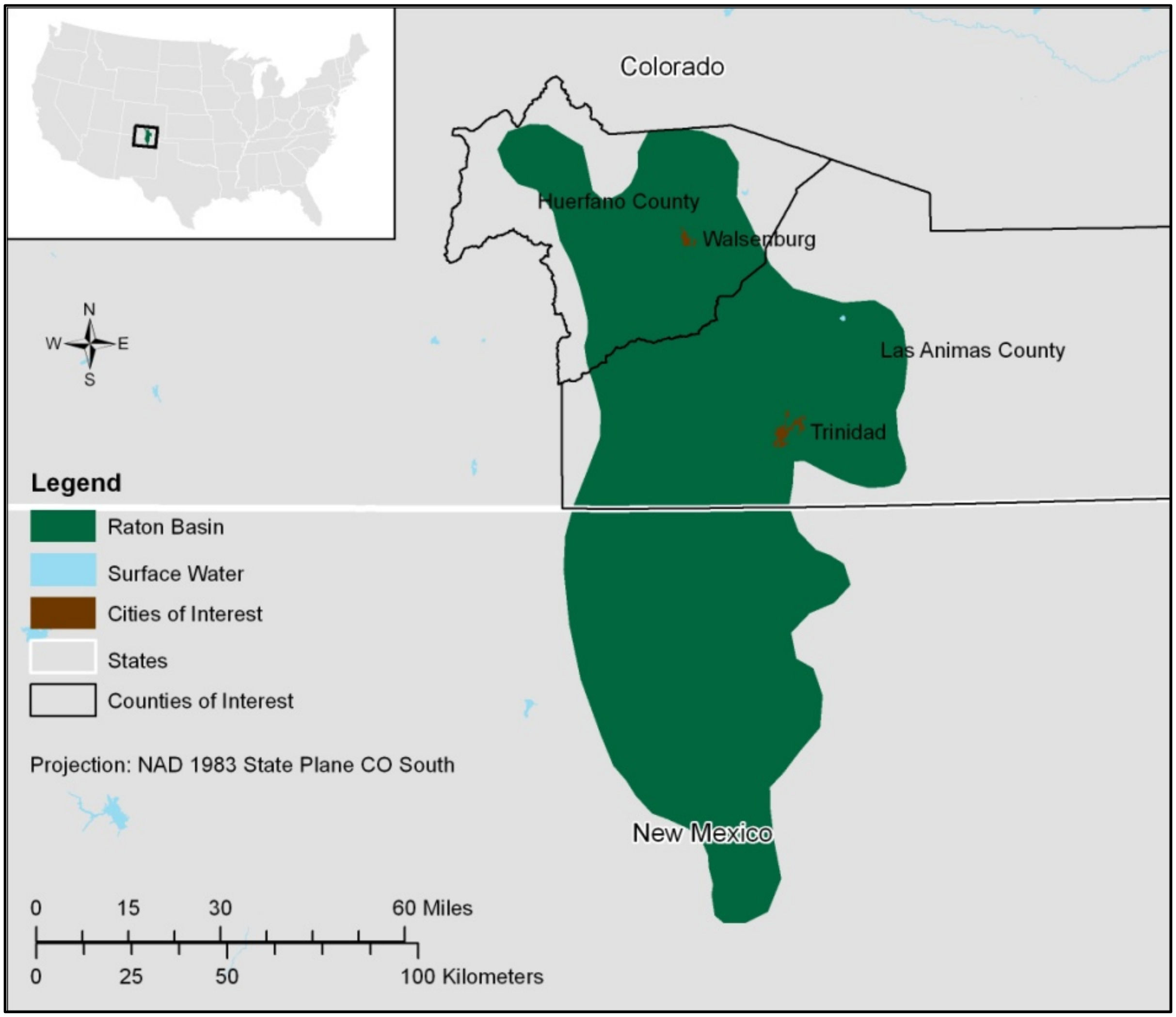

Figure 28. Extent of the Raton Basin in southeastern Colorado and northeastern New Mexico (ESRI, 2012; US EIA, 2011d; USCB, 2012a, b, c). The case study includes two locations: "North Fork Ranch," located northwest of the city of Trinidad in western Las Animas County, and "Little Creek," located southwest of the city of Walsenburg in Huerfano County.

Study site locations in Las Animas and Huerfano Counties were selected in response to ongoing complaints about changes in appearance, odor, and taste associated with drinking water in domestic wells. These sites include "North Fork Ranch," located northwest of the city of Trinidad in western Las Animas County, and "Little Creek," located southwest of the city of Walsenburg in Huerfano County. In some locations, point-of-use water treatment systems have been installed on properties to treat elevated methane and sulfide concentrations in well water. This case study focuses on the potential impacts of hydraulic fracturing on drinking water resources near these two study sites. Potential sources of ground water contamination under consideration include activities associated with natural sources, CBM extraction (such as leaking or abandoned pits), gas well completion and enhancement techniques, improperly plugged and abandoned wells, gas migration, and residential impacts.

7.2.2. Site Background

Geology. The Raton Basin is a north-south trending sedimentary and structural depression located along the eastern edge of the Rocky Mountains, between the Sangre de Cristo Mountains to the west and the Apishapa, Las Animas, and Sierra Grande arches on the east (Watts, 2006a). This chevron-shaped basin encompasses roughly 2,200 square miles of southeastern Colorado and northeastern New Mexico, extending from southern Colfax County, New Mexico, through Las Animas County, Colorado, and northward into Huerfano County, Colorado, as shown in Figure 28 (Tremain, 1980). It is the southernmost of the several major coal-bearing basins located along the eastern margin of the Rocky Mountains (Johnson and Finn, 2001). Within the Raton Basin, the Vermejo and Raton Formations contain CBM resources being extracted using hydraulic fracturing.

Las Animas and Huerfano Counties are underlain by sedimentary bedrock ranging in age from the late Cretaceous to the Eocene (see Appendix D for a geologic timeline). Igneous intrusions, dating to the Eocene, Miocene, and Pliocene epochs, occur throughout the area. The sedimentary sequence exposed within the Raton Basin was deposited in association with regression of the Cretaceous Interior Seaway, and the stratigraphy reflects deposition in fluvial systems and peat-forming swamps (Cooper et al., 2007; Flores, 1993). Numerous discontinuous and thin coalbeds are located in the Vermejo and Raton Formations, which lie directly above the Trinidad Sandstone. The upper Trinidad intertongues with, and is overlain by, the coal-bearing Vermejo Formation (Topper et al., 2011). No coal is found below this sandstone (Greg Lewicki & Associates, 2001).

Individual coalbeds in the Vermejo Formation consist of interbedded shales, sandstones, and coalbeds. The Vermejo Formation ranges in thickness from 150 feet in the southern part of the basin to 410 feet in the northern part (Greg Lewicki & Associates, 2001). This formation contains from 3 to 14 coalbeds over 14 inches thick throughout the entire basin, and total coal thickness typically ranges from 5 to 35 feet (US EPA, 2004b).

The Raton Formation overlies the Vermejo Formation. The Raton Formation ranges from 0 to 2,100 feet thick and is composed of a basal conglomerate, a middle coal-bearing zone, and an upper transitional zone (Johnson and Finn, 2001; US EPA, 2004b). Its middle coal-bearing zone is approximately 1,000 feet thick and consists of shales, sandstones, and coalbeds (Greg Lewicki & Associates, 2001). This zone also contains coal seams that have been mined extensively; total coal thickness ranges from 10 feet to more than 140 feet in this zone, with individual seams ranging in thickness from several inches to more than 10 feet (US EPA, 2004b). Sandstones are interbedded with coalbeds that are currently being developed for CBM, and the coalbeds are the likely source for gas found in the sandstones (Johnson and Finn, 2001).

Water Resources. Las Animas and Huerfano Counties are located in the Arkansas River Basin and are drained by the Purgatoire, Apishapa, and Cucharas Rivers. The coal-bearing region of the Raton Basin is predominantly drained by the Purgatoire and Apishapa Rivers; many stream segments of these rivers are currently on Colorado's list of impaired waters (CDPHE, 2012). Annual precipitation in the Raton Basin is generally correlated to elevation, ranging from over 30 inches per year in the Spanish Peaks to less than 16 inches per year in eastern portions of the basin, which are at lower elevation. Much of the precipitation falls as winter snow in the mountains or as intense summer rain in the plains (Abbott, 1985; S.S. Papadopulos & Associates Inc, 2008). Ground water-based drinking water resources in Las Animas and Huerfano Counties reside in four bedrock aquifers: (1) the Dakota Sandstone and Purgatoire Formation; (2) the Raton Formation, Vermejo Formation, and Trinidad Sandstone; (3) the Cuchara-Poison Canyon Formation; and (4) volcanic rocks (Abbott et al., 1983). Sources of recharge to the aquifers include runoff from the Sangre de Cristo Mountains, precipitation infiltration, and infiltration from streams and lakes (Abbott et al., 1983; CDM and GBSM, 2004). The depth to ground water depends mostly on topographic position. In all areas but the southeast corner of the basin, water can be encountered at less than 200 feet below ground surface (CDM and GBSM, 2004). Regional ground water flow is generally from west to east, except where it is intercepted by valleys that cut into the rock (Watts, 2006b).

Within the hydrogeologic units of the Raton Basin, sandstone and conglomerate layers transmit most of the water; shale and coal layers generally retard flow. However, fracture networks in the shales and coal provide pathways which can transmit fluids or gas. Talus and alluvium may yield large quantities of water, but are limited in size, and discharges from these units fluctuate seasonally (Abbott et al., 1983). Aquifer tests in the Raton-Vermejo aquifers indicate hydraulic conductivities that range from 0 to 45 feet per day (Abbott et al., 1983).

Geologic formations have distinctive ground water chemistry. The Cuchara-Poison Canyon Formation is typically calcium-bicarbonate type with less than 500 milligrams per liter TDS content, while the Raton-Vermejo-Trindad aquifer is typically sodium-bicarbonate with TDS concentrations less than 1,500 milligrams per liter. Abbott et al. (1983) note that concentrations of boron, fluoride, iron, manganese, mercury, nitrate, selenium, and zinc are locally elevated due to a variety of geologic processes and human activities. High concentrations of fluoride occur in the Poison Canyon and Raton Formations, possibly due to the dissolution of detrital fluorite. Iron and manganese concentrations may be also elevated, particularly in areas where coals are present, due to the dissolution of pyrite and/or siderite contained in the coal seams. Nitrate enrichment often occurs in alluvial aquifers where fertilizers or animal wastes add nitrogen (Abbott et al., 1983).

Oil and Gas Exploration and Production. The Raton Basin contains substantial amounts of high- and medium-volatile bituminous coals, which extend from outcrops along the periphery of the region to depths of at least 3,000 feet in the deepest parts of the region (Jurich and Adams, 1984). Most of these coal resources are in the Vermejo and Raton Formations, which are the target formations for CBM production (Macartney, 2011; Tyler, 1995). These coalbeds have been extensively mined in the peripheral outcrop belt along major stream valleys, as well as in a few structural uplifts within the interior of the basin (Dolly and Meissner, 1977). Total coal resources estimated in the basin range from 1.5 billion to more than 17 billion short tons (Flores and Bader, 1999).

Production of natural gas in the Raton Basin began in the 1980s, but before 1995, there were no gas distribution lines out of the basin and fewer than 60 wells had been drilled (S.S. Papadopulos & Associates Inc, 2008). The Raton Basin is estimated to contain as much as 18.4 trillion cubic feet of CBM (Tyler, 1995). This area has recently seen a rapid expansion in the production of natural gas with recent advances in hydraulic fracturing technology. Between 1999 and 2004, annual production of Raton Basin CBM in Las Animas and Huerfano Counties increased from about 28 billion cubic feet to about 80 billion cubic feet, and the number of producing wells grew from 478 wells to 1,543 wells. During the same period, annual ground water withdrawals for CBM production increased from about 1.45 billion gallons to about 3.64 billion gallons (Watts, 2006b). Expansion of CBM wells has focused on the development of the Vermejo coals, since these coals are thicker and more continuous than those located in the Raton Formation (US EPA, 2004b).

7.2.3. Research Approach

A detailed description of the sampling methods and procedures for this case study can be found in the project's QAPP (US EPA, 2012o). Ground water and surface water sampling in this area is intended to provide a survey of water quality in Las Animas and Huerfano Counties. Data collection involves sampling water from domestic wells, surface water bodies (streams), monitoring wells,[76] and gas production wells at locations in both Las Animas and Huerfano Counties, as indicated in Figure 29. The locations of these sampling sites were chosen based on their proximity to production activity.

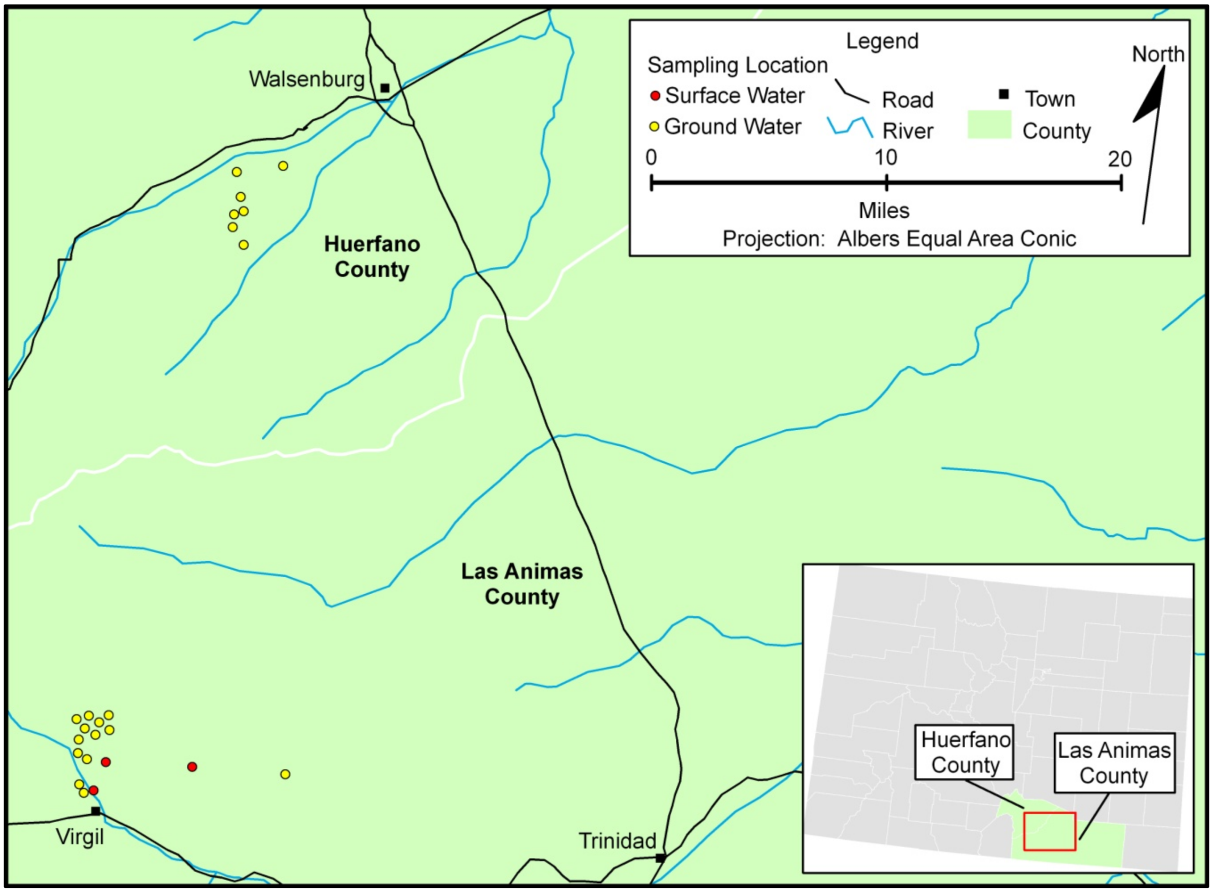

Figure 29. Locations of sampling sites in Las Animas and Huerfano Counties, Colorado. Water samples have been taken from domestic wells, surface water bodies (streams), monitoring wells, and gas production wells.

In addition to the analytes discussed in Section 7.1.1, the stable isotope compositions of carbon and hydrogen in methane, as well as the stable carbon isotope composition of dissolved inorganic carbon and the stable sulfur isotope composition of dissolved sulfate and dissolved sulfide, are

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[76] Monitoring wells were installed by either Pioneer Natural Resources or Petroglyph Energy.

being analyzed as part of this case study. Microbial analyses are also being conducted on water samples collected at this case study location in order to better understand the biogeochemical cycling of carbon and sulfur in ground water. Together, these measurements support the objective of determining if ground water resources have been impacted, and, if so, whether they were impacted by hydraulic fracturing activities or other sources of contamination.

7.2.4. Status and Preliminary Data

As of August 2012, two sampling trips have been conducted: one in October 2011 and another in May 2012. During the October 2011 sampling trip, two production wells, five monitoring wells, 14 domestic water wells, and one surface water location were sampled. During the May 2012 sampling trip, two production wells, three monitoring wells, 12 domestic water wells, and three surface water locations were sampled. The locations of sampling sites are displayed in Figure 29.

7.2.5. Next Steps

Additional fieldwork to collect ground and surface water at each sampling location is tentatively scheduled for late 2012 and spring 2013. Sampling locations and analytes measured may be refined based on the results of the first two sets of samples. More focused investigations will also be conducted, if warranted, at locations where potential impacts associated with hydraulic fracturing may have occurred.

7.2.6. Quality Assurance Summary

The initial QAPP for this case study, “Hydraulic Fracturing Retrospective Case Study, Raton Basin, CO,” was approved by the designated EPA QA Manager on September 20, 2011 (US EPA, 2012o). A revision to the QAPP was made before the second sampling event and was approved on April 30, 2012, to update project organization, update lab accreditation information, update sampling methodology, add sulfur isotope analyses, modify critical analytes, and change the analytical method for determining hydrogen and oxygen stable isotope ratios in water . There have been no significant deviations from the QAPP during any sampling event, and therefore no impact on data quality. A field TSA was conducted on October 4, 2011, during the first sample collection event; no findings were identified. See Section 7.1.1 for information related to the laboratory TSAs.

As results are reported and raw data are provided from the laboratories, ADQs are performed to verify that the quality requirements specified in the approved QAPP were met. Data will be qualified, if necessary, based on these ADQs. The results of these ADQs will be reported in the final report on this project.

7.3. Dunn County, North Dakota

7.3.1. Project Introduction

Dunn County, North Dakota, is a rural county with a population of 3,500 and an average population density of 1.8 people per square mile (USCB, 2010b); Killdeer is its largest city. This part of North Dakota is currently experiencing renewed natural gas exploration and a boom in oil production from the Bakken Shale, which extends domestically from western North Dakota to parts of northeastern Montana (Figure 30). The area's increased oil and gas exploration has relied greatly upon both horizontal drilling and hydraulic fracturing technologies.

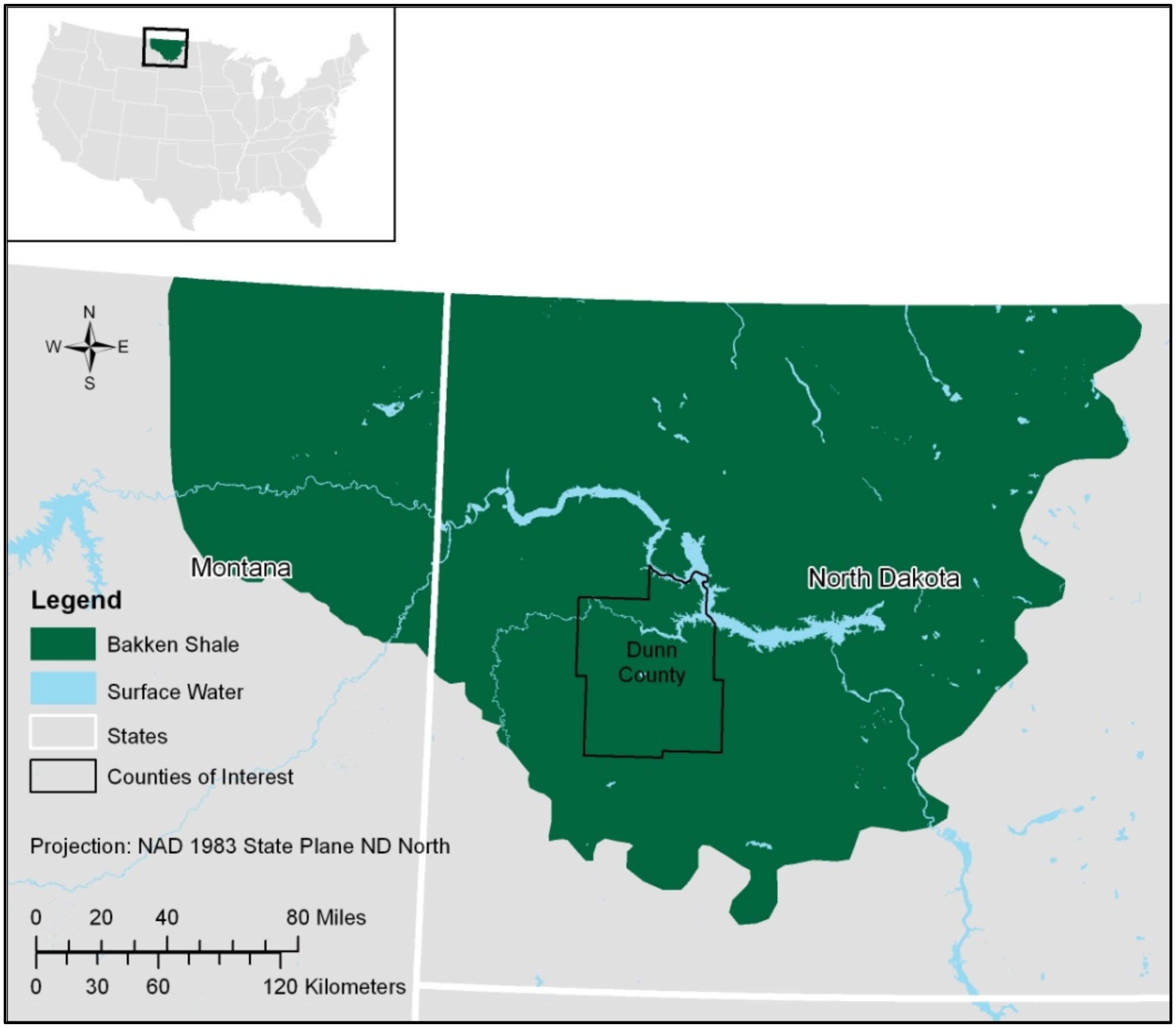

Figure 30. Extent of the Bakken Shale in North Dakota and Montana (US EIA, 2011d; USCB, 2012a, c). The case study focuses on a well blowout that occurred in Dunn County, North Dakota, in September 2010.

The EPA's case study site in Killdeer, North Dakota, was chosen at the request of the state to specifically examine any water resource impacts from a well blowout in September 2010 that resulted in an uncontrolled release of hydraulic fracturing fluids and formation fluids. The Killdeer Aquifer, the main source of drinking water for the city of Killdeer, underlies the study site. The blowout occurred at the Franchuk 44-20 SWH well, which is just outside the Killdeer municipal water supply well's 2.5 mile wellhead protection zone.

The uncontrolled blowout occurred on September 1, 2010, during the fifth stage of a hydraulic fracturing treatment of the Franchuk 44-20 SWH well. The intermediate well casing burst because of a 8,390 pounds per square inch pressure spike that released the pop-off relief valve. Hydraulic fracturing fluids and formation fluids began flowing from the ground around the well at several points and then flowed toward the northeast corner of the well pad, where they were contained by a 2 foot berm. During that day, 47,544 gallons of fluids were removed from the site. The following day, 88,000 gallons of fluids were removed from the site, and 15,120 gallons of mud were circulated into the well to kill it. Three monitoring wells were installed, but not sampled. Two down-gradient homeowner wells, an up-gradient homeowner well, and two municipal water wells were sampled on September 2. Three cement plugs were installed beginning at 9,000 feet in the wellbore, and 105,252 gallons of fluid were removed from the site. A bridge plug was set at 9,969 feet on September 6. From September 30 to October 15, 2,000 tons of contaminated soil were removed and disposed of (Jacob, 2011). Since the blowout, the State of North Dakota has overseen site cleanup and has required the well's operator to conduct ground water monitoring on a quarterly basis. In November 2010, the state asked the EPA to consider this site as part of this study, and the EPA agreed to do so.

7.3.2. Site Background

Geology. Dunn County is located in west-central North Dakota and is underlain by the sedimentary rocks of the Williston Basin. Although Dunn County marks the southern extent of glaciations in North Dakota, most of the glacial deposits have been eroded and the surface sediments are characterized by post-glacial, channel-fill deposits (Murphy, 2001). As described in Nordeng (2010), the Bakken formation is primarily composed of shale and dolomite, with some sandstone and siltstone. The Bakken Shale is of Late Devionian-Early Mississippian age (Appendix D) and is an organic-rich marine shale. It has no surface outcrop and is constrained by the Madison Formation above and the Wabamum, Big Valley, and Torquary Formations below (Murphy, 2001; Nordeng, 2010). The depths to the Bakken Shale range from 9,500 to 10,500 feet and its thickness ranges from very thin up to 140 feet (Carlson, 1985; Murphy, 2001).

Water Resources. Dunn County is a semi-arid region. Surface water in Dunn County is in the Missouri River Basin and includes the Little Missouri River to the northwest of the county and Lake Sakakawea to the northeast. These water resources supply water for domestic use, irrigation, industrial water, and hydraulic fracturing.

One of the major sources of drinking water in Killdeer is the Killdeer Aquifer: a glacial outwash aquifer, composed of fine to medium sand with course gravel near its base. It is shallow, with a maximum thickness of 233 feet. The aquifer is generally overlain by clay and silt soils (Klausing, 1979). Yields from the Killdeer Aquifer are high, ranging from 50 to 1,000 gallons per minute (Klausing, 1979). The major water types in the Killdeer Aquifer are sodium bicarbonate and sodium sulfate. Table 52 shows background water quality data for the Killdeer Aquifer, compiled by Klausing (1979).

Table 52. Background water quality data for the Killdeer Aquifer in North Dakota (Klausing, 1979). The range of boron, chloride, and iron in some samples was below the detection limit (BDL).

Parameter	Concentration Range (milligrams per liter)	Mean Concentration (milligrams per liter)
Bicarbonate	374–1,250	713
Boron	BDL–3.70	0.53
Chloride	BDL–25	4.5
Fluoride	0.1–2	0.66
Iron	BDL–5.50	1.03
Nitrate	0.3–6.7	1.2
Sodium	50–1,350	413
Sulfate	333–3,000	626
TDS	234–5,030	1,531

Oil and Gas Exploration and Production. Although it was known to contain large volumes of oil as early as the 1950s, difficulties in extracting the oil from the Bakken Shale kept production rates low (NDIC, 2012a). Hydraulic fracturing and horizontal drilling technologies have created greater access to the Bakken Shale oil reserves. In January 2003, Dunn County had 99 wells, producing approximately 86,000 barrels of oil (NDIC, 2003). By July 2012, the county had 854 wells, producing approximately 3.2 million barrels of oil (NDIC, 2012b).

7.3.3. Research Approach

A detailed description of this case study's sampling methods and procedures can be found in the QAPP (US EPA, 2011i). The primary objective of this case study is to assess the impacts of the Franchuk 44-20 SWH well blowout that occurred on September 1, 2010. Unlike the EPA's other four retrospective case studies, the Killdeer case study does not use a tiered approach because the potential source of contamination is known. Ground water sampling includes domestic, municipal, water supply, and monitoring wells.[77] Figure 31 shows the sampling locations in Dunn County, North Dakota.

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[77] Terracon Consultants was contracted by the well operator, Denbury Resources, for the installation of monitoring wells.

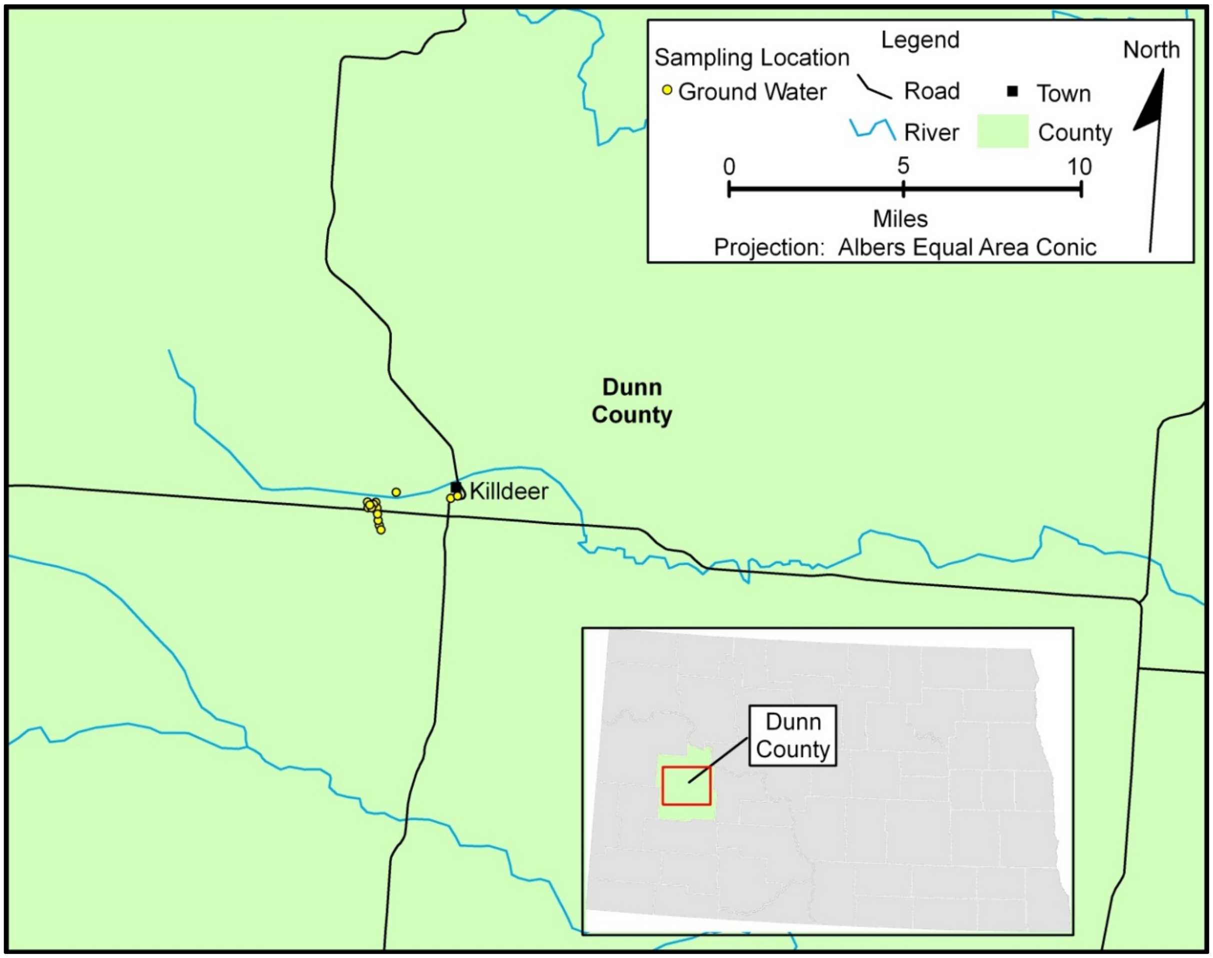

Figure 31. Location of sampling sites in Dunn County, North Dakota.

Domestic, municipal, and supply wells are being sampled at a tap as close to the wellhead as possible, before any treatment has occurred. Monitoring wells have been installed and have dedicated bladder pumps for sampling and purging operations. Water samples collected at these locations are being analyzed for the chemicals listed in Section 7.1.1 as well as the chemicals listed in the QAPP (US EPA, 2011i). The data collected as part of this case study will be compared to existing background data as part of the initial screening phase (Tier 2 in Table 50) to determine if any contamination has occurred in the study location.

7.3.4. Status and Preliminary Data

Two rounds of sampling were conducted in Killdeer in July and October 2011. Samples were collected at 10 monitoring wells, three domestic water wells, two water supply wells, and one municipal water well. The locations of sampling sites are displayed in Figure 31.

7.3.5. Next Steps

At least one more round of sampling is planned to verify data collected from the first two rounds of sampling. Additional sampling locations or analytes may be included in future rounds as analytical data are evaluated and additional pertinent information becomes available.

7.3.6. Quality Assurance Summary

The initial QAPP for this case study, "Hydraulic Fracturing Retrospective Case Study, Bakken Shale, Killdeer and Dunn County," was approved by the designated EPA QA Manager on June 20, 2011 (US EPA, 2011i). A revision to the QAPP was made before the second sampling event and was approved on August 31, 2011, to address the collection of isotopic samples; revised sampling protocols for domestic, supply, and municipal wells; and analytical lab information. Another QAPP revision has been submitted for review by QA staff in preparation for the third sampling event. There have been no significant deviations from the QAPPs during earlier sampling events, and therefore no impact to data quality. A field TSA was conducted on July 19, 2011; no findings were identified. See Section 7.1.1 for information related to the laboratory TSAs.

As results are reported and raw data are provided from the laboratories, ADQs will be performed to verify that the quality requirements specified in the approved QAPP were met. Data will be qualified if necessary, based on these ADQs. The results of these ADQs will be reported in the final report on this project.

7.4. Bradford County, Pennsylvania

7.4.1. Project Introduction

Bradford County is a rural county in northeastern Pennsylvania with an approximate total population of 63,000 and an average population density of 55 people per square mile (USCB, 2010a). As shown in Figure 32, the Marcellus Shale underlies Bradford County, extending through much of New York, Pennsylvania, Ohio, and West Virginia. Recently, natural gas drilling in the Marcellus Shale has increased significantly in northeastern Pennsylvania, including Bradford County.

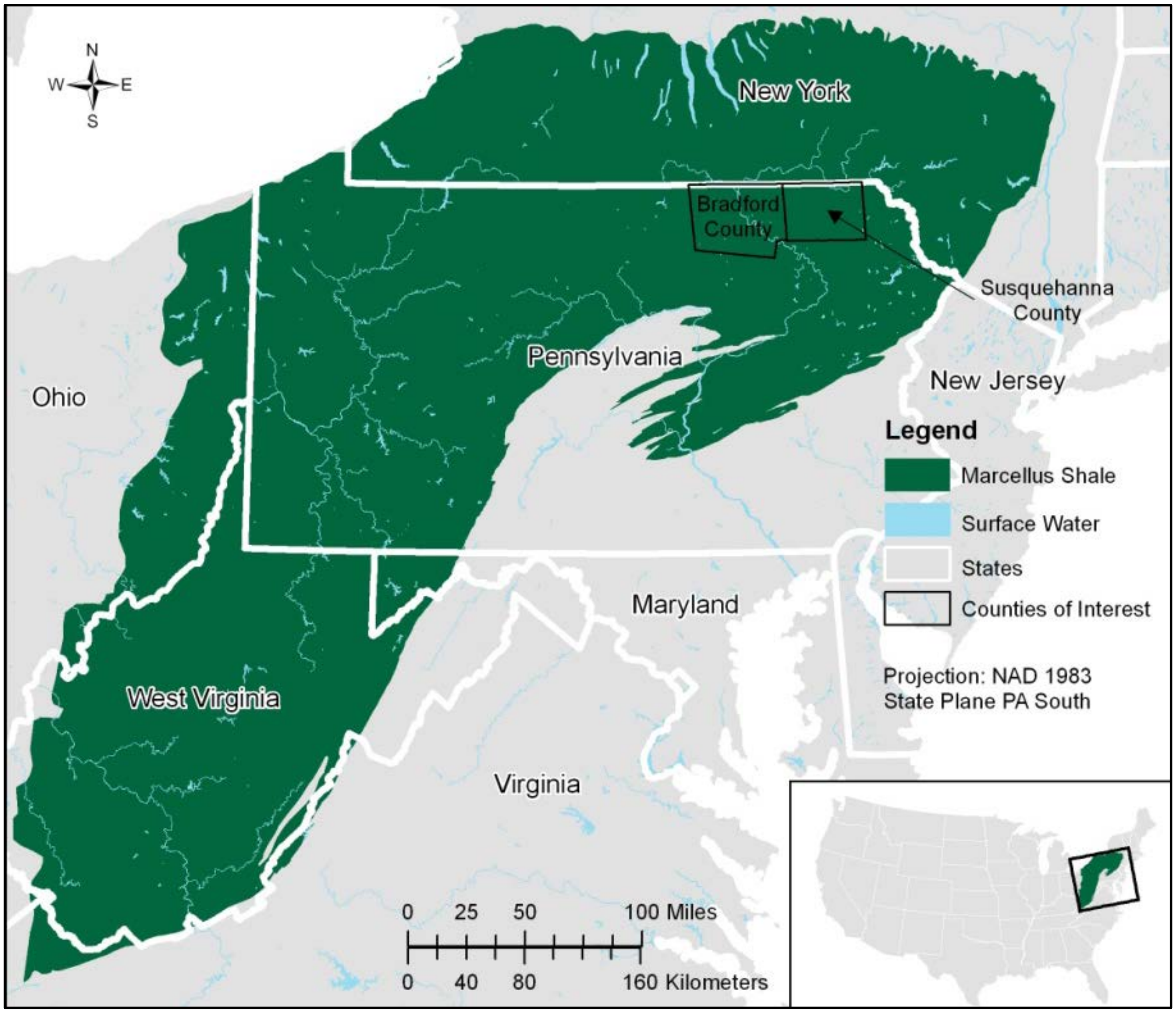

Figure 32. Extent of the Marcellus Shale, which underlies large portions of New York, Ohio, Pennsylvania, and West Virginia (US EIA, 2011d; USCB, 2012a, c). The case study focuses on reported changes in drinking water quality in Bradford County, Pennsylvania, with a few water samples taken in neighboring Susquehanna County.

The EPA chose Bradford County, and parts of neighboring Susquehanna County,[78] as a retrospective case study location because of the extensive hydraulic fracturing activities occurring there, coincident with the large number of homeowner complaints regarding the appearance, odor, and possible health impacts associated with water from domestic wells. Additionally, the Pennsylvania Department of Environmental Protection has issued notices of violation for infractions at wells in this area, including a gas well blowout in Leroy Township of Bradford County in April 2011 that released a reported 10,000 gallons of flowback and produced water (SAIC Energy Environment & Infrastructure LLC and Groundwater & Environmental Services Inc., 2011). Initial sampling locations for this retrospective case study were chosen primarily based on individual homeowner complaints or concerns regarding potential adverse impacts to their well water from nearby hydraulic fracturing activities. If anomalies in ground water quality are found during sampling, all potential sources of contamination in the study area will be considered, including those not related to hydraulic fracturing.

7.4.2. Site Background

Geology. The geology of the study area has been extensively described in other studies and is summarized below (Carter and Harper, 2002; Milici and Swezey, 2006; Taylor, 1984; Williams et al., 1998). The Bradford County study area is underlain by unconsolidated deposits of glacial and post-glacial origin and the nearly flat-lying sedimentary bedrock of the Appalachian Basin. The glacial and post-glacial deposits consist of till, stratified drift, alluvium, and swamp deposits. The bedrock consists primarily of shale, siltstone, and sandstone of Devonian to Pennsylvanian age. The Devonian bedrock includes the Loch Haven and Catskill formations, both of which are important sources of drinking water in the study area. The Marcellus Shale, also known as the Marcellus Formation, is a Middle Devonian-age (Appendix D) shale with a black color, low density, and high organic carbon content. It occurs in the subsurface beneath much of Ohio, West Virginia, Pennsylvania, and New York (Figure 32). Smaller areas of Maryland, Kentucky, Tennessee, and Virginia are also underlain by the Marcellus Shale. In Bradford County, the Marcellus Shale generally lies 4,000 to 7,000 feet below the surface and ranges in thickness from 150 to 300 feet (Marcellus Center for Outreach and Research, 2012a, b). The Marcellus Shale is part of a transgressive sedimentary package, formed by the deposition of terrestrial and marine material in a shallow, inland sea. It is underlain by the sandstones and siltstones of the Onondaga Formation and overlain by the carbonate rocks of the Mahantango Formation.

Within the Marcellus Shale, natural gas occurs within the pore spaces of the shale, within vertical fractures or joints of the shale, and adsorbed onto mineral grains and organic material. An assessment conducted by the USGS in 2011 suggested that the Marcellus Shale contains an estimated 84 trillion cubic feet of technically recoverable natural gas (Coleman et al., 2011).

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[78] Four wells were sampled in Susquehanna County during the first round of sampling. Soon after, EPA Region 3 began an investigation of potential drinking water contamination in Dimock, located in Susquehanna County (see http://www.epa.gov/aboutepa/states/pa.html). In order to avoid duplication of effort, this case study focuses on reported changes in drinking water quality in Bradford County. Subsequent sampling for this case study has been, and will continue to be, done in Bradford County.

Water Resources. The average precipitation in Bradford County is 33 inches per year. Summer storms produce about half of this precipitation; the remainder of the precipitation, and much of the ground water recharge, occurs during winter and spring (PADEP, 2012). Surface water in the study area is part of the Upper Susquehanna River Basin. The main branches of the Susquehanna River flow to the south, while the smaller tributaries are constrained by the northeast-southwest orientation of the Appalachian Mountains. Stratified drift aquifers and the Loch Haven and Catskill bedrock formations serve as primary ground water drinking sources in the study area. Glacial till is also tapped as a drinking water source at some locations (Williams et al., 1998). These resources provide water for domestic use, municipal water, manufacturing, irrigation, and hydraulic fracturing.

The stratified drift aquifers in Bradford County occur as either confined or unconfined aquifers. The confined aquifers in the study area are composed of sand and gravel deposits of glacial, ice-contact origin and are typically buried by pro-glacial lake deposits; the unconfined aquifers are composed of sand and gravel deposited by glacial outwash or melt-waters. Depth to ground water varies throughout Bradford County and ranged from 1 to 300 feet for the wells sampled in the study. The median specific capacity of confined stratified drift aquifers is 11 gallons per minute per foot; the median specific capacity of unconfined stratified drift aquifers is 24 gallons per minute per foot (Williams et al., 1998). The specific capacity of wells completed in till or bedrock is typically 10 times lower than in the stratified drift aquifers.

Ground water in the study area is generally of two types: a calcium bicarbonate type in zones of unconfined flow and a sodium chloride type in zones of confined flow. Data from Williams et al. (1998) show that water wells completed in zones with more confined flow contain higher TDS (median concentration of 830 milligrams per liter), dissolved barium (median concentration of 2.0 milligrams per liter), and dissolved chloride (median concentration of 349 milligrams per liter) compared to zones with unconfined flow. This is also true for concentrations of iron and manganese in the study area. Table 53 presents a summary of median and maximum concentrations of inorganic parameters in Bradford County ground water, based on the study conducted by Williams et al. (1998).

Table 53. Background (pre-drill) water quality data for ground water wells in Bradford County, Pennsylvania (Williams et al., 1998).

Parameter	Pre Drill Data		
	Median Concentration (milligrams per liter)	Maximum Concentration (milligrams per liter)	Number of Samples
Arsenic	0.009	0.072	16
Barium	0.175	98	50
Chloride	11	3,500	93
Iron	0.320	15.9	95
Manganese	0.120	1.03	77
TDS	246	6,100	102
pH (pH units)	7.25	8.8	102

Naturally high levels of TDS, barium, and chloride found in ground water make it difficult to assess the potential impacts of hydraulic fracturing activities in this part of the country since these analytes would normally serve as indicators of potential impacts. In addition, methane occurs naturally in ground water in the study area, making an assessment of potential impacts of methane due to hydraulic fracturing on drinking water resources more challenging than at other study locations.

Oil and Gas Exploration and Production. Gas drilling to depths of the Marcellus Shale and beyond dates back to the 1930s, although at that time, the Marcellus Shale was of little interest as a source of gas. Instead, gas was sought primarily from sandstone and limestone deposits, and the Marcellus Shale was only encountered during drilling to deeper targeted zones like the Oriskany Sandstone. Upon penetrating the Marcellus Shale, significant but generally short-lived gas flow would be observed. With the advent of modern hydraulic fracturing technology and the increasing price of gas, the Marcellus Shale has become an economical source of natural gas with the potential to produce several hundred trillion cubic feet (Milici and Swezey, 2006). In July 2008, there were only 48 active permitted natural gas wells in Bradford County; by January 2012, there were 2,015 (Bradford County Government, 2012). The wells are located throughout the county with an average density of actively permitted wells of 1.8 wells per square mile.

7.4.3. Research Approach

Methods for sampling ground water and surface water are described in detail in the QAPP (US EPA, 2012m). The primary objective of this case study is to determine if ground water resources have been impacted, and whether or not those impacts were caused by hydraulic fracturing activities or other sources. Water samples have been taken from domestic wells, springs, ponds, and streams near gas well pads. Figure 33 shows the sampling locations, which were primarily chosen based on individual homeowner complaints or concerns regarding potential adverse impacts to water resources from nearby hydraulic fracturing activities.

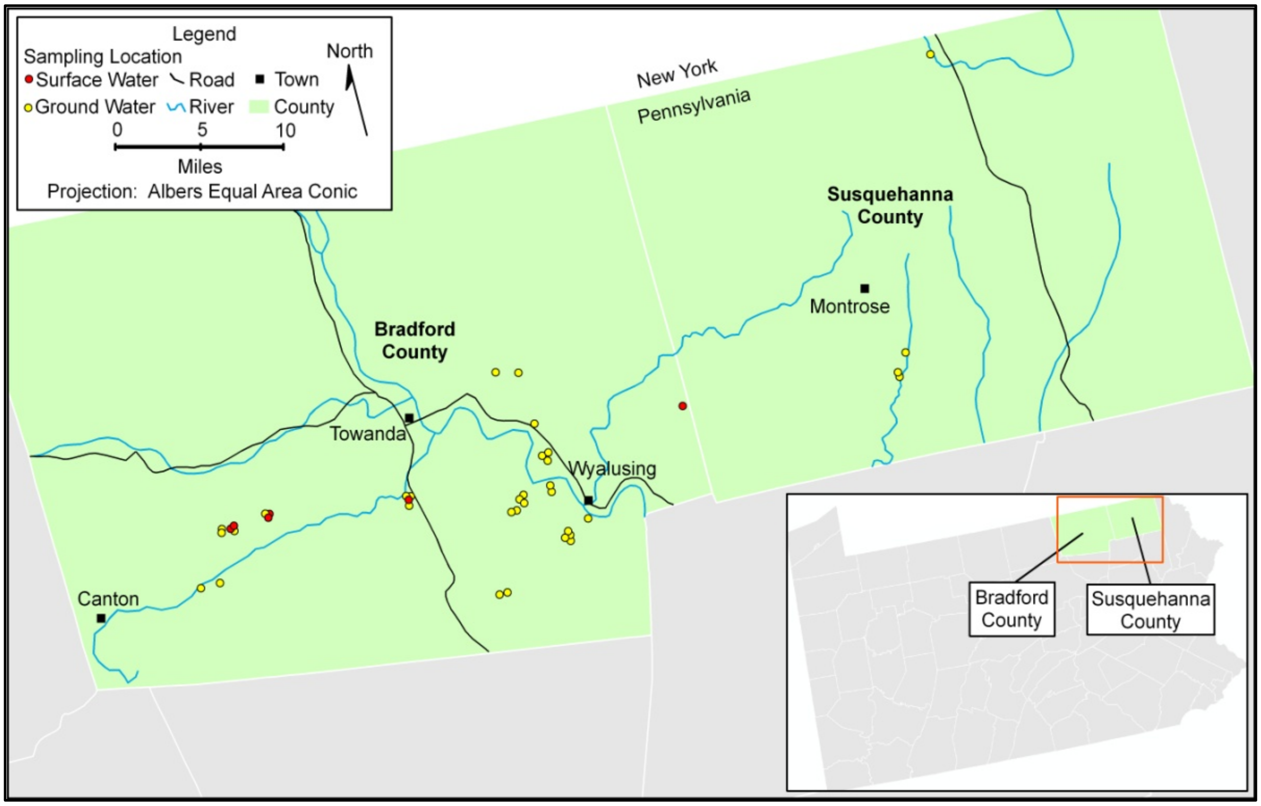

Figure 33. Location of sampling sites in Bradford and Susquehanna Counties, Pennsylvania. Samples were taken in Susquehanna County during the first round of sampling. Later rounds of sampling are focused only in Bradford County.

In addition to the analytes described in Section 7.1.1, the stable isotope compositions of carbon and hydrogen in dissolved methane and of carbon in dissolved inorganic carbon are being measured to determine the potential origin of the methane (i.e., biogenic versus thermogenic).[79] Since methane is known to be naturally present in the ground water of northeastern Pennsylvania, it is critical to understand the origin of any methane detected as part of this case study. Samples are also being analyzed for radium-226, radium-228, and gross alpha and beta radiation, as they may be potential indicators of hydraulic fracturing impacts to ground water in northeast Pennsylvania. Together, these measurements support the objective of determining if ground water resources have been impacted by hydraulic fracturing activities or other sources of contamination.

7.4.4. Status and Preliminary Data

Two rounds of sampling have been completed from 34 domestic wells, two springs, one pond, and one stream. The first sampling round was conducted in October and November of 2011 and the second round in April and May of 2012. The locations of sampling sites are displayed in Figure 33.

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[79] Biogenic methane is formed as methane-producing microorganisms chemically break down organic material. Thermogenic methane results from the geologic formation of fossil fuel.

7.4.5. Next Steps

A third round of sampling to verify data collected from the first two rounds of sampling is already planned. Additional sampling locations may be included and there may be future rounds of sampling as analytical data from the first three rounds are evaluated and additional pertinent information becomes available. More focused investigations may also be conducted, if warranted, at locations where potential impacts associated with hydraulic fracturing are suspected.

7.4.6. Quality Assurance Summary

The initial QAPP for this case study, "Hydraulic Fracturing Retrospective Case Study, Bradford-Susquehanna Couties, PA," was approved by the designated EPA QA Manager on October 3, 2011 (US EPA, 2012m). A revision to the QAPP was made prior to the second sampling event and was approved on April 12, 2012, to address the addition of analytes such as radium-226, radium-228, lithium, and thorium; updated project organization and accreditation information; and clarification on some sampling and laboratory QA/QC issues. There have been no significant deviations from the QAPP during any sampling event, and therefore no impact to data quality. A field TSA was conducted on October 27, 2011; no findings were identified. See Section 7.1.1 for information related to the laboratory TSAs.

As results are reported and raw data are provided from the laboratories, ADQs are performed to verify that the quality requirements specified in the approved QAPP were met. Data will be qualified if necessary, based on these ADQs. The results of these ADQs will be reported in the final report on this project.

7.5. *Washington County, Pennsylvania*

7.5.1. Project Introduction

Washington County, located about 30 miles southwest of Pittsburgh, Pennsylvania, has a population of about 208,000 with approximately 240 people per square mile (USCB, 2010e). Figure 34 shows its position in the western region of the Marcellus Shale. Recently, oil and gas exploration and production in this area have increased, primarily due to production of natural gas from the Marcellus Shale using hydraulic fracturing.

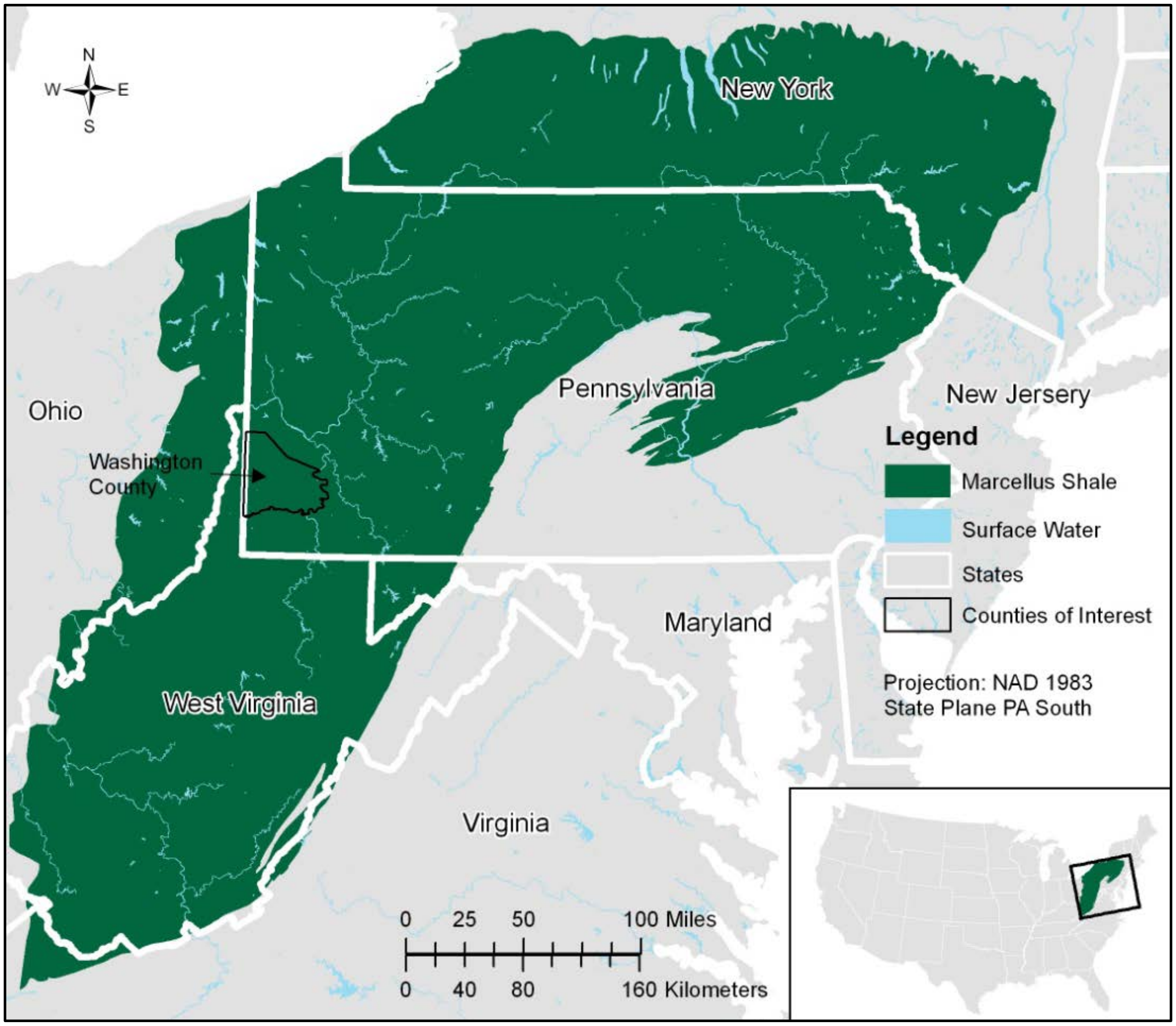

Figure 34. Extent of the Marcellus Shale, which underlies large portions of New York, Ohio, Pennsylvania, and West Virginia (US EIA, 2011d; USCB, 2012a, c). The case study focuses on reported changes in drinking water quality and quantity in Washington County, Pennsylvania.

The location of this case study was chosen in response to homeowner complaints about changes to water quality and water quantity in Washington County. Residents in several areas of Washington County have reported impacts to their private drinking water wells, specifically increased turbidity, discoloration of sinks, and transient organic odors. Sampling locations were selected in May 2011 by interviewing individuals about their water quality and the timing of any possible water quality changes in relation to gas production activities. Potential sources of ground water and surface water contamination under consideration at this case study site may include activities associated with oil and gas production (such as leaking or abandoned pits), gas well completion and enhancement techniques, and improperly plugged and abandoned wells, as well as activities associated with residential and agricultural practices.

7.5.2. Site Background

Geology. Washington County, like Bradford County, is located in the Appalachian Basin. The geology of this area of Pennsylvania consists of thick sequences of Paleozoic Era (Appendix D) sedimentary formations that dip and thicken to the southeast toward the basin axis. The surface geology in Washington County consists of Quaternary alluvial deposits, predominantly in stream valleys of the county. Alluvial deposits are generally less than 60 feet thick and consist of clay, silt, sand, and gravel derived from local bedrock. The formations of the Appalachian Basin are derived from a variety of clastic and biochemical sedimentary deposits, ranging from terrestrial swamps to near-shore environments and deep marine basins, which created shales, limestones, sandstones, coalbeds, and other sedimentary rocks (Shultz, 1999). As previously noted, the Marcellus Shale formation is of particular importance to recent gas exploration and production in the Appalachian Basin. In Washington County, the depth to the Marcellus Shale ranges from about 5,000 to 7,000 feet below ground surface (Marcellus Center for Outreach and Research, 2012a). The thickness of the Marcellus Shale in Washington County is less than 150 feet (Marcellus Center for Outreach and Research, 2012b).

Water Resources. The rivers and streams of Washington County drain into the Ohio River to the west. Drinking water aquifers in the county exist in both the alluvial deposits overlying bedrock in the stream valleys and in the bedrock. Ground water flow in the shallow aquifer system generally follows the topography, moving from recharge areas near hilltops to discharge areas in valleys.

Background information on the geology and hydrology of Washington County is summarized from reports published by Newport (1973) and Williams et al. (1993). Ground water in Washington County occurs in both confined and unconfined aquifers, with well yields ranging from a fraction of a gallon per minute to over 350 gallons per minute. In this area, water-bearing zones are generally no deeper than 150 feet below ground surface, and the depth to water varies from 20 to 60 feet below land surface depending on topographic setting. In addition to alluvial aquifers, ground water is derived from bedrock aquifers, including the Monongahela Group, the Conemaugh Group, and the Greene and Washington formations, which consist of limestones, shales, and sandstone units. In general, ground water derived from these formations has yields ranging from less than 1 to over 70 gallons per minute, and the formations range in depth from less than 40 feet to over 400 feet. The Conemaugh Group generally provides the greatest yield; the median yield for wells in this aquifer is 5 gallons per minute.

The quality of ground water in Washington County is variable and depends on factors such as formation lithology and residence time. For example, recharge ground water sampled from hilltops and hillsides is typically calcium-bicarbonate type and usually low in TDS (about 500 milligrams per liter). Ground water from valley settings in areas of discharge is typically sodium-bicarbonate or sodium-chloride type, with higher TDS values (up to 2,000 milligrams per liter). Williams et al.

(1993) report that background concentrations of iron and manganese in the ground water from Washington County are frequently above the EPA's secondary MCLs: over 33% of water samples had iron concentrations greater than 0.3 milligrams per liter, and 30% of water samples had manganese concentrations above 0.05 milligrams per liter. Hard water was also reported as being a common problem in the county, with TDS levels in more than one-third of the wells sampled by Williams et al. (1993) exceeding 500 milligrams per liter. Arsenic, cadmium, chromium, copper, lead, mercury, selenium, silver, and zinc were also detected at low levels. Historically, ground water quality in Washington County has been altered due to drainage from coal mining operations (Newport, 1973). Additionally, fresh water aquifers in some locations have been contaminated by brine from deeper non-potable aquifers through historic oil and gas wells that were improperly abandoned or have corroded casings (Newport, 1973).

Oil and Gas Exploration and Production. The oil and gas development in Washington County dates back to the 1800s, but generally did not target the Marcellus Shale (Ashley and Robinson, 1922). The first test gas well into the Marcellus Shale was drilled in Mount Pleasant Township in Washington County in 2003 and was hydraulically fractured in 2004. Data provided by the Pennsylvania Department of Environmental Protection indicate that the number of permitted gas wells in the Washington County area of the Marcellus Shale increased rapidly, from 10 wells in 2005 to 205 wells in 2009 (MarcellusGas.Org, 2012b). From 2009 to 2012, the number of newly permitted wells per year has remained below 240 (MarcellusGas.Org, 2012c). The anticipated water usage for all permitted wells in Washington County is estimated to be nearly 5 billion gallons (MarcellusGas.Org, 2012a).

7.5.3. Research Approach

Methods for sampling ground water and surface water are described in detail in the QAPP (US EPA, 2012n). Samples have been taken from domestic wells and surface water bodies. The EPA chose sampling locations by interviewing individuals about their water quality and the timing of water quality changes in relation to gas production activities. The locations of sampling sites are shown in Figure 35.

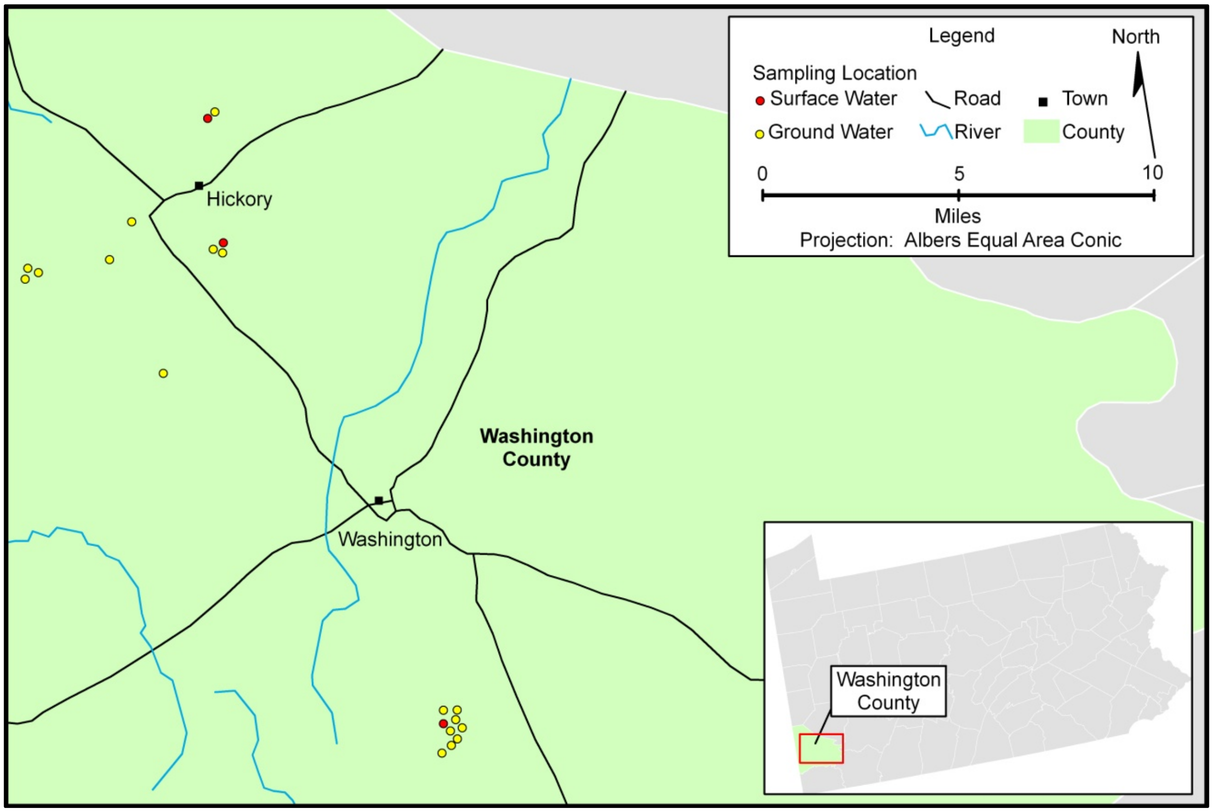

Figure 35. Sampling locations in Washington County, Pennsylvania.

Water samples collected at these locations are being analyzed for the chemicals listed in Section 7.1.1 as well as the chemicals listed in the QAPP (US EPA, 2012n). Together these measurements support the objective of determining if ground water resources have been impacted by hydraulic fracturing activities, or other sources of contamination.

7.5.4. Status and Preliminary Data

Two rounds of sampling have been completed: the first in July 2011 and the second in March 2012. During July 2011, 13 domestic wells and three surface water locations (small streams and spring discharges) were sampled. During March 2012, 13 domestic wells and two surface water locations were sampled. The locations of sampling sites are displayed in Figure 35.

7.5.5. Next Steps

Additional sampling rounds will be conducted to verify data collected from the first two rounds of sampling. Additional sampling locations may be included in the future as analytical data is evaluated and additional pertinent information becomes available. More focused investigations may also be conducted, if warranted, at locations where impacts associated with hydraulic fracturing may have occurred.

7.5.6. Quality Assurance Summary

The initial QAPP for this case study, "Hydraulic Fracturing Retrospective Case Study, Marcellus Shale, Washington County, PA," was approved by the designated EPA QA Manager on July 21, 2011 (US EPA, 2012n). A revision to the QAPP was made before the second sampling event and was approved on March 5, 2012, to update project organization, lab accreditation information, sampling methodology, to add radium isotope analyses and gross alpha/beta analyses, to modify critical analytes, and to change the analytical method for determining water isotope values. There have been no significant deviations from the QAPP during any sampling event, and therefore no impact on data quality. A field TSA was conducted on March 26, 2011; no findings were identified. See Section 7.1.1 for information related to the laboratory TSAs.

As results are reported and raw data are provided from the laboratories, ADQs are performed to verify that the quality requirements specified in the approved QAPP were met. Data will be qualified if necessary, based on these ADQs. The results of these ADQs will be reported in the final report on this project.

7.6. Wise County, Texas

7.6.1. Project Introduction

Wise County, Texas, is mostly rural, with a total population of about 60,000 and about 66 people per square mile (USCB, 2010f). Current gas development activities in Wise County are in the Barnett Shale, which is an unconventional shale in the Fort Worth Basin adjoining the Bend Arch Basin of north-central Texas. Figure 36 shows the extent of the Barnett Shale in Texas. In recent years, gas production in Wise County has increased due to improvements in horizontal drilling and hydraulic fracturing technologies.

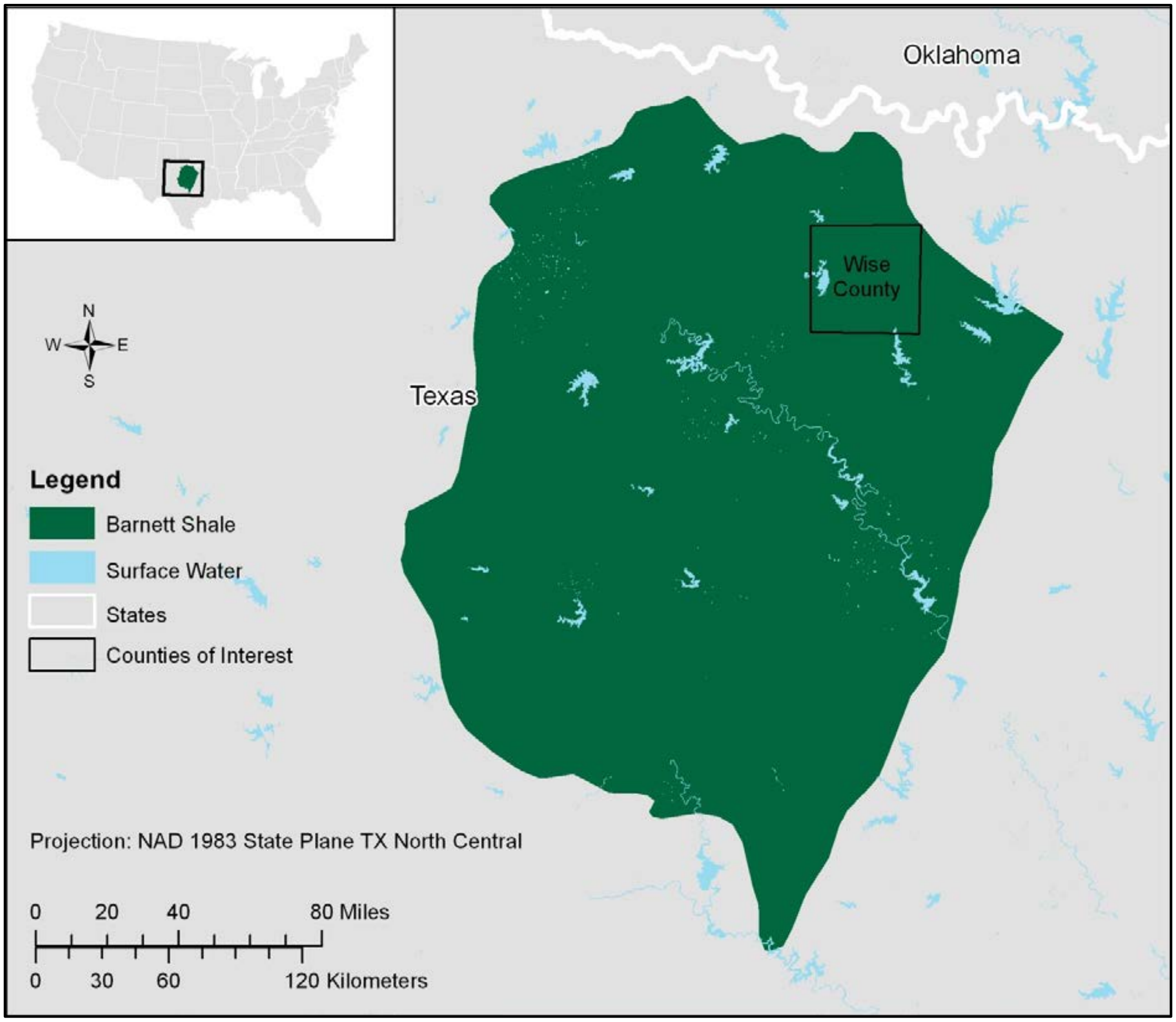

Figure 36. Extent of the Barnett Shale in north-central Texas (US EIA, 2011e; USCB, 2012a, c). The case study focuses on three distinct locations within Wise County.

The intent of this case study is to investigate homeowner concerns about changes in the ground water quality in Wise County that may be related to the recent increase in the hydraulic fracturing of oil and gas wells. Sampling locations in Wise County were chosen based on reported complaints of changes in drinking water quality and are clustered in three distinct locations: two near Decatur and one near Alvord. Homeowners in the two locations near Decatur reported changes in water quality, including changes in turbidity, color, smell, and taste. Homeowners near Alvord also reported changes in drinking water quality, although no more specific concerns were identified. Concerns about potential hydraulic fracturing impacts to ground water resources in Wise County are related to flowback fluid discharge to shallow aquifers, gas migration to shallow aquifers, spills on well pads, and leaking impoundments. Residential or agricultural practices, or aquifer drawdown unrelated to oil and gas development, may also be sources of ground water contamination at these sites.

7.6.2. Site Background

Geology. Wise County is located in the Bend Arch-Fort Worth Basin, which was formed during the late Paleozoic Ouachita Orogeny by the convergence of Laurussia and Gondwana in a narrow, restricted, inland seaway (Bruner and Smosna, 2011). The stratigraphy of the Bend Arch-Fort Worth Basin is characterized by limestones, sandstones, and shales. The Barnett Shale is of Mississippian age (Appendix D) and extends throughout the Bend Arch-Fort Worth Basin: south from the Muenster Arch, near the Oklahoma border, to the Llano Uplift in Burnet County and west from the Ouachita Thrust Front, near Dallas, to Taylor County (Bruner and Smosna, 2011). The Barnett Shale ranges from about 50 to 1,000 feet thick and occurs at depths ranging from 4,000 to 8,500 feet (Bruner and Smosna, 2011). In the northeastern portion of the Fort Worth Basin, the Barnett Shale is divided by the presence of the Forestburg Limestone, but this formation tapers out toward the southern edge of Wise County (Bruner and Smosna, 2011). The Barnett Shale is bounded by the Chappel Limestone below it and the Marble Falls Limestone above it (Bruner and Smosna, 2011). A recent estimate of the potential total gas yield was 820 billion cubic feet of gas per square mile, which is a significant increase from earlier estimates (Bruner and Smosna, 2011).

Water Resources. Wise County is drained by the Trinity River. Residents in the county often rely on the Trinity Aquifer as a major source of drinking water. In addition to drinking water, the Trinity Aquifer is also used for irrigation, industrial water, and hydraulic fracturing source water. The aquifer is composed of three formations, deposited in the Cretaceous: Paluxy, Glen Rose, and Twin Mountain (Nordstrom, 1982; Reutter and Dunn, 2000; Scott and Armstrong, 1932). In the northern part of Wise County, the Glen Rose formation pinches out, leaving only the Paluxy and Twin Mountain Formations, which together are occasionally referred to as the Antlers Formation (Nordstrom, 1982; Reutter and Dunn, 2000). The composition of the Paluxy Formation is fine sand, sandy shale, and shale and yields small to moderate quantities of water (Nordstrom, 1982). The Glen Rose Formation is composed of limestone, marl, shale, and anhydrite. The Glen Rose yields small quantities of water in localized areas (Nordstrom, 1982). Finally, the composition of the Twin Mountain Formation is fine to coarse sand, shale, clay, and basal gravel and conglomerate. This formation yields moderate to large quantities of water (Nordstrom, 1982). The Trinity Aquifer is overlain by the Walnut Creek Formation and is underlain by Graham Formation, both of which act as confining layers (Scott and Armstrong, 1932). Before modern water usage, it was artesian.

Table 54 summarizes background water quality data for the Trinity Aquifer in Wise County (Reutter and Dunn, 2000). The water quality is expected to be slightly different in the northern portion of the county than the southern portion of the county due to the “pinching out” of the Glen Rose Formation. From the reported data, the major water types in Wise County are calcium bicarbonate, calcium chloride, and sodium bicarbonate (Reutter and Dunn, 2000). All three water types are present in northern Wise County, but only the calcium bicarbonate and calcium chloride water types were observed in southern Wise County. The data collected at study locations will be compared to this compiled background data as part of the initial screening to determine if any contamination has occurred in study locations.

Table 54. Background water quality data for all of Wise County, Texas, and its northern and southern regions (Reutter and Dunn, 2000). Range of concentrations shown, with median values reported in parentheses.

Parameter	Units	Concentration Ranges		
		Wise County	North Wise County	South Wise County
Alkalinity	mg CaCO$_3$/L	130–430 (335)	190–430 (330)	130–420 (360)
Aluminum	µg/L	1–5 (2)	2–5 (2)	1–5 (2)
Ammonia	mg N/L	<0.01–1.10 (0.06)	<0.01–0.57 (0.6)	0.01–1.10 (0.10)
Antimony	µg/L	<1	<1	<1
Arsenic	µg/L	<1–4 (2)	<1–4 (3)	<1–2 (2)
Barium	µg/L	24–990 (95)	28–990 (95)	24–200 (94)
Beryllium	µg/L	<1	<1	<1
Bicarbonate	mg HCO$_3$/L	160–527 (407)	230–527 (406)	160–517 (424)
Bromide	mg/L	0.03–8.40 (0.22)	0.03–8.40 (0.18)	0.03–3.00 (0.30)
Cadmium	µg/L	<1	<1	<1
Calcium	mg/L	1–570 (88)	62–570 (110)	1–200 (70)
Chloride	mg/L	5–1,300 (45)	12–1,300 (194)	5–500 (49)
Chromium	µg/L	<1–8 (5)	<1–2 (1)	1–8 (5)
Cobalt	µg/L	<1	<1	<1
Copper	µg/L	<1–18 (5)	<1–8 (3)	<1–8 (7)
Fluoride	mg/L	<0.10–1.20 (0.20)	<0.10–0.60 (0.20)	<0.10–1.20 (0.20)
Iron	mg/L	<3–4,400 (10)	<3–4,400 (27)	<3–160 (9)
Lead	µg/L	<1–5 (2)	<1	<1–5 (2)
Magnesium	mg/L	1–86 (18)	2.8–65 (33)	1–86 (9)
Manganese	µg/L	<1–140 (27)	<1–140 (49)	<1–27 (4)
Molybdenum	µg/L	<1–2 (1)	<1	<1–2 (1)
Nickel	µg/L	<1–6 (1)	<1–6 (2)	<1–4 (1)
Nitrate + nitrite	mg N/L	<0.05–7.20 (1.70)	<0.05–7.20 (2.30)	<0.05–6.30 (1.25)
pH	pH units	6.6–9.1 (7.1)	6.7–7.8 (7.0)	6.6–9.1 (7.2)
Phosphate	mg P/L	<0.01–0.40 (0.03)	<0.01–0.03 (0.02)	<0.01–0.40 (0.04)
Potassium	mg/L	0.6–4.6 (2.4)	1–4.6 (2.7)	0.6–3.8 (1.9)
Selenium	µg/L	<1–14 (2)	<1–3 (2)	<1–14 (3)
Silica	mg/L	8.8–26 (19.5)	17–24 (20)	9–26 (19)
Silver	µg/L	<1	<1	<1
Sodium	mg/L	10–310 (58)	18–220 (51)	10–310 (87)

Table continued on next page

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Parameter	Units	Concentration Ranges		
		Wise County	North Wise County	South Wise County
Specific conductance	µS/cm	710–4,590 (913)	71–4,590 (911)	510–2,380 (914)
Sulfate	mg/L	10–250 (46)	26–250 (45)	10–160 (46)
Uranium	µg/L	<1–93 (4)	<1–93 (4)	<1–13 (5)
Zinc	µg/L	1–590 (18)	4–590 (18)	1–96 (18)

Oil and Gas Exploration and Production. Wise County has experienced a dramatic increase in gas production from the Barnett Shale since the late 1990s, concurrent with the recent improvements in hydraulic fracturing and horizontal drilling technologies (RRC, 2012). From 2003 to 2011, Wise County gas production increased almost 10-fold, from approximately 200 to 1,800 billion cubic feet (RRC, 2012).

7.6.3. Research Approach

A detailed description of this study's sampling methods and procedures can be found in the QAPP (US EPA, 2012p). Sampling in Wise County includes surface water, industrial wells, and homeowners' domestic wells in three general locations, as shown in Figure 37. Because of the standard water well design in Wise County,[80] it is not possible to sample directly from these drinking water wells, nor is it possible to measure water levels to establish ground water flow gradients and direction. Instead, both domestic and industrial wells are sampled at a tap as close to the wellhead as possible and before any water treatment has occurred.[81]

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[80] The water wells in Wise County are sealed, with no access ports. To sample the wells directly, it would require a crane or drilling rig to pull the pump string out of the well, due to the weight of the pump string, safety concerns, and costs.

[81] To control for the possible effects of household plumbing, sampling of the domestic wells at or near the well head is done upstream of the home, and the sampled water never enters the home plumbing or water treatment systems. The wells are purged at 8–30 gallons per minute for at least 30 minutes before the flow is reduced. The initial purge is such that an estimated three screen volumes of water are purged from the well. After that, the purge rate is reduced to less than 2 liters per minute and is continued until stable geochemical parameters are obtained.

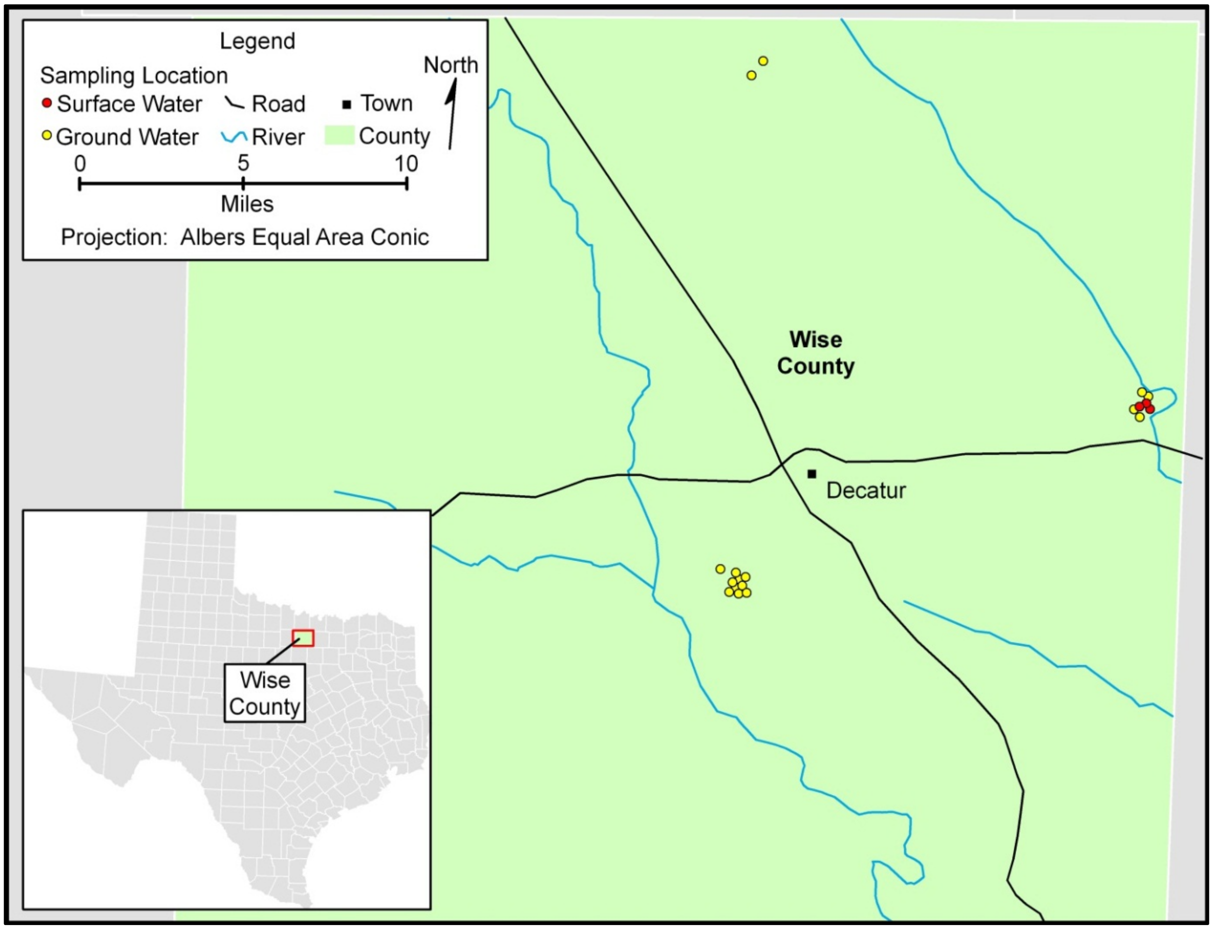

Figure 37. Location of sampling sites in Wise County, Texas.

Water samples collected at these locations are being analyzed for the chemicals listed in Section 7.1.1 as well as the chemicals listed in the QAPP (US EPA, 2012p). Together these measurements support the objective of determining if ground water resources have been impacted by hydraulic fracturing activities, or other sources of contamination.

7.6.4. Status and Preliminary Data

Two rounds of sampling have been conducted at all locations in Wise County: one round in September 2011 and one round in March 2012. The September 2011 sampling event included 11 domestic wells, one industrial well, and three surface water (pond) samples. The March 2012 sampling event included the same wells as the September 2011 sampling event, with an additional four domestic wells and the loss of one domestic well. The locations of all sampling sites are displayed in Figure 37.

7.6.5. Next Steps

Additional sampling rounds will be conducted to verify data collected from the first two rounds of sampling. Additional sampling locations may be included in the future as analytical data are evaluated and additional pertinent information becomes available. More focused investigations may also be conducted, if warranted, at locations where impacts may have occurred.

7.6.6. Quality Assurance Summary

The initial QAPP for this case study, "Hydraulic Fracturing Retrospective Case Study, Wise, TX," was approved by the designated EPA QA Manager on June 20, 2011 (US EPA, 2012p). A revision to the QAPP was made before the second sampling event and was approved on February 27, 2012. The revision included the addition of isotopic analysis, USGS laboratory information,[82] revised sampling locations, Region 8 laboratory accreditation status, geophysical measurement methods and QC, data qualifiers, personnel changes, and analytical method updates. A second revision was approved on May 25, 2012, for the next sampling event to include the Phase 2 sampling information, the method for qualifying field blanks, and the modified sampling schedule. The second QAPP revision also replaced EPA Method 200.7 with 6010C and replaced metals QC criteria with revised criteria. A third revision to the QAPP was approved on September 10, 2012, to add information on March 2012 sampling, add strontium and stable water isotopes to analytes list, and delete diesel range organics and gasoline range organics. The third QAPP revision also replaced EPA Method 6010C with 200.7.[83] There have been no significant deviations from the QAPP during any sampling event, and therefore no impact on data quality. A field TSA was conducted on September 21, 2011; no findings were identified. See Section 7.1.1 for information related to the laboratory TSAs.

As results are reported and raw data are provided from the laboratories, ADQs are performed to verify that the quality requirements specified in the approved QAPP were met. Data will be qualified if necessary, based on these ADQs. The results of these ADQs will be reported in the final report on this project.

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[82] USGS provided isotope support for the Wise County retrospective case study. A detailed account of the role of USGS can be found in Appendix A of the Wise County QAPP.

[83] EPA Method 200.7 was referenced in the initial QAPP and the first QAPP revision. It was changed in the second QAPP revision to EPA Method 6010C, but since then it was determined by QA staff that the use of 200.7 as the "base" method was appropriate as 200.7 incorporates 6010C by reference.

8. Conducting High-Quality Science

The EPA ensures that its research activities result in high-quality science through the use of QA and peer review activities. Specific 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. Peer review ensures that the data are sound and used appropriately. The use of QA measures and peer review helps ensure that the EPA conducts high-quality science that can be used to inform policymakers, industry, and the public.

8.1. Quality Assurance

All agency research projects that generate or use environmental data to make conclusions or recommendations must comply with the EPA QA program requirements. The EPA laboratories and external organizations involved with the generation or use of environmental data are supported by QA professionals who oversee the implementation of the QA program for their organization. To ensure scientifically defensible results, this study complies with the agency-wide Quality Policy CIO 2106 (US EPA, 2008), EPA Order CIO 2105.0 (US EPA, 2000a, c), the EPA's Information Quality Guidelines (US EPA, 2002), the EPA's Laboratory Competency Policy (US EPA, 2004a), and Chapter 13 of the Office of Research and Development's *Policies and Procedures Manual* (US EPA, 2006).

Given the cross-organizational nature of this study, a Quality Management Plan was developed (US EPA, 2012t) and a Program QA Manager was chosen to coordinate a rigorous QA approach and oversee its implementation across all participating organizations within the EPA. The Quality Management Plan defines the QA-related policies, procedures, roles, responsibilities, and authorities for the study and documents how the EPA will plan, implement, and assess the effectiveness of its QA and QC operations. In light of the importance and organizational complexity of the study, the Quality Management Plan was created to make certain that all research be conducted with integrity and strict quality controls.

The Quality Management Plan sets forth the following rigorous QA approach:

- Individual research projects must comply with agency requirements and guidance for QAPPs.
- TSAs and audits of data quality will be conducted for individual research projects as described in the QAPPs.
- Performance evaluations of analytical systems will be conducted.
- Products will undergo QA review. Applicable products may include reports, journal articles, symposium/conference papers, extended abstracts, computer products/ software/models/databases, and scientific data.
- Reports will have readily identifiable QA sections.

Research records will be managed according to EPA Records Schedule 501, "Applied and Directed Scientific Research"(US EPA, 2011c).

The Quality Management Plan applies to all research activities conducted under the EPA's *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*. More information about specific QA protocols, including management, organization, quality-system components, personnel qualification and training, procurement of items and services, documentation and records, computer requirements, planning, implementation, assessment, and quality improvement, can be found in the Quality Management Plan.[84]

Project-specific details of individual research projects are documented in a QAPP. All work performed or funded by the EPA that involves the acquisition of environmental data must have an approved QAPP. The QAPP documents the planning, implementation, and assessment procedures for a particular project, as well as any specific QA and QC activities. It integrates all the technical and quality aspects of the project in order to provide a guide for obtaining the type and quality of environmental data and information needed for a specific decision or use. Quality assurance project plans are living documents that undergo revisions as needed. Individual QAPPs for the various research projects included in this study are available on the study website (http://www.epa.gov/hfstudy) and are summarized in Appendix C.

Regular technical assessments of project operation, systems, and data related to the study are conducted as detailed in the Quality Management Plan. A technical assessment is "a systematic and objective examination of a project to determine whether environmental data collection activities and related results comply with the project's QAPP, whether the activities are implemented effectively, and whether they are sufficient and adequate to achieve QAPP's data quality goals" (US EPA, 2000b). Assessment components include quality system assessments, technical system assessments, verification of data, audits of data quality, and surveillance. More details about assessments and audits required for this study can be found in the Quality Management Plan and project-specific QAPPs.

Quality Assurance and Projects Involving the Generation of New Data. Research projects that generate new data (e.g., case studies, laboratory studies, some toxicity assessments) will contribute to the growing body of scientific literature about environmental issues associated with hydraulic fracturing. The QA/QC procedures detailed in these QAPPs meet the requirements of the hydraulic fracturing Quality Management Plan, detailed above, and also focus on those practices necessary for assuring the quality of measurement data generated by the EPA. Samples must be collected, preserved, transported, and stored in a manner that retains their integrity; these issues are addressed in individual QAPPs. Also described in QAPPs are the methods used for sample analysis, including details about the appropriate frequency of calibration of analytical instrumentation and measurement devices. Quality control samples are identified that can be used to check for potential contamination of samples and to check for measurement errors that can be caused by difficult sample matrices. The QAPPs for generation of new data provide details on the logistics of who, where, when and how new data will be generated.

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[84] Research initiated prior to the implementation of the study-specific Quality Management Plan was conducted under Quality Management Plans associated with each of the EPA Office of Research and Development's individual labs and centers.

Quality Assurance and Projects Involving Existing Data. Research projects that involve acquiring and analyzing existing data (i.e., data that are not new data generated by or for the EPA) must conform to the requirements of the Quality Management Plan, including the development of a QAPP. The focus of QAPPs for existing data is on setting criteria that will filter out any data that are of insufficient quality to meet project needs. This starts with describing the process for locating and acquiring the data. How the data will be evaluated for their planned use and how the integrity of the data will be maintained throughout the collection, storing, evaluation, and analysis processes are also important features of a QAPP for existing data.

Quality Assurance and Report Preparation. Quality assurance requirements also extend to the two primary products of this study: this progress report and the report of results. As required by the Quality Management Plan, this progress report has undergone QA review before its release, and the report of results will do the same. These requirements serve to ensure that the reports are defensible and scientifically sound.

8.2. Peer Review

Peer review, an important part of every scientific study, is a documented critical review of a specific scientific and/or technical work product (e.g., paper, report, presentation). It is an in-depth assessment of the assumptions, calculations, extrapolations, alternate interpretations, methodology, acceptance criteria, and conclusions in the work product and the documents that support them. Peer review is conducted by individuals (or organizations) independent of those who performed the work and equivalent in technical expertise (US EPA, 2012e; US OMB, 2004). Feedback from the review process is used to revise the draft product to make certain the final work product reflects sound technical information and analyses.

Peer review can take many forms depending on the nature of the work product. Work products generated through the EPA's *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* will be subjected to both internal and external peer review. Internal peer review occurs when work products are reviewed by independent experts within the EPA, while external peer review engages experts outside of the agency, often through scientific journals, letter reviews, or *ad hoc* panels.

The EPA often engages the Science Advisory Board, an external federal advisory committee, to conduct peer reviews of high-profile scientific matters relevant to the agency. Members of an *ad hoc* panel convened under the auspices of the Science Advisory will provide comment on this progress report.[85] Panel members are nominated by the public and chosen based on factors such as technical expertise, knowledge, experience, and absence of any real or perceived conflicts of interest to create a balanced review panel. In August 2012, the EPA issued a *Federal Register* notice requesting public nominations for technical experts to form a Science Advisory Board *ad hoc* panel to provide advice on the status of the research described in this progress report (US EPA, 2012v). This panel is

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

also expected to review the report of results, which has been classified as a Highly Influential Scientific Assessment.[86]

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[86] The Office of Management and Budget's Peer Review Bulletin (US OMB, 2004) defines Highly Influential Scientific Assessments as scientific assessments that could (1) have a potential impact of more than $500 million in any year or (2) are novel, controversial, or precedent-setting or have significant interagency interest. The Peer Review Bulletin describes specific peer review requirements for Highly Influential Scientific Assessments.

9. Research Progress Summary and Next Steps

This report describes the progress made for each of the research projects conducted as part of the EPA's *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*. This chapter provides an overview of the progress made for each research activity as well as the progress made for each stage of the water cycle presented in Section 2.1. It also describes, in more detail, the report of results.

9.1. Summary of Progress by Research Activity

The EPA is using a transdisciplinary research approach to investigate the potential relationship between hydraulic fracturing and drinking water resources. This approach includes compiling and analyzing data from existing sources, evaluating scenarios using computer models, carrying out laboratory studies, assessing the toxicity associated with hydraulic fracturing-related chemicals, and conducting case studies.

Analysis of Existing Data. To date, data from seven sources have been obtained for review and ongoing analysis, including:

- Information provided by nine hydraulic fracturing service companies.
- 333 well files supplied by nine oil and gas operators.
- Over 12,000 chemical disclosure records from FracFocus, the national hydraulic fracturing chemical registry managed by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission.
- Spill reports from four different sources, including databases from the National Response Center, Colorado, New Mexico, and Pennsylvania.

As part of its literature review, the EPA has compiled, and continues to search for, literature relevant to the secondary research questions listed in Section 2.1. This includes documents provided by stakeholders and recommended by the Science Advisory Board during its review of the draft study plan.[87] A *Federal Register* notice requesting peer-reviewed data and publications relevant to the study, including information on advances in industry practices and technologies, has recently been published (US EPA, 2012u).

Scenario Evaluations. Potential impacts to drinking water sources from withdrawing large volumes of water in both a semi-arid and a humid river basin—the Upper Colorado River Basin in the west and the Susquehanna River Basin in the east—are being assessed. Additionally, complex computer models are being used to explore the possibility of subsurface gas and fluid migration from deep shale formations to overlying aquifers in six different scenarios. These scenarios include poor well

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[87] Additional information on the Science Advisory Board review of the EPA's *Draft Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* is available at http://www.epa.gov/hfstudy/peer-review.html.

construction and hydraulic communication via fractures (natural and created) and nearby existing wells. As a first step, the subsurface migration simulations will examine realistic scenarios to assess the conditions necessary for hydraulic communication rather than the probability of migration occurring. In a separate research project, the EPA is using surface water transport models to estimate concentrations of bromide and radium at public water supply intakes downstream from wastewater treatment facilities that discharge treated hydraulic fracturing wastewater.

Laboratory Studies. The ability to analyze and determine the presence and concentration of chemicals in environmental samples is critical to the EPA's study. In most cases, standard EPA methods are being used for laboratory analyses. In other cases, however, standard methods do not exist for the low-level detection of chemicals of interest or for use in the complex matrices associated with hydraulic fracturing wastewater. Where necessary, existing analytical methods are being tested, modified, and verified for use in this study and by others. Analytical methods are currently being tested and modified for several classes of chemicals, including glycols, acrylamides, ethoxylated alcohols, DBPs, radionuclides, and inorganic chemicals.

Laboratory studies focusing on the potential impacts of inadequate treatment of hydraulic fracturing wastewater on drinking water resources are being planned and conducted. The studies include assessing the ability of hydraulic fracturing wastewater to create brominated DBPs and testing the efficacy of common wastewater treatment processes on removing selected contaminants from hydraulic fracturing wastewater. Samples of surface water, raw hydraulic fracturing wastewater, and treated effluent have been collected for the source apportionment studies, which aim to identify the source of high chloride and bromide levels in rivers accepting treated hydraulic fracturing wastewater.

Toxicity Assessment. The EPA has evaluated data to identify chemicals reportedly used in hydraulic fracturing fluids from 2005 to 2011 and chemicals found in flowback and produced water. Appendix A contains tables of these chemicals, with over 1,000 chemicals identified. Chemical, physical, and toxicological properties have been compiled for chemicals with known chemical structures. Existing models are being used to estimate properties in cases where information is lacking. At this time, the EPA has not made any judgment about the extent of exposure to these chemicals when used in hydraulic fracturing fluids or found in hydraulic fracturing wastewater, or their potential impacts on drinking water resources.

Case Studies. Two rounds of sampling at all five retrospective case study locations have been completed. In total, water samples have been collected from over 70 domestic water wells, 15 monitoring wells, and 13 surface water sources, among others. A third round of sampling is expected to occur this fall in Las Animas and Huerfano Counties, Colorado; Dunn County, North Dakota; and Wise County, Texas. Additional sampling in Bradford and Washington Counties, Pennsylvania, is projected to take place in spring 2013.

The EPA continues to work with industry partners to plan and begin research activities for prospective case studies.

9.2. Summary of Progress by Water Cycle Stage

Figures 38 and 39 illustrate the research underway for each stage of the hydraulic fracturing water cycle. The fundamental research questions and research focus areas are briefly described below for each water cycle stage; for more detail on the stages of the hydraulic fracturing water cycle and their associated research projects, see Section 2.1.

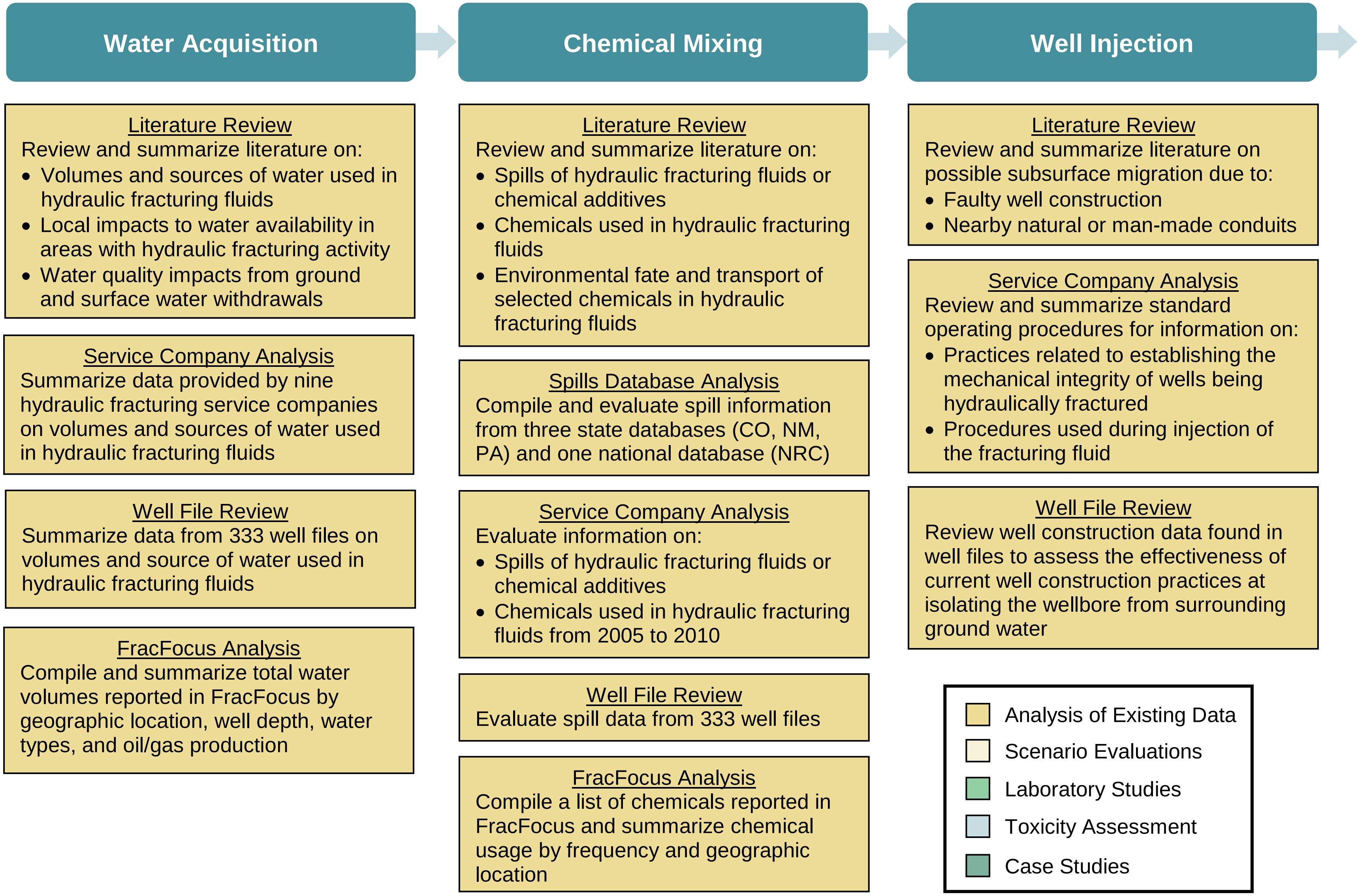
Water Acquisition: What are the possible impacts of large volume water withdrawals from ground and surface waters on drinking water resources? Work in this area focuses on understanding the volumes and sources of water needed for hydraulic fracturing operations, and the potential impacts of water withdrawals on drinking water quantity and quality. Effects of recently emerging trends in water recycling will be considered in the report of results.

Chemical Mixing: What are the possible impacts of surface spills on or near well pads of hydraulic fracturing fluids on drinking water resources? Spill reports from several databases are being reviewed to identify volumes and causes of spills of hydraulic fracturing fluids and wastewater. Information on the chemicals used in hydraulic fracturing fluids and their known chemical, physical, and toxicological properties has been compiled.

Well Injection: What are the possible impacts of the injection and fracturing process on drinking water resources? Work currently underway is focused on identifying conditions that may be associated with the subsurface migration of gases and fluids to drinking water resources. The EPA is exploring gas and fluid migration due to inadequate well construction as well as the presence of nearby natural faults and fractures or man-made wells.

Flowback and Produced Water: What are the possible impacts of surface spills on or near well pads of flowback and produced water on drinking water resources? As with chemical mixing, research in this area focuses on reviewing spill reports of flowback and produced water as well as collecting information on the composition of hydraulic fracturing wastewater. Known chemical, physical, and toxicological properties of the components of flowback and produced water are being compiled.

Wastewater Treatment and Waste Disposal: What are the possible impacts of inadequate treatment of hydraulic fracturing wastewater on drinking water resources? Work in this area focuses on evaluating treatment and disposal practices for hydraulic fracturing wastewater. Since some wastewater is known to be discharged to surface water after treatment in POTWs or commercial treatment systems, the EPA is investigating the efficacy of common treatment processes at removing selected components in flowback and produced water. Potential impacts to downstream public water supplies from discharge of treated hydraulic fracturing wastewater are also being investigated, including the potential for the formation of Br-DBPs.



Water Acquisition

Literature Review
Review and summarize literature on:
- Volumes and sources of water used in hydraulic fracturing fluids
- Local impacts to water availability in areas with hydraulic fracturing activity
- Water quality impacts from ground and surface water withdrawals

Service Company Analysis
Summarize data provided by nine hydraulic fracturing service companies on volumes and sources of water used in hydraulic fracturing fluids

Well File Review
Summarize data from 333 well files on volumes and source of water used in hydraulic fracturing fluids

FracFocus Analysis
Compile and summarize total water volumes reported in FracFocus by geographic location, well depth, water types, and oil/gas production

Chemical Mixing

Literature Review
Review and summarize literature on:
- Spills of hydraulic fracturing fluids or chemical additives
- Chemicals used in hydraulic fracturing fluids
- Environmental fate and transport of selected chemicals in hydraulic fracturing fluids

Spills Database Analysis
Compile and evaluate spill information from three state databases (CO, NM, PA) and one national database (NRC)

Service Company Analysis
Evaluate information on:
- Spills of hydraulic fracturing fluids or chemical additives
- Chemicals used in hydraulic fracturing fluids from 2005 to 2010

Well File Review
Evaluate spill data from 333 well files

FracFocus Analysis
Compile a list of chemicals reported in FracFocus and summarize chemical usage by frequency and geographic location

Well Injection

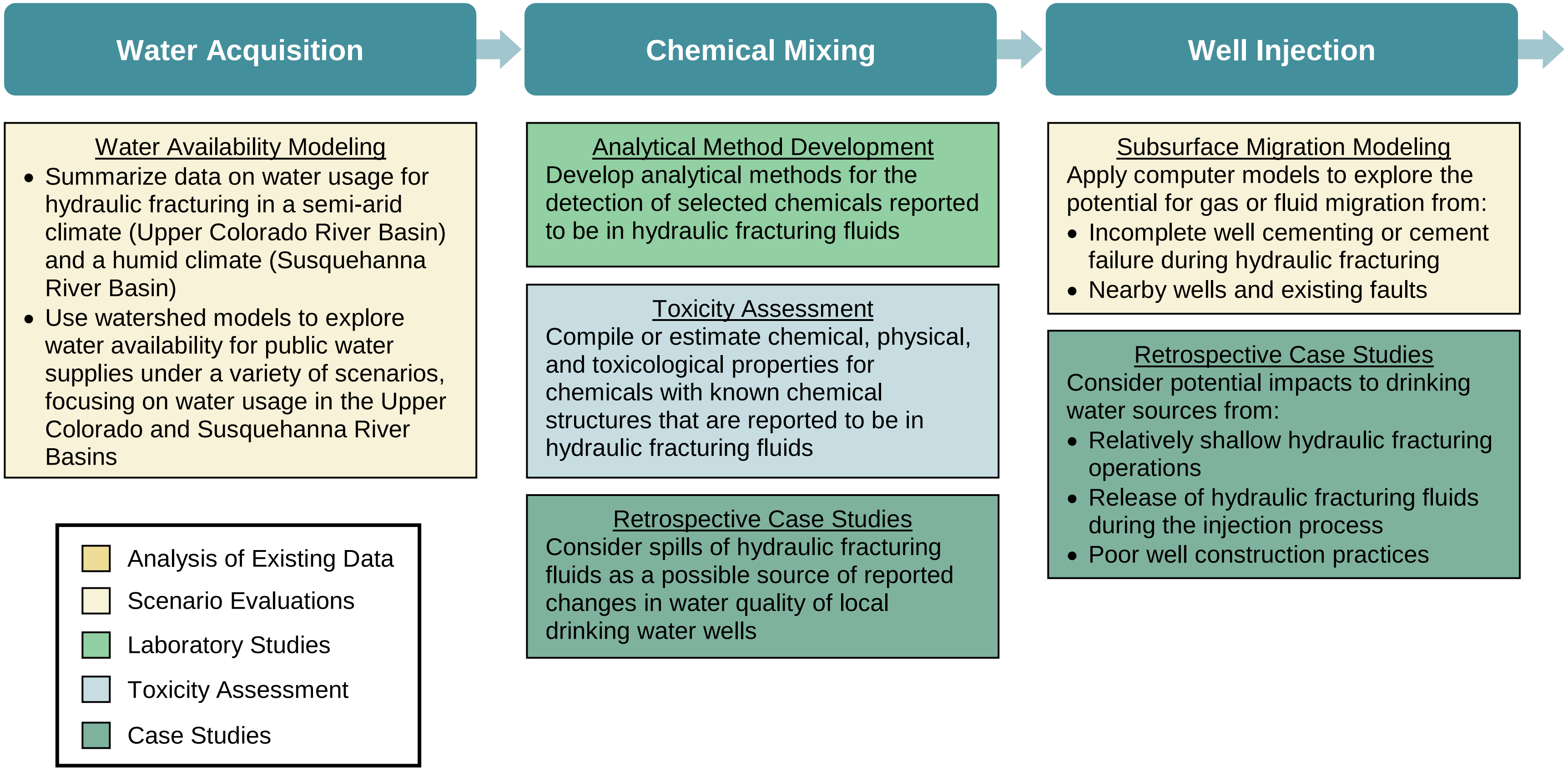
Literature Review
Review and summarize literature on possible subsurface migration due to:
- Faulty well construction
- Nearby natural or man-made conduits

Service Company Analysis
Review and summarize standard operating procedures for information on:
- Practices related to establishing the mechanical integrity of wells being hydraulically fractured
- Procedures used during injection of the fracturing fluid

Well File Review
Review well construction data found in well files to assess the effectiveness of current well construction practices at isolating the wellbore from surrounding ground water

🟨 Analysis of Existing Data
⬜ Scenario Evaluations
🟩 Laboratory Studies
🟦 Toxicity Assessment
▨ Case Studies

Figure 38a. Summary of research projects underway for the first three stages of the hydraulic fracturing water cycle.



Water Acquisition

Water Availability Modeling

- Summarize data on water usage for hydraulic fracturing in a semi-arid climate (Upper Colorado River Basin) and a humid climate (Susquehanna River Basin)
- Use watershed models to explore water availability for public water supplies under a variety of scenarios, focusing on water usage in the Upper Colorado and Susquehanna River Basins

Chemical Mixing

Analytical Method Development
Develop analytical methods for the detection of selected chemicals reported to be in hydraulic fracturing fluids

Toxicity Assessment
Compile or estimate chemical, physical, and toxicological properties for chemicals with known chemical structures that are reported to be in hydraulic fracturing fluids

Retrospective Case Studies
Consider spills of hydraulic fracturing fluids as a possible source of reported changes in water quality of local drinking water wells

Well Injection

Subsurface Migration Modeling
Apply computer models to explore the potential for gas or fluid migration from:

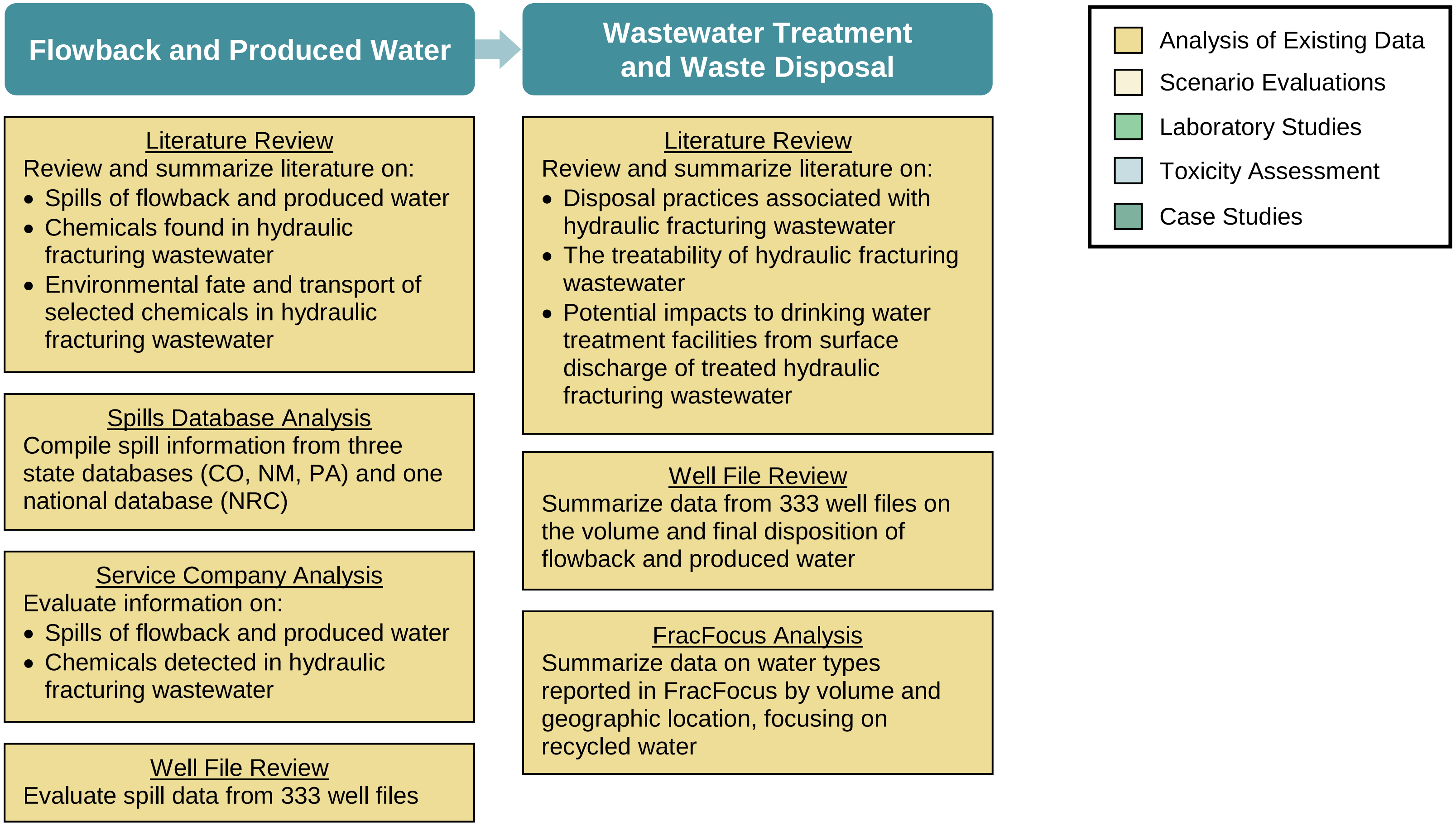
- Incomplete well cementing or cement failure during hydraulic fracturing
- Nearby wells and existing faults

Retrospective Case Studies
Consider potential impacts to drinking water sources from:

- Relatively shallow hydraulic fracturing operations
- Release of hydraulic fracturing fluids during the injection process
- Poor well construction practices

🟨 Analysis of Existing Data
⬜ Scenario Evaluations
🟩 Laboratory Studies
🟦 Toxicity Assessment
■ Case Studies

Figure 38b. Summary of research projects underway for the first three stages of the hydraulic fracturing water cycle.



Flowback and Produced Water

Literature Review
Review and summarize literature on:

- Spills of flowback and produced water
- Chemicals found in hydraulic fracturing wastewater
- Environmental fate and transport of selected chemicals in hydraulic fracturing wastewater

Spills Database Analysis
Compile spill information from three state databases (CO, NM, PA) and one national database (NRC)

Service Company Analysis
Evaluate information on:

- Spills of flowback and produced water
- Chemicals detected in hydraulic fracturing wastewater

Well File Review
Evaluate spill data from 333 well files

Wastewater Treatment and Waste Disposal

Literature Review
Review and summarize literature on:

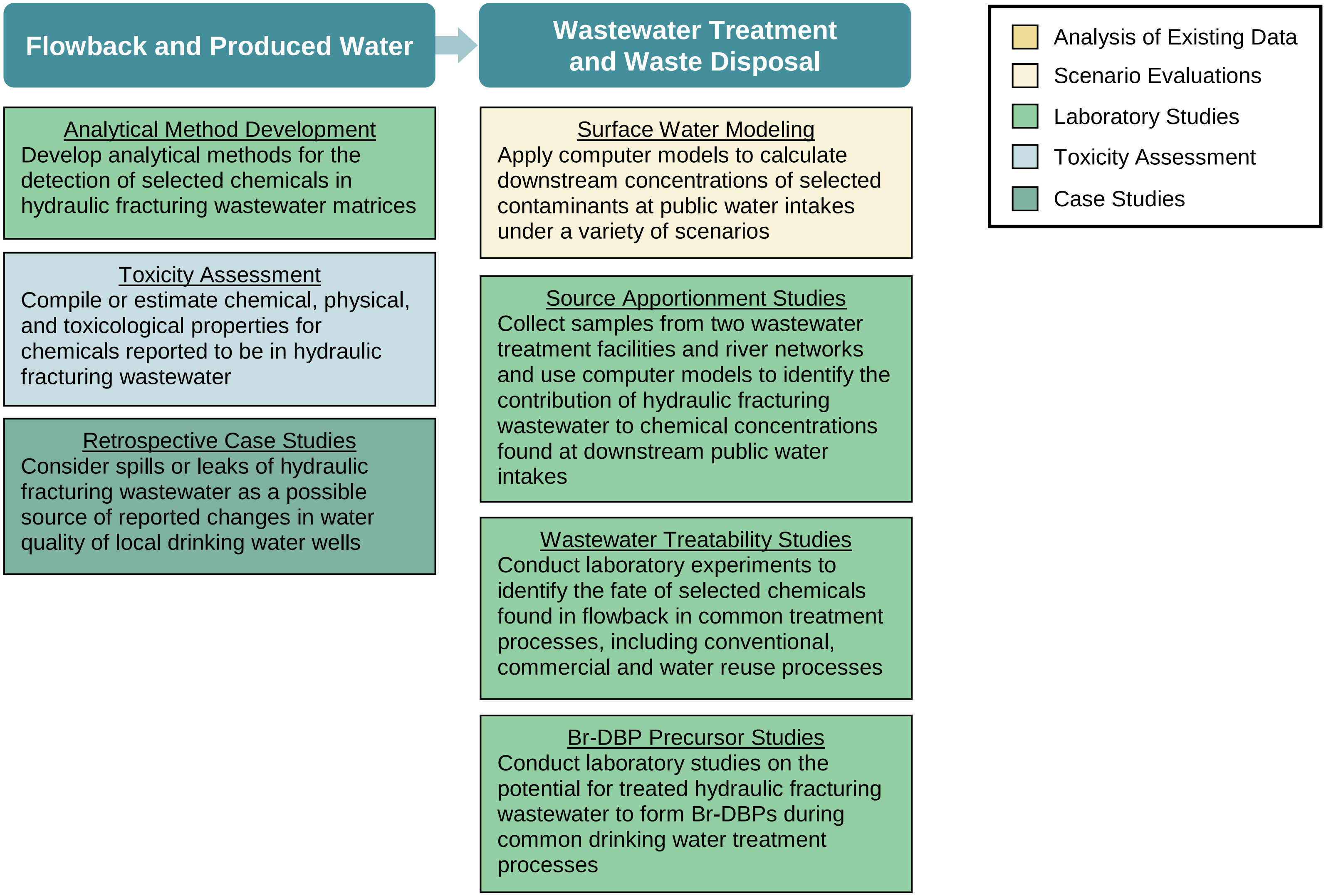
- Disposal practices associated with hydraulic fracturing wastewater
- The treatability of hydraulic fracturing wastewater
- Potential impacts to drinking water treatment facilities from surface discharge of treated hydraulic fracturing wastewater

Well File Review
Summarize data from 333 well files on the volume and final disposition of flowback and produced water

FracFocus Analysis
Summarize data on water types reported in FracFocus by volume and geographic location, focusing on recycled water

🟨 Analysis of Existing Data
⬜ Scenario Evaluations
🟩 Laboratory Studies
⬜ Toxicity Assessment
🟩 Case Studies

Figure 39a. Summary of research projects underway for the last two stages of the hydraulic fracturing water cycle.



Flowback and Produced Water → **Wastewater Treatment and Waste Disposal**

- 🟨 Analysis of Existing Data
- ⬜ Scenario Evaluations
- 🟩 Laboratory Studies
- ⬜ Toxicity Assessment
- 🟩 Case Studies

Flowback and Produced Water

<u>Analytical Method Development</u>
Develop analytical methods for the detection of selected chemicals in hydraulic fracturing wastewater matrices

<u>Toxicity Assessment</u>
Compile or estimate chemical, physical, and toxicological properties for chemicals reported to be in hydraulic fracturing wastewater

<u>Retrospective Case Studies</u>
Consider spills or leaks of hydraulic fracturing wastewater as a possible source of reported changes in water quality of local drinking water wells

Wastewater Treatment and Waste Disposal

<u>Surface Water Modeling</u>
Apply computer models to calculate downstream concentrations of selected contaminants at public water intakes under a variety of scenarios

<u>Source Apportionment Studies</u>
Collect samples from two wastewater treatment facilities and river networks and use computer models to identify the contribution of hydraulic fracturing wastewater to chemical concentrations found at downstream public water intakes

<u>Wastewater Treatability Studies</u>
Conduct laboratory experiments to identify the fate of selected chemicals found in flowback in common treatment processes, including conventional, commercial and water reuse processes

<u>Br-DBP Precursor Studies</u>
Conduct laboratory studies on the potential for treated hydraulic fracturing wastewater to form Br-DBPs during common drinking water treatment processes

Figure 39b. Summary of research projects underway for the last two stages of the hydraulic fracturing water cycle.

9.3. Report of Results

This is a status report, describing the current progress made on the research projects that make up the agency's S*tudy of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*. Results from individual research projects will undergo peer review prior to publication either as articles in scientific journals or EPA reports. The EPA plans to synthesize results from the published reports with a critical literature review in a report of results that will answer as completely as possible the research questions identified in the Study Plan. The report of results has been determined to be a Highly Influential Scientific Assessment and will undergo peer review by the Science Advisory Board. Ultimately, the results of this study are expected to inform the public and provide policymakers at all levels with high-quality scientific knowledge that can be used in decision-making processes.

The report of results will also be informed by information provided through the ongoing stakeholder engagement process described in Section 1.1. This process is anticipated to provide agency scientists with updates on changes in industry practices and technologies relevant to the study. While the EPA expects hydraulic fracturing technology to develop between now and the publication of the report of results, the agency believes that the research described here will provide timely information that will contribute to the state of knowledge on the relationship between hydraulic fracturing and drinking water resources. For example, some companies may adopt new injection or wastewater treatment technologies and practices, while others may continue to use current technologies and practices. Many of the practices, including wastewater treatment and disposal technologies used by POTWs, are not expected to change significantly between now and the report of results.

Results from the study are expected to identify potential impacts to drinking water resources, if any, from water withdrawals, the fate and transport of chemicals associated with hydraulic fracturing, and wastewater treatment and waste disposal. Information on the toxicity of hydraulic fracturing-related chemicals is also being gathered. Although these data may be used to assess the potential risks to drinking water resources from hydraulic fracturing activities, the report of results is not intended to quantify risks. Results presented in the report of results will be appropriately discussed and all uncertainties will be described.

The EPA will strive to make the report of results as clear and definitive as possible in answering all of the primary and secondary research questions, at that time. Science and technology evolve, however: the agency does not believe that the report of results will provide definitive answers on all research questions for all time and fully expects that additional research needs will be identified.

9.4. Conclusions

This report presents the EPA's progress in conducting its *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*. Chapters 3 through 7 provide individual progress reports for each of the research projects that make up this study. Each project progress report describes the project's relationship to the study, research methods, and status and summarizes QA activities. Information presented as part of this report cannot be used to draw conclusions about potential impacts to drinking water resources from hydraulic fracturing.

The EPA is committed to conducting a study that uses the best available science, independent sources of information, and a transparent, peer-reviewed process that ensures the validity and accuracy of the results. The EPA will seek input from individual members of an *ad hoc* expert panel convened under the auspices of the EPA's Science Advisory Board. Information about this process is available at http://yosemite.epa.gov/sab/sabproduct.nsf/02ad90b136fc21ef85256eba00436459/b436304ba804e3f885257a5b00521b3b!OpenDocument. The individual members of the *ad hoc* panel will consider public comment. The EPA will consider feedback from the individual experts, as informed by the public's comments, in the development of the report of results.

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Appendix A: Chemicals Identified in Hydraulic Fracturing Fluids and Wastewater

This appendix contains tables of chemicals reported to be used in hydraulic fracturing fluids and chemicals detected in flowback and produced water. Sources of information include federal and state government documents, industry-provided data, and other reliable sources based on the availability of clear scientific methodology and verifiable original sources; the full list of information sources is available in Section A.1. The EPA at this time has not made any judgment about the extent of exposure to these chemicals when used in hydraulic fracturing fluids or found in hydraulic fracturing wastewater, or their potential impacts on drinking water resources.

The tables in this appendix include information provided by nine hydraulic fracturing service companies (see Section 3.3), nine oil and gas operators (Section 3.4), and FracFocus (Section 3.5). Over 150 entries in Tables A-1 and A-2 were provided by the service companies, and roughly 60 entries were provided by FracFocus; these entries were not included in easily obtained public sources. The nine oil and gas operators provided data on chemicals and properties of flowback and produced water; the chemicals and properties are listed in Tables A-3 and A-4.

Much of the information provided in response to the EPA's September 2010 information request to the nine hydraulic fracturing service companies was claimed as confidential business information (CBI) under the Toxic Substances Control Act. In many cases, the service companies have agreed to publicly release chemical names and Chemical Abstract Services Registration Numbers (CASRNs) in Table A-1. However, 82 chemicals with known chemical names and CASRNs continue to be claimed as CBI, and are not included in this appendix. In some instances, generic chemical names have been provided for these chemicals in Table A-2.

In order to standardize chemical names, chemical name and structure annotation quality control methods have been applied to chemicals with CASRNs.[88] These methods ensure correct chemical names and CASRNs and include combining duplicates where appropriate.

The EPA is creating a Distributed Structure-Searchable Toxicity (DSSTox)[89] chemical inventory for chemicals reported to be used in hydraulic fracturing fluids and/or detected in flowback and produced water. The hydraulic fracturing DSSTox chemical inventory will contain CASRNs, chemical names and synonyms, and structure data files (where available). The structure data files can be used with existing computer software to calculate physicochemical properties, as described in Chapter 6.

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[88] Additional information on this process can be found at http://www.epa.gov/ncct/dsstox/ChemicalInfQAProcedures.html.

[89] The DSSTox website provides a public forum for publishing downloadable, structure-searchable, standardized chemical structure files associated with chemical inventories or toxicity datasets of environmental relevance. For more information, see http://www.epa.gov/ncct/dsstox/.

Table A-1 lists chemicals reported to be used in hydraulic fracturing fluids between 2005 and 2011. This table lists chemicals with their associated CASRNs. Structure data files are expected to be in the hydraulic fracturing DSSTox chemical inventory for some chemicals on Table A-1; these chemicals are marked with a "✓" in the "IUPAC Name and Structure" column.

Table A-1. List of CASRNs and names of chemicals reportedly used in hydraulic fracturing fluids. Chemical structures and IUPAC names have been identified for the chemicals with an "✓" in the "IUPAC Name and Structure" column. A few chemicals have structures, but no assigned CASRNs; these chemicals have "NA" entered in the CASRN column.

CASRN	Chemical Name	IUPAC Name and Structure	Reference
120086-58-0	(13Z)-N,N-bis(2-hydroxyethyl)-N-methyldocos-13-en-1-aminium chloride	✓	1
123-73-9	(E)-Crotonaldehyde	✓	1, 4
2235-43-0	[Nitrilotris(methylene)]tris-phosphonic acid pentasodium salt	✓	1
65322-65-8	1-(1-Naphthylmethyl)quinolinium chloride	✓	1
68155-37-3	1-(Alkyl* amino)-3-aminopropane *(42%C12, 26%C18, 15%C14, 8%C16, 5%C10, 4%C8)	✓	8
68909-18-2	1-(Phenylmethyl)pyridinium Et Me derivs., chlorides	✓	1, 2, 3, 4, 6, 8
526-73-8	1,2,3-Trimethylbenzene	✓	1, 4
95-63-6	1,2,4-Trimethylbenzene	✓	1, 2, 3, 4, 5
2634-33-5	1,2-Benzisothiazolin-3-one	✓	1, 3, 4
35691-65-7	1,2-Dibromo-2,4-dicyanobutane	✓	1, 4
95-47-6	1,2-Dimethylbenzene	✓	4
138879-94-4	1,2-Ethanediaminium, N, N'-bis[2-[bis(2-hydroxyethyl)methylammonio]ethyl]-N,N'bis(2-hydroxyethyl)-N,N'-dimethyl-,tetrachloride	✓	1, 4
57-55-6	1,2-Propanediol	✓	1, 2, 3, 4, 8
75-56-9	1,2-Propylene oxide	✓	1, 4
4719-04-4	1,3,5-Triazine-1,3,5(2H,4H,6H)-triethanol	✓	1, 4
108-67-8	1,3,5-Trimethylbenzene	✓	1, 4
123-91-1	1,4-Dioxane	✓	2, 3, 4
9051-89-2	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	✓	1, 4, 8
124-09-4	1,6-Hexanediamine	✓	1, 2
6055-52-3	1,6-Hexanediamine dihydrochloride	✓	1
20324-33-8	1-[2-(2-Methoxy-1-methylethoxy)-1-methylethoxy]-2-propanol	✓	4
78-96-6	1-Amino-2-propanol	✓	8

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CASRN	Chemical Name	IUPAC Name and Structure	Reference
15619-48-4	1-Benzylquinolinium chloride	✓	1, 3, 4
71-36-3	1-Butanol	✓	1, 2, 3, 4, 7
112-30-1	1-Decanol	✓	1, 4
2687-96-9	1-Dodecyl-2-pyrrolidinone	✓	1, 4
3452-07-1	1-Eicosene	✓	3
629-73-2	1-Hexadecene	✓	3
111-27-3	1-Hexanol	✓	1, 4, 8
68909-68-7	1-Hexanol, 2-ethyl-, manuf. of, by products from, distn. residues		4
68442-97-7	1H-Imidazole-1-ethanamine, 4,5-dihydro-, 2-nortall-oil alkyl derivs.		2, 4
107-98-2	1-Methoxy-2-propanol	✓	1, 2, 3, 4
2190-04-7	1-Octadecanamine, acetate (1:1)	✓	8
124-28-7	1-Octadecanamine, N,N-dimethyl-	✓	1, 3, 4
112-88-9	1-Octadecene	✓	3
111-87-5	1-Octanol	✓	1, 4
71-41-0	1-Pentanol	✓	8
61789-39-7	1-Propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-, N-coco acyl derivs., chlorides, sodium salts		1
61789-40-0	1-Propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-, N-coco acyl derivs., inner salts		1, 2, 3, 4
68139-30-0	1-Propanaminium, N-(3-aminopropyl)-2-hydroxy-N,N-dimethyl-3-sulfo-, N-coco acyl derivs., inner salts		1, 3, 4
149879-98-1	1-Propanaminium, N-(carboxymethyl)-N,N-dimethyl-3-[[(13Z)-1-oxo-13-docosen-1-yl]amino]-,	✓	1, 3
5284-66-2	1-Propanesulfonic acid	✓	3
71-23-8	1-Propanol	✓	1, 2, 4, 5
23519-77-9	1-Propanol, zirconium(4+) salt	✓	1, 4, 8
115-07-1	1-Propene	✓	2
1120-36-1	1-Tetradecene	✓	3
112-70-9	1-Tridecanol	✓	1, 4
112-42-5	1-Undecanol	✓	2
112-34-5	2-(2-Butoxyethoxy)ethanol	✓	2, 4
111-90-0	2-(2-Ethoxyethoxy)ethanol	✓	1, 4
112-15-2	2-(2-Ethoxyethoxy)ethyl acetate	✓	1, 4
102-81-8	2-(Dibutylamino)ethanol	✓	1, 4

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
34375-28-5	2-(Hydroxymethylamino)ethanol	✓	1, 4
21564-17-0	2-(Thiocyanomethylthio)benzothiazole	✓	2
27776-21-2	2,2'-(Azobis(1-methylethylidene))bis(4,5-dihydro-1H-imidazole)dihydrochloride	✓	3
10213-78-2	2,2'-(Octadecylimino)diethanol	✓	1
929-59-9	2,2'-[Ethane-1,2-diylbis(oxy)]diethanamine	✓	1, 4
9003-11-6	2,2'-[propane-1,2-diylbis(oxy)]diethanol	✓	1, 3, 4, 8
25085-99-8	2,2'-[propane-2,2-diylbis(4,1-phenyleneoxymethylene)]dioxirane	✓	1, 4, 8
10222-01-2	2,2-Dibromo-3-nitrilopropionamide	✓	1, 2, 3, 4, 6, 7, 8
73003-80-2	2,2-Dibromopropanediamide	✓	3
24634-61-5	2,4-Hexadienoic acid, potassium salt, (2E,4E)-	✓	3
915-67-3	2,7-Naphthalenedisulfonic acid, 3-hydroxy-4-[2-(4-sulfo-1-naphthalenyl) diazenyl] -, sodium salt (1:3)	✓	4
9002-93-1	2-[4-(1,1,3,3-tetramethylbutyl)phenoxy]ethanol	✓	1, 3, 4
NA	2-Acrylamide - 2-propanesulfonic acid and N,N-dimethylacrylamide copolymer	✓	2
NA	2-acrylamido -2-methylpropanesulfonic acid copolymer	✓	2
15214-89-8	2-Acrylamido-2-methyl-1-propanesulfonic acid	✓	1, 3
124-68-5	2-Amino-2-methylpropan-1-ol	✓	8
2002-24-6	2-Aminoethanol hydrochloride	✓	4, 8
52-51-7	2-Bromo-2-nitropropane-1,3-diol	✓	1, 2, 3, 4, 6
1113-55-9	2-Bromo-3-nitrilopropionamide	✓	1, 2, 3, 4, 5
96-29-7	2-Butanone oxime	✓	1
143106-84-7	2-Butanone, 4-[[[(1R,4aS,10aR)-1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-1-phenanthrenyl]methyl](3-oxo-3-phenylpropyl)amino]-, hydrochloride (1:1)	✓	1, 4
68442-77-3	2-Butenediamide, (2E)-, N,N'-bis[2-(4,5-dihydro-2-nortall-oil alkyl-1H-imidazol-1-yl)ethyl] derivs.		3, 8
111-76-2	2-Butoxyethanol	✓	1, 2, 3, 4, 6, 7, 8
110-80-5	2-Ethoxyethanol	✓	6
104-76-7	2-Ethyl-1-hexanol	✓	1, 2, 3, 4, 5
645-62-5	2-Ethyl-2-hexenal	✓	2
5444-75-7	2-Ethylhexyl benzoate	✓	4

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
818-61-1	2-Hydroxyethyl acrylate	✓	1, 4
13427-63-9	2-Hydroxyethylammonium hydrogen sulphite	✓	1
60-24-2	2-Mercaptoethanol	✓	1, 4
109-86-4	2-Methoxyethanol	✓	4
78-83-1	2-Methyl-1-propanol	✓	1, 2, 4
107-41-5	2-Methyl-2,4-pentanediol	✓	1, 2, 4
2682-20-4	2-Methyl-3(2H)-isothiazolone	✓	1, 2, 4
115-19-5	2-Methyl-3-butyn-2-ol	✓	3
78-78-4	2-Methylbutane	✓	2
62763-89-7	2-Methylquinoline hydrochloride	✓	3
37971-36-1	2-Phosphono-1,2,4-butanetricarboxylic acid	✓	1, 4
93858-78-7	2-Phosphonobutane-1,2,4-tricarboxylic acid, potassium salt (1:x)	✓	1
555-31-7	2-Propanol, aluminum salt	✓	1
26062-79-3	2-Propen-1-aminium, N,N-dimethyl-N-2-propenyl-, chloride, homopolymer	✓	3
13533-05-6	2-Propenoic acid, 2-(2-hydroxyethoxy)ethyl ester	✓	4
113221-69-5	2-Propenoic acid, ethyl ester, polymer with ethenyl acetate and 2,5-furandione, hydrolyzed	✓	4, 8
111560-38-4	2-Propenoic acid, ethyl ester, polymer with ethenyl acetate and 2,5-furandione, hydrolyzed, sodium salt	✓	8
9003-04-7	2-Propenoic acid, homopolymer, sodium salt	✓	1, 2, 3, 4
9003-06-9	2-Propenoic acid, polymer with 2-propenamide	✓	4, 8
25987-30-8	2-Propenoic acid, polymer with 2-propenamide, sodium salt		3, 4, 8
37350-42-8	2-Propenoic acid, sodium salt (1:1), polymer with sodium 2-methyl-2-((1-oxo-2-propen-1-yl)amino)-1-propanesulfonate (1:1)	✓	1
151006-66-5	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		4
71050-62-9	2-Propenoic, polymer with sodium phosphinate	✓	3, 4
75673-43-7	3,4,4-Trimethyloxazolidine	✓	8
51229-78-8	3,5,7-Triazatricyclo(3.3.1.1(superscript 3,7))decane, 1-(3-chloro-2-propenyl)-, chloride, (Z)-	✓	3
5392-40-5	3,7-Dimethyl-2,6-octadienal	✓	3

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
104-55-2	3-Phenylprop-2-enal	✓	1, 2, 3, 4, 7
12068-08-5	4-(Dodecan-6-yl)benzenesulfonic acid – morpholine (1:1)	✓	1, 4
51200-87-4	4,4-Dimethyloxazolidine	✓	8
5877-42-9	4-Ethyloct-1-yn-3-ol	✓	1, 2, 3, 4
121-33-5	4-Hydroxy-3-methoxybenzaldehyde	✓	3
122-91-8	4-Methoxybenzyl formate	✓	3
150-76-5	4-Methoxyphenol	✓	4
108-11-2	4-Methyl-2-pentanol	✓	1, 4
108-10-1	4-Methyl-2-pentanone	✓	5
104-40-5	4-Nonylphenol	✓	8
26172-55-4	5-Chloro-2-methyl-3(2H)-isothiazolone	✓	1, 2, 4
106-22-9	6-Octen-1-ol, 3,7-dimethyl-	✓	3
75-07-0	Acetaldehyde	✓	1, 4
64-19-7	Acetic acid	✓	1, 2, 3, 4, 5, 6, 7, 8
25213-24-5	Acetic acid ethenyl ester, polymer with ethenol		1, 4
90438-79-2	Acetic acid, C6-8-branched alkyl esters	✓	4
68442-62-6	Acetic acid, hydroxy-, reaction products with triethanolamine	✓	3
5421-46-5	Acetic acid, mercapto-, monoammonium salt	✓	2, 8
108-24-7	Acetic anhydride	✓	1, 2, 3, 4, 7
67-64-1	Acetone	✓	1, 3, 4, 6
7327-60-8	Acetonitrile, 2,2',2''-nitrilotris-	✓	1, 4
98-86-2	Acetophenone	✓	1
77-89-4	Acetyltriethyl citrate	✓	1, 4
107-02-8	Acrolein	✓	2
79-06-1	Acrylamide	✓	1, 2, 3, 4
25085-02-3	Acrylamide/ sodium acrylate copolymer	✓	1, 2, 3, 4, 8
38193-60-1	Acrylamide-sodium-2-acrylamido-2-methlypropane sulfonate copolymer	✓	1, 2, 3, 4
79-10-7	Acrylic acid	✓	2, 4
110224-99-2	Acrylic acid, with sodium-2-acrylamido-2-methyl-1-propanesulfonate and sodium phosphinate	✓	8
67254-71-1	Alcohols, C10-12, ethoxylated	✓	3
68526-86-3	Alcohols, C11-14-iso-, C13-rich	✓	3

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
228414-35-5	Alcohols, C11-14-iso-, C13-rich, butoxylated ethoxylated		1
78330-21-9	Alcohols, C11-14-iso-, C13-rich, ethoxylated	✓	3, 4, 8
126950-60-5	Alcohols, C12-14-secondary	✓	1, 3, 4
84133-50-6	Alcohols, C12-14-secondary, ethoxylated		3, 4, 8
78330-19-5	Alcohols, C7-9-iso-, C8-rich, ethoxylated	✓	2, 4, 8
68603-25-8	Alcohols, C8-10, ethoxylated propoxylated		3
78330-20-8	Alcohols, C9-11-iso-, C10-rich, ethoxylated	✓	1, 2, 4, 8
93924-07-3	Alkanes, C10-14	✓	1
90622-52-9	Alkanes, C10-16-branched and linear		4
68551-19-9	Alkanes, C12-14-iso-	✓	2, 4, 8
68551-20-2	Alkanes, C13-16-iso-	✓	1, 4
64743-02-8	Alkenes, C>10 .alpha.-	✓	1, 3, 4, 8
68411-00-7	Alkenes, C>8		1
68607-07-8	Alkenes, C24-25 alpha-, polymers with maleic anhydride, docosyl esters	✓	8
71011-24-0	Alkyl quaternary ammonium with bentonite		4
85409-23-0	Alkyl* dimethyl ethylbenzyl ammonium chloride *(50%C12, 30%C14, 17%C16, 3%C18)	✓	8
42615-29-2	Alkylbenzenesulfonate, linear	✓	1, 4, 6
1302-62-1	Almandite and pyrope garnet		1, 4
60828-78-6	alpha-[3.5-dimethyl-1-(2-methylpropyl)hexyl]-omega-hydroxy-poly(oxy-1,2-ethandiyl)	✓	3
9000-90-2	alpha-Amylase		4
98-55-5	Alpha-Terpineol	✓	3
1302-42-7	Aluminate (AlO_2^{1-}), sodium	✓	2, 4
7429-90-5	Aluminum	✓	1, 4, 6
12042-68-1	Aluminum calcium oxide (Al_2CaO_4)		2
7446-70-0	Aluminum chloride	✓	1, 4
1327-41-9	Aluminum chloride, basic	✓	3, 4
1344-28-1	Aluminum oxide	✓	1, 2, 4
12068-56-3	Aluminum oxide silicate	✓	1, 2, 4
12141-46-7	Aluminum silicate	✓	1, 2, 4
10043-01-3	Aluminum sulfate	✓	1, 4
68155-07-7	Amides, C8-18 and C18-unsatd., N,N-bis(hydroxyethyl)		3
68140-01-2	Amides, coco, N-[3-(dimethylamino)propyl]		1, 4

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
70851-07-9	Amides, coco, N-[3-(dimethylamino)propyl], alkylation products with chloroacetic acid, sodium salts		1, 4
68155-09-9	Amides, coco, N-[3-(dimethylamino)propyl], N-oxides		1, 3, 4
68876-82-4	Amides, from C16-22 fatty acids and diethylenetriamine		3
68155-20-4	Amides, tall-oil fatty, N,N-bis(hydroxyethyl)		3, 4
68647-77-8	Amides, tallow, N-[3-(dimethylamino)propyl],N-oxides		1, 4
68155-39-5	Amines, C14-18; C16-18-unsaturated, alkyl, ethoxylated		1
68037-94-5	Amines, C8-18 and C18-unsatd. alkyl		5
61788-46-3	Amines, coco alkyl		4
61790-57-6	Amines, coco alkyl, acetates		1, 4
61788-93-0	Amines, coco alkyldimethyl		8
61790-59-8	Amines, hydrogenated tallow alkyl, acetates		4
68966-36-9	Amines, polyethylenepoly-, ethoxylated, phosphonomethylated		1, 4
68603-67-8	Amines, polyethylenepoly-, reaction products with benzyl chloride	✓	1
61790-33-8	Amines, tallow alkyl		8
61791-26-2	Amines, tallow alkyl, ethoxylated		1, 3
68551-33-7	Amines, tallow alkyl, ethoxylated, acetates (salts)		1, 3, 4
68308-48-5	Amines, tallow alkyl, ethoxylated, phosphates		4
6419-19-8	Aminotrimethylene phosphonic acid	✓	1, 4, 8
7664-41-7	Ammonia	✓	1, 2, 3, 4, 7
32612-48-9	Ammonium (lauryloxypolyethoxy)ethyl sulfate	✓	4
631-61-8	Ammonium acetate	✓	1, 3, 4, 5, 8
10604-69-0	Ammonium acrylate	✓	8
26100-47-0	Ammonium acrylate-acrylamide polymer	✓	2, 4, 8
7803-63-6	Ammonium bisulfate	✓	2
10192-30-0	Ammonium bisulfite	✓	1, 2, 3, 4, 7
12125-02-9	Ammonium chloride	✓	1, 2, 3, 4, 5, 6, 8
7632-50-0	Ammonium citrate (1:1)	✓	3
3012-65-5	Ammonium citrate (2:1)	✓	8
2235-54-3	Ammonium dodecyl sulfate	✓	1
12125-01-8	Ammonium fluoride	✓	1, 4
1066-33-7	Ammonium hydrogen carbonate	✓	1, 4

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
1341-49-7	Ammonium hydrogen difluoride	✓	1, 3, 4, 7
13446-12-3	Ammonium hydrogen phosphonate	✓	4
1336-21-6	Ammonium hydroxide	✓	1, 3, 4
8061-53-8	Ammonium ligninsulfonate		2
6484-52-2	Ammonium nitrate	✓	1, 2, 3
7722-76-1	Ammonium phosphate	✓	1, 4
7783-20-2	Ammonium sulfate	✓	1, 2, 3, 4, 6
99439-28-8	Amorphous silica	✓	1, 7
104-46-1	Anethole	✓	3
62-53-3	Aniline	✓	2, 4
1314-60-9	Antimony pentoxide	✓	1, 4
10025-91-9	Antimony trichloride	✓	1, 4
1309-64-4	Antimony trioxide	✓	8
7440-38-2	Arsenic		4
68131-74-8	Ashes, residues		4
68201-32-1	Asphalt, sulfonated, sodium salt		2
12174-11-7	Attapulgite		2, 3
31974-35-3	Aziridine, polymer with 2-methyloxirane	✓	4, 8
7727-43-7	Barium sulfate	✓	1, 2, 4
1318-16-7	Bauxite		1, 2, 4
1302-78-9	Bentonite		1, 2, 4, 6
121888-68-4	Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex		3, 4
80-08-0	Benzamine, 4,4'-sulfonylbis-	✓	1, 4
71-43-2	Benzene	✓	1, 3, 4
98-82-8	Benzene, (1-methylethyl)-		1, 2, 3, 4
119345-03-8	Benzene, 1,1'-oxybis-, tetrapropylene derivs., sulfonated		8
119345-04-9	Benzene, 1,1'-oxybis-, tetrapropylene derivs., sulfonated, sodium salts		3, 4, 8
611-14-3	Benzene, 1-ethyl-2-methyl-	✓	4
68648-87-3	Benzene, C10-16-alkyl derivs.	✓	1
9003-55-8	Benzene, ethenyl-, polymer with 1,3-butadiene	✓	2, 4
74153-51-8	Benzenemethanaminium, N,N-dimethyl-N-(2-((1-oxo-2-propen-1-yl)oxy)ethyl)-, chloride (1:1), polymer with 2-propenamide	✓	3
98-11-3	Benzenesulfonic acid	✓	2

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
37953-05-2	Benzenesulfonic acid, (1-methylethyl)-,	✓	4
37475-88-0	Benzenesulfonic acid, (1-methylethyl)-, ammonium salt	✓	3, 4
28348-53-0	Benzenesulfonic acid, (1-methylethyl)-, sodium salt	✓	8
68584-22-5	Benzenesulfonic acid, C10-16-alkyl derivs.	✓	1, 4
255043-08-4	Benzenesulfonic acid, C10-16-alkyl derivs., compds. with cyclohexylamine	✓	1
68584-27-0	Benzenesulfonic acid, C10-16-alkyl derivs., potassium salts	✓	1, 4, 8
90218-35-2	Benzenesulfonic acid, dodecyl-, branched, compds. with 2-propanamine	✓	4
26264-06-2	Benzenesulfonic acid, dodecyl-, calcium salt	✓	4
68648-81-7	Benzenesulfonic acid, mono-C10-16 alkyl derivs., compds. with 2-propanamine	✓	1, 4
65-85-0	Benzoic acid	✓	1, 4, 7
100-44-7	Benzyl chloride	✓	1, 2, 4, 8
139-07-1	Benzyldimethyldodecylammonium chloride	✓	2, 8
122-18-9	Benzylhexadecyldimethylammonium chloride	✓	8
68425-61-6	Bis(1-methylethyl)naphthalenesulfonic acid, cyclohexylamine salt	✓	1
111-44-4	Bis(2-chloroethyl) ether	✓	8
80-05-7	Bisphenol A	✓	4
65996-69-2	Blast furnace slag		2, 3
1303-96-4	Borax	✓	1, 2, 3, 4, 6
10043-35-3	Boric acid	✓	1, 2, 3, 4, 6, 7
1303-86-2	Boric oxide	✓	1, 2, 3, 4
11128-29-3	Boron potassium oxide		1
1330-43-4	Boron sodium oxide	✓	1, 2, 4
12179-04-3	Boron sodium oxide pentahydrate	✓	8
106-97-8	Butane	✓	2, 5
2373-38-8	Butanedioic acid, sulfo-, 1,4-bis(1,3-dimethylbutyl) ester, sodium salt	✓	1
2673-22-5	Butanedioic acid, sulfo-, 1,4-ditridecyl ester, sodium salt	✓	4
2426-08-6	Butyl glycidyl ether	✓	1, 4
138-22-7	Butyl lactate	✓	1, 4
3734-67-6	C.I. Acid red 1	✓	4

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
6625-46-3	C.I. Acid violet 12, disodium salt	✓	4
6410-41-9	C.I. Pigment Red 5	✓	4
4477-79-6	C.I. Solvent Red 26	✓	4
70592-80-2	C10-16-Alkyldimethylamines oxides	✓	4
68002-97-1	C10-C16 ethoxylated alcohol	✓	1, 2, 3, 4, 8
68131-40-8	C11-15-Secondary alcohols ethoxylated	✓	1, 2, 8
73138-27-9	C12-14 tert-alkyl ethoxylated amines	✓	3
66402-68-4	Calcined bauxite		2, 8
12042-78-3	Calcium aluminate	✓	2
7789-41-5	Calcium bromide	✓	4
10043-52-4	Calcium chloride	✓	1, 2, 3, 4, 7
10035-04-8	Calcium dichloride dihydrate	✓	1, 4
7789-75-5	Calcium fluoride	✓	1, 4
1305-62-0	Calcium hydroxide	✓	1, 2, 3, 4
7778-54-3	Calcium hypochlorite	✓	1, 2, 4
58398-71-3	Calcium magnesium hydroxide oxide		4
1305-78-8	Calcium oxide	✓	1, 2, 4, 7
1305-79-9	Calcium peroxide	✓	1, 3, 4, 8
7778-18-9	Calcium sulfate	✓	1, 2, 4
10101-41-4	Calcium sulfate dihydrate	✓	2
76-22-2	Camphor	✓	3
1333-86-4	Carbon black	✓	1, 2, 4
124-38-9	Carbon dioxide	✓	1, 3, 4, 6
471-34-1	Carbonic acid calcium salt (1:1)	✓	1, 2, 4
584-08-7	Carbonic acid, dipotassium salt	✓	1, 2, 3, 4, 8
39346-76-4	Carboxymethyl guar gum, sodium salt		1, 2, 4
61791-12-6	Castor oil, ethoxylated		1, 3
8000-27-9	Cedarwood oil		3
9005-81-6	Cellophane		1, 4
9012-54-8	Cellulase		1, 2, 3, 4, 5
9004-34-6	Cellulose	✓	1, 2, 3, 4
9004-32-4	Cellulose, carboxymethyl ether, sodium salt		2, 3, 4
16887-00-6	Chloride	✓	4, 8
7782-50-5	Chlorine	✓	2

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
10049-04-4	Chlorine dioxide	✓	1, 2, 3, 4, 8
78-73-9	Choline bicarbonate	✓	3, 8
67-48-1	Choline chloride	✓	1, 3, 4, 7, 8
16065-83-1	Chromium (III), insoluble salts	✓	2, 6
18540-29-9	Chromium (VI)	✓	6
39430-51-8	Chromium acetate, basic	✓	2
1066-30-4	Chromium(III) acetate	✓	1, 2
77-92-9	Citric acid	✓	1, 2, 3, 4, 7
8000-29-1	Citronella oil		3
94266-47-4	Citrus extract		1, 3, 4, 8
50815-10-6	Coal, granular		1, 2, 4
71-48-7	Cobalt(II) acetate	✓	1, 4
68424-94-2	Coco-betaine		3
68603-42-9	Coconut oil acid/Diethanolamine condensate (2:1)		1
61789-18-2	Coconut trimethylammonium chloride	✓	1, 8
7440-50-8	Copper	✓	1, 4
7758-98-7	Copper sulfate	✓	1, 4, 8
7758-89-6	Copper(I) chloride	✓	1, 4
7681-65-4	Copper(I) iodide	✓	1, 2, 4, 6
7447-39-4	Copper(II) chloride	✓	1, 3, 4
68525-86-0	Corn flour		4
11138-66-2	Corn sugar gum		1, 2, 4
1302-74-5	Corundum (Aluminum oxide)	✓	4, 8
68308-87-2	Cottonseed, flour		2, 4
91-64-5	Coumarin	✓	3
14464-46-1	Cristobalite	✓	1, 2, 4
15468-32-3	Crystalline silica, tridymite	✓	1, 2, 4
10125-13-0	Cupric chloride dihydrate	✓	1, 4, 7
110-82-7	Cyclohexane	✓	1, 7
108-94-1	Cyclohexanone	✓	1, 4
18472-87-2	D&C Red 28	✓	4
533-74-4	Dazomet	✓	1, 2, 3, 4, 7, 8
1120-24-7	Decyldimethylamine	✓	3, 4
7789-20-0	Deuterium oxide	✓	8

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
50-70-4	D-Glucitol	✓	1, 3, 4
526-95-4	D-Gluconic acid	✓	1, 4
3149-68-6	D-Glucopyranoside, methyl	✓	2
50-99-7	D-Glucose	✓	1, 4
117-81-7	Di(2-ethylhexyl) phthalate	✓	1, 4
7727-54-0	Diammonium peroxydisulfate	✓	1, 2, 3, 4, 6, 7, 8
68855-54-9	Diatomaceous earth		2, 4
91053-39-3	Diatomaceous earth, calcined		1, 2, 4
3252-43-5	Dibromoacetonitrile	✓	1, 2, 3, 4, 8
10034-77-2	Dicalcium silicate	✓	1, 2, 4
7173-51-5	Didecyldimethylammonium chloride	✓	1, 2, 4, 8
111-42-2	Diethanolamine	✓	1, 2, 3, 4, 6
25340-17-4	Diethylbenzene	✓	1, 3, 4
111-46-6	Diethylene glycol	✓	1, 2, 3, 4, 7
111-77-3	Diethylene glycol monomethyl ether	✓	1, 2, 4
111-40-0	Diethylenetriamine	✓	1, 2, 4, 5
68647-57-4	Diethylenetriamine reaction product with fatty acid dimers		2
38640-62-9	Diisopropylnaphthalene	✓	3, 4
627-93-0	Dimethyl adipate	✓	8
1119-40-0	Dimethyl glutarate	✓	1, 4
63148-62-9	Dimethyl polysiloxane	✓	1, 2, 4
106-65-0	Dimethyl succinate	✓	8
108-01-0	Dimethylaminoethanol	✓	2, 4
7398-69-8	Dimethyldiallylammonium chloride	✓	3, 4
101-84-8	Diphenyl oxide	✓	3
7758-11-4	Dipotassium monohydrogen phosphate	✓	5
25265-71-8	Dipropylene glycol	✓	1, 3, 4
31291-60-8	Di-sec-butylphenol	✓	1
28519-02-0	Disodium dodecyl(sulphonatophenoxy)benzenesulphonate	✓	1
38011-25-5	Disodium ethylenediaminediacetate	✓	1, 4
6381-92-6	Disodium ethylenediaminetetraacetate dihydrate	✓	1
12008-41-2	Disodium octaborate	✓	4, 8
12280-03-4	Disodium octaborate tetrahydrate	✓	1, 4

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
68477-31-6	Distillates, petroleum, catalytic reformer fractionator residue, low-boiling		1, 4
68333-25-5	Distillates, petroleum, hydrodesulfurized light catalytic cracked		1
64742-80-9	Distillates, petroleum, hydrodesulfurized middle		1
64742-52-5	Distillates, petroleum, hydrotreated heavy naphthenic		1, 2, 3, 4
64742-54-7	Distillates, petroleum, hydrotreated heavy paraffinic		1, 2, 4
64742-47-8	Distillates, petroleum, hydrotreated light		1, 2, 3, 4, 5, 7, 8
64742-53-6	Distillates, petroleum, hydrotreated light naphthenic		1, 2, 8
64742-55-8	Distillates, petroleum, hydrotreated light paraffinic		8
64742-46-7	Distillates, petroleum, hydrotreated middle		1, 2, 3, 4, 8
64741-59-9	Distillates, petroleum, light catalytic cracked		1, 4
64741-77-1	Distillates, petroleum, light hydrocracked		3
64742-65-0	Distillates, petroleum, solvent-dewaxed heavy paraffinic		1
64741-96-4	Distillates, petroleum, solvent-refined heavy naphthenic		1, 4
64742-91-2	Distillates, petroleum, steam-cracked		1, 4
64741-44-2	Distillates, petroleum, straight-run middle		1, 2, 4
64741-86-2	Distillates, petroleum, sweetened middle		1, 4
71011-04-6	Ditallow alkyl ethoxylated amines		3
10326-41-7	D-Lactic acid	✓	1, 4
5989-27-5	D-Limonene	✓	1, 3, 4, 5, 7, 8
577-11-7	Docusate sodium	✓	1
112-40-3	Dodecane	✓	8
123-01-3	Dodecylbenzene	✓	3, 4
27176-87-0	Dodecylbenzene sulfonic acid		2, 3, 4, 8
26836-07-7	Dodecylbenzenesulfonic acid, monoethanolamine salt	✓	1, 4
12276-01-6	EDTA, copper salt	✓	1, 5, 6
37288-54-3	Endo-1,4-.beta.-mannanase.		3, 8
106-89-8	Epichlorohydrin	✓	1, 4, 8
44992-01-0	Ethanaminium, N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]-, chloride	✓	3
69418-26-4	Ethanaminium, N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]-, chloride, polymer with 2-propenamide	✓	1, 3, 4

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
26006-22-4	Ethanaminium, N,N,N-trimethyl-2[(2-methyl-1-oxo-2-propen-1-yl0oxy]-, methyl sulfate 91:1), polymer with 2-propenamide		1, 4
27103-90-8	Ethanaminium, N,N,N-trimethyl-2-[(2-methyl-1-oxo-2-propenyl)oxy]-, methyl sulfate, homopolymer	✓	8
74-84-0	Ethane	✓	2, 5
64-17-5	Ethanol	✓	1, 2, 3, 4, 5, 6, 8
68171-29-9	Ethanol, 2,2',2''-nitrilotris-, tris(dihydrogen phosphate) (ester), sodium salt	✓	4
61791-47-7	Ethanol, 2,2'-iminobis-, N-coco alkyl derivs., N-oxides		1
61791-44-4	Ethanol, 2,2'-iminobis-, N-tallow alkyl derivs.		1
68909-77-3	Ethanol, 2,2'-oxybis-, reaction products with ammonia, morpholine derivs. residues		4, 8
68877-16-7	Ethanol, 2,2-oxybis-, reaction products with ammonia, morpholine derivs. residues, acetates (salts)		4
102424-23-7	Ethanol, 2,2-oxybis-, reaction products with ammonia, morpholine derivs. residues, reaction products with sulfur dioxide		4
25446-78-0	Ethanol, 2-[2-[2-(tridecyloxy)ethoxy]ethoxy]-, hydrogen sulfate, sodium salt	✓	1, 4
34411-42-2	Ethanol, 2-amino-, polymer with formaldehyde	✓	4
68649-44-5	Ethanol, 2-amino-, reaction products with ammonia, by-products from, phosphonomethylated		4
141-43-5	Ethanolamine	✓	1, 2, 3, 4, 6
66455-15-0	Ethoxylated C10-14 alcohols	✓	3
66455-14-9	Ethoxylated C12-13 alcohols	✓	4
68439-50-9	Ethoxylated C12-14 alcohols	✓	2, 3, 4, 8
68131-39-5	Ethoxylated C12-15 alcohols	✓	3, 4
68551-12-2	Ethoxylated C12-16 alcohols	✓	3, 4, 8
68951-67-7	Ethoxylated C14-15 alcohols	✓	3, 4, 8
68439-45-2	Ethoxylated C6-12 alcohols	✓	3, 4, 8
68439-46-3	Ethoxylated C9-11 alcohols	✓	3, 4
9002-92-0	Ethoxylated dodecyl alcohol	✓	4
61790-82-7	Ethoxylated hydrogenated tallow alkylamines		4
68439-51-0	Ethoxylated propoxylated C12-14 alcohols	✓	1, 3, 4, 8
52624-57-4	Ethoxylated, propoxylated trimethylolpropane	✓	3
141-78-6	Ethyl acetate	✓	1, 4, 7

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
141-97-9	Ethyl acetoacetate	✓	1, 4
93-89-0	Ethyl benzoate	✓	3
97-64-3	Ethyl lactate	✓	3
118-61-6	Ethyl salicylate	✓	3
100-41-4	Ethylbenzene	✓	1, 2, 3, 4, 7
9004-57-3	Ethylcellulose	✓	2
107-21-1	Ethylene glycol	✓	1, 2, 3, 4, 6, 7, 8
75-21-8	Ethylene oxide	✓	1, 2, 3, 4
107-15-3	Ethylenediamine	✓	2, 4
60-00-4	Ethylenediaminetetraacetic acid	✓	1, 2, 4
64-02-8	Ethylenediaminetetraacetic acid tetrasodium salt	✓	1, 2, 3, 4
67989-88-2	Ethylenediaminetetraacetic acid, diammonium copper salt	✓	4
139-33-3	Ethylenediaminetetraacetic acid, disodium salt	✓	1, 3, 4, 8
74-86-2	Ethyne	✓	7
68604-35-3	Fatty acids, C 8-18 and C18-unsaturated compounds with diethanolamine		3
70321-73-2	Fatty acids, C14-18 and C16-18-unsatd., distn. residues		2
61788-89-4	Fatty acids, C18-unsatd., dimers	✓	2
61791-29-5	Fatty acids, coco, ethoxylated		3
61791-08-0	Fatty acids, coco, reaction products with ethanolamine, ethoxylated		3
61790-90-7	Fatty acids, tall oil, hexa esters with sorbitol, ethoxylated		1, 4
68188-40-9	Fatty acids, tall oil, reaction products with acetophenone, formaldehyde and thiourea		3
61790-12-3	Fatty acids, tall-oil		1, 2, 3, 4
61790-69-0	Fatty acids, tall-oil, reaction products with diethylenetriamine		1, 4
8052-48-0	Fatty acids, tallow, sodium salts		1, 3
68153-72-0	Fatty acids, vegetable-oil, reaction products with diethylenetriamine		3
3844-45-9	FD&C Blue no. 1	✓	1, 4
7705-08-0	Ferric chloride	✓	1, 3, 4
10028-22-5	Ferric sulfate	✓	1, 4
17375-41-6	Ferrous sulfate monohydrate	✓	2

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
65997-17-3	Fiberglass		2, 3, 4
50-00-0	Formaldehyde	✓	1, 2, 3, 4
NA	Formaldehyde amine	✓	8
29316-47-0	Formaldehyde polymer with 4,1,1-(dimethylethyl)phenol and methyloxirane	✓	3
63428-92-2	Formaldehyde polymer with methyl oxirane, 4-nonylphenol and oxirane	✓	4, 8
28906-96-9	Formaldehyde, polymer with 2-(chloromethyl)oxirane and 4,4'-(1-methylethylidene)bis[phenol]	✓	1, 4
30704-64-4	Formaldehyde, polymer with 4-(1,1-dimethylethyl)phenol, 2-methyloxirane and oxirane	✓	1, 2, 4, 8
30846-35-6	Formaldehyde, polymer with 4-nonylphenol and oxirane	✓	1, 4
35297-54-2	Formaldehyde, polymer with ammonia and phenol	✓	1, 4
25085-75-0	Formaldehyde, polymer with bisphenol A	✓	4
70750-07-1	Formaldehyde, polymer with N1-(2-aminoethyl)-1,2-ethanediamine, benzylated	✓	8
55845-06-2	Formaldehyde, polymer with nonylphenol and oxirane	✓	4
153795-76-7	Formaldehyde, polymers with branched 4-nonylphenol, ethylene oxide and propylene oxide	✓	1, 3
75-12-7	Formamide	✓	1, 2, 3, 4
64-18-6	Formic acid	✓	1, 2, 3, 4, 6, 7
590-29-4	Formic acid, potassium salt	✓	1, 3, 4
68476-30-2	Fuel oil, no. 2		1, 2
68334-30-5	Fuels, diesel		2
68476-34-6	Fuels, diesel, no. 2		2, 4, 8
8031-18-3	Fuller's earth		2
110-17-8	Fumaric acid	✓	1, 2, 3, 4, 6
98-01-1	Furfural	✓	1, 4
98-00-0	Furfuryl alcohol	✓	1, 4
64741-43-1	Gas oils, petroleum, straight-run		1, 4
9000-70-8	Gelatin		1, 4
12002-43-6	Gilsonite		1, 2, 4
133-42-6	Gluconic acid	✓	7
111-30-8	Glutaraldehyde	✓	1, 2, 3, 4, 7
56-81-5	Glycerin, natural	✓	1, 2, 3, 4, 5

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
135-37-5	Glycine, N-(carboxymethyl)-N-(2-hydroxyethyl)-, disodium salt	✓	1
150-25-4	Glycine, N,N-bis(2-hydroxyethyl)-	✓	1, 4
5064-31-3	Glycine, N,N-bis(carboxymethyl)-, trisodium salt	✓	1, 2, 3, 4
139-89-9	Glycine, N-[2-[bis(carboxymethyl)amino]ethyl]-N-(2-hydroxyethyl)-, trisodium salt	✓	1
79-14-1	Glycolic acid	✓	1, 3, 4
2836-32-0	Glycolic acid sodium salt	✓	1, 3, 4
107-22-2	Glyoxal	✓	1, 2, 4
298-12-4	Glyoxylic acid	✓	1
9000-30-0	Guar gum		1, 2, 3, 4, 7, 8
68130-15-4	Guar gum, carboxymethyl 2-hydroxypropyl ether, sodium salt		1, 2, 3, 4, 7
13397-24-5	Gypsum	✓	2, 4
67891-79-6	Heavy aromatic distillate		1, 4
1317-60-8	Hematite		1, 2, 4
9025-56-3	Hemicellulase enzyme concentrate		3, 4
142-82-5	Heptane	✓	1, 2
68526-88-5	Heptene, hydroformylation products, high-boiling		1, 4
57-09-0	Hexadecyltrimethylammonium bromide	✓	1
110-54-3	Hexane	✓	5
124-04-9	Hexanedioic acid	✓	1, 2, 4, 6
1415-93-6	Humic acids, commercial grade		2
68956-56-9	Hydrocarbons, terpene processing by-products		1, 3, 4
7647-01-0	Hydrochloric acid	✓	1, 2, 3, 4, 5, 6, 7, 8
7664-39-3	Hydrogen fluoride	✓	1, 2, 4
7722-84-1	Hydrogen peroxide	✓	1, 3, 4
7783-06-4	Hydrogen sulfide	✓	1, 2
9004-62-0	Hydroxyethylcellulose	✓	1, 2, 3, 4
4719-04-4	Hydroxylamine hydrochloride	✓	1, 3, 4
10039-54-0	Hydroxylamine sulfate (2:1)	✓	4
9004-64-2	Hydroxypropyl cellulose	✓	2, 4
39421-75-5	Hydroxypropyl guar gum		1, 3, 4, 5, 6, 8

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
120-72-9	Indole	✓	2
430439-54-6	Inulin, carboxymethyl ether, sodium salt		1, 4
12030-49-8	Iridium oxide	✓	8
7439-89-6	Iron	✓	2, 4
1317-61-9	Iron oxide ($Fe3O4$)	✓	4
1332-37-2	Iron(II) oxide	✓	1, 4
7720-78-7	Iron(II) sulfate	✓	2
7782-63-0	Iron(II) sulfate heptahydrate	✓	1, 2, 3, 4
1309-37-1	Iron(III) oxide	✓	1, 2, 4
89-65-6	Isoascorbic acid	✓	1, 3, 4
75-28-5	Isobutane	✓	2
26952-21-6	Isooctanol	✓	1, 4, 5
123-51-3	Isopentyl alcohol	✓	1, 4
67-63-0	Isopropanol	✓	1, 2, 3, 4, 6, 7
42504-46-1	Isopropanolamine dodecylbenzenesulfonate	✓	1, 3, 4
75-31-0	Isopropylamine	✓	1, 4
68909-80-8	Isoquinoline, reaction products with benzyl chloride and quinoline	✓	3
35674-56-7	Isoquinolinium, 2-(phenylmethyl)-, chloride	✓	3
9043-30-5	Isotridecanol, ethoxylated	✓	1, 3, 4, 8
1332-58-7	Kaolin	✓	1, 2, 4
8008-20-6	Kerosine (petroleum)		1, 2, 3, 4, 8
64742-81-0	Kerosine, petroleum, hydrodesulfurized		1, 2, 4
61790-53-2	Kieselguhr	✓	1, 2, 4
1302-76-7	Kyanite		1, 2, 4
50-21-5	Lactic acid	✓	1, 4, 8
63-42-3	Lactose	✓	3
13197-76-7	Lauryl hydroxysultaine	✓	1
8022-15-9	Lavandula hybrida abrial herb oil		3
4511-42-6	L-Dilactide	✓	1, 4
7439-92-1	Lead	✓	1, 4
8002-43-5	Lecithin		4
129521-66-0	Lignite		2
8062-15-5	Lignosulfuric acid		2

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
1317-65-3	Limestone	✓	1, 2, 3, 4
8001-26-1	Linseed oil		8
79-33-4	L-Lactic acid	✓	1, 4, 8
546-93-0	Magnesium carbonate (1:1)	✓	1, 3, 4
7786-30-3	Magnesium chloride	✓	1, 2, 4
7791-18-6	Magnesium chloride hexahydrate	✓	4
1309-42-8	Magnesium hydroxide	✓	1, 4
19086-72-7	Magnesium iron silicate		1, 4
10377-60-3	Magnesium nitrate	✓	1, 2, 4
1309-48-4	Magnesium oxide	✓	1, 2, 3, 4
14452-57-4	Magnesium peroxide	✓	1, 4
12057-74-8	Magnesium phosphide	✓	1
1343-88-0	Magnesium silicate	✓	1, 4
26099-09-2	Maleic acid homopolymer	✓	8
25988-97-0	Methanamine-N-methyl polymer with chloromethyl oxirane	✓	4
74-82-8	Methane	✓	2, 5
67-56-1	Methanol	✓	1, 2, 3, 4, 5, 6, 7, 8
100-97-0	Methenamine	✓	1, 2, 4
625-45-6	Methoxyacetic acid	✓	8
9004-67-5	Methyl cellulose	✓	8
119-36-8	Methyl salicylate	✓	1, 2, 3, 4, 7
78-94-4	Methyl vinyl ketone	✓	1, 4
108-87-2	Methylcyclohexane	✓	1
6317-18-6	Methylene bis(thiocyanate)	✓	2
66204-44-2	Methylenebis(5-methyloxazolidine)	✓	2
68891-11-2	Methyloxirane polymer with oxirane, mono (nonylphenol) ether, branched	✓	3
12001-26-2	Mica		1, 2, 4, 6
8012-95-1	Mineral oil - includes paraffin oil		4, 8
64475-85-0	Mineral spirits		2
26038-87-9	Monoethanolamine borate (1:x)	✓	1, 4
1318-93-0	Montmorillonite		2
110-91-8	Morpholine	✓	1, 2, 4

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
78-21-7	Morpholinium, 4-ethyl-4-hexadecyl-, ethyl sulfate	✓	8
1302-93-8	Mullite		1,2, 4, 8
46830-22-2	N-(2-Acryloyloxyethyl)-N-benzyl-N,N-dimethylammonium chloride	✓	3
54076-97-0	N,N,N-Trimethyl-2[1-oxo-2-propenyl]oxy ethanaminimum chloride, homopolymer	✓	3
19277-88-4	N,N,N-Trimethyl-3-((1-oxooctadecyl)amino)-1-propanaminium methyl sulfate	✓	1
112-03-8	N,N,N-Trimethyloctadecan-1-aminium chloride	✓	1, 3, 4
109-46-6	N,N'-Dibutylthiourea	✓	1, 4
2605-79-0	N,N-Dimethyldecylamine oxide	✓	1, 3, 4
68-12-2	N,N-Dimethylformamide	✓	1, 2, 4, 5, 8
593-81-7	N,N-Dimethylmethanamine hydrochloride	✓	1, 4, 5, 7
1184-78-7	N,N-Dimethyl-methanamine-N-oxide	✓	3
1613-17-8	N,N-Dimethyloctadecylamine hydrochloride	✓	1, 4
110-26-9	N,N'-Methylenebisacrylamide	✓	1, 4
64741-68-0	Naphtha, petroleum, heavy catalytic reformed		1, 2, 3, 4
64742-48-9	Naphtha, petroleum, hydrotreated heavy		1, 2, 3, 4, 8
91-20-3	Naphthalene	✓	1, 2, 3, 4, 5, 7
93-18-5	Naphthalene, 2-ethoxy-	✓	3
28757-00-8	Naphthalenesulfonic acid, bis(1-methylethyl)-	✓	1, 3, 4
99811-86-6	Naphthalenesulphonic acid, bis (1-methylethyl)-methyl derivatives	✓	1
68410-62-8	Naphthenic acid ethoxylate	✓	4
7786-81-4	Nickel sulfate	✓	2
10101-97-0	Nickel(II) sulfate hexahydrate	✓	1, 4
61790-29-2	Nitriles, tallow, hydrogenated		4
4862-18-4	Nitrilotriacetamide	✓	1, 4, 7
139-13-9	Nitrilotriacetic acid	✓	1, 4
18662-53-8	Nitrilotriacetic acid trisodium monohydrate	✓	1, 4
7727-37-9	Nitrogen	✓	1, 2, 3, 4, 6
872-50-4	N-Methyl-2-pyrrolidone	✓	1, 4
105-59-9	N-Methyldiethanolamine	✓	2, 4, 8
109-83-1	N-Methylethanolamine	✓	4
68213-98-9	N-Methyl-N-hydroxyethyl-N-hydroxyethoxyethylamine	✓	4

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
13127-82-7	N-Oleyl diethanolamide	✓	1, 4
25154-52-3	Nonylphenol (mixed)	✓	1, 4
8000-48-4	Oil of eucalyptus		3
8007-02-1	Oil of lemongrass		3
8000-25-7	Oil of rosemary		3
112-80-1	Oleic acid	✓	2, 4
1317-71-1	Olivine		4
8028-48-6	Orange terpenes		4
68649-29-6	Oxirane, methyl-, polymer with oxirane, mono-C10-16-alkyl ethers, phosphates		1, 4
51838-31-4	Oxiranemethanaminium, N,N,N-trimethyl-, chloride, homopolymer	✓	1, 2, 3, 4, 5, 8
7782-44-7	Oxygen	✓	4
10028-15-6	Ozone	✓	8
8002-74-2	Paraffin waxes and Hydrocarbon waxes		1
30525-89-4	Paraformaldehyde	✓	2
4067-16-7	Pentaethylenehexamine	✓	4
109-66-0	Pentane	✓	2, 5
628-63-7	Pentyl acetate	✓	3
540-18-1	Pentyl butyrate	✓	3
79-21-0	Peracetic acid	✓	8
93763-70-3	Perlite		4
64743-01-7	Petrolatum, petroleum, oxidized		3
8002-05-9	Petroleum		1, 2
6742-47-8	Petroleum distillate hydrotreated light		8
85-01-8	Phenanthrene	✓	6
108-95-2	Phenol	✓	1, 2, 4
25068-38-6	Phenol, 4,4'-(1-methylethylidene)bis-, polymer with 2-(chloromethyl)oxirane	✓	1, 2, 4
9003-35-4	Phenol, polymer with formaldehyde	✓	1, 2, 4, 7
7803-51-2	Phosphine	✓	1, 4
13598-36-2	Phosphonic acid	✓	1, 4
29712-30-9	Phosphonic acid (dimethylamino(methylene))	✓	1
129828-36-0	Phosphonic acid, (((2-[(2-hydroxyethyl)(phosphonomethyl)amino)ethyl)imino]bis(methylene))bis-, compd. with 2-aminoethanol	✓	1

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
67953-76-8	Phosphonic acid, (1-hydroxyethylidene)bis-, potassium salt	✓	4
3794-83-0	Phosphonic acid, (1-hydroxyethylidene)bis-, tetrasodium salt	✓	1, 4
15827-60-8	Phosphonic acid, [[(phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-	✓	1, 2, 4
70714-66-8	Phosphonic acid, [[(phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-, ammonium salt (1:x)	✓	3
22042-96-2	Phosphonic acid, [[(phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-, sodium salt	✓	3
34690-00-1	Phosphonic acid, [[(phosphonomethyl)imino]bis[6,1-hexanediylnitrilobis(methylene)]]tetrakis-	✓	1, 4, 8
7664-38-2	Phosphoric acid	✓	1, 2, 4
7785-88-8	Phosphoric acid, aluminium sodium salt	✓	1, 2
7783-28-0	Phosphoric acid, diammonium salt	✓	2
68412-60-2	Phosphoric acid, mixed decyl and Et and octyl esters		1
10294-56-1	Phosphorous acid	✓	1
85-44-9	Phthalic anhydride	✓	1, 4
8002-09-3	Pine oils		1, 2, 4
25038-54-4	Policapram (Nylon 6)		1, 4
62649-23-4	Poly (acrylamide-co-acrylic acid), partial sodium salt	✓	3, 4
26680-10-4	Poly(lactide)	✓	1
9014-93-1	Poly(oxy-1,2-ethanediyl), .alpha.-(dinonylphenyl)-.omega.-hydroxy-	✓	4
9016-45-9	Poly(oxy-1,2-ethanediyl), .alpha.-(nonylphenyl)-.omega.-hydroxy-	✓	1, 2, 3, 4, 8
51811-79-1	Poly(oxy-1,2-ethanediyl), .alpha.-(nonylphenyl)-.omega.-hydroxy-, phosphate	✓	1, 4
68987-90-6	Poly(oxy-1,2-ethanediyl), .alpha.-(octylphenyl)-.omega.-hydroxy-, branched	✓	1, 4
26635-93-8	Poly(oxy-1,2-ethanediyl), .alpha.,.alpha.'-[[(9Z)-9-octadecenylimino]di-2,1-ethanediyl]bis[.omega.-hydroxy-	✓	1, 4
9004-96-0	Poly(oxy-1,2-ethanediyl), .alpha.-[(9Z)-1-oxo-9-octadecenyl]-.omega.-hydroxy-	✓	8
68891-38-3	Poly(oxy-1,2-ethanediyl), .alpha.-sulfo-.omega.-hydroxy-, C12-14-alkyl ethers, sodium salts		1, 4

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
61723-83-9	Poly(oxy-1,2-ethanediyl), a-hydro-w-hydroxy-, ether with D-glucitol (2:1), tetra-(9Z)-9-octadecenoate	✓	8
68015-67-8	Poly(oxy-1,2-ethanediyl), alpha-(2,3,4,5-tetramethylnonyl)-omega-hydroxy	✓	1
68412-53-3	Poly(oxy-1,2-ethanediyl), alpha-(nonylphenyl)-omega-hydroxy-,branched, phosphates	✓	1
31726-34-8	Poly(oxy-1,2-ethanediyl), alpha-hexyl-omega-hydroxy		3, 8
56449-46-8	Poly(oxy-1,2-ethanediyl), alpha-hydro-omega-hydroxy-, (9Z)-9-octadecenoate	✓	3
65545-80-4	Poly(oxy-1,2-ethanediyl), alpha-hydro-omega-hydroxy-, ether with alpha-fluoro-omega-(2-hydroxyethyl)poly(difluoromethylene) (1:1)		1
27306-78-1	Poly(oxy-1,2-ethanediyl), alpha-methyl-omega-(3-(1,3,3,3-tetramethyl-1-((trimethylsilyl)oxy)-1-disiloxanyl)propoxy)-	✓	1
52286-19-8	Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-(decyloxy)-, ammonium salt (1:1)	✓	4
63428-86-4	Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-(hexyloxy)-, ammonium salt (1:1)	✓	1, 3, 4
68037-05-8	Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-(hexyloxy)-, C6-10-alkyl ethers, ammonium salts	✓	3, 4
9081-17-8	Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega--(nonylphenoxy)-	✓	4
52286-18-7	Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-(octyloxy)-, ammonium salt (1:1)	✓	4
68890-88-0	Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-hydroxy-, C10-12-alkyl ethers, ammonium salts	✓	8
24938-91-8	Poly(oxy-1,2-ethanediyl), alpha-tridecyl-omega-hydroxy-	✓	1, 3, 4
127036-24-2	Poly(oxy-1,2-ethanediyl), alpha-undecyl-omega-hydroxy-, branched and linear	✓	1
68412-54-4	Poly(oxy-1,2-ethanediyl),alpha-(4-nonylphenyl)-omega-hydroxy-,branched	✓	2, 3, 4
34398-01-1	Poly-(oxy-1,2-ethanediyl)-alpha-undecyl-omega-hydroxy	✓	1, 3, 4, 8
127087-87-0	Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy branched	✓	1, 2, 3, 4
25704-18-1	Poly(sodium-p-styrenesulfonate)	✓	1, 4
32131-17-2	Poly[imino(1,6-dioxo-1,6-hexanediyl)imino-1,6-hexanediyl]	✓	2
9003-05-8	Polyacrylamide	✓	1, 2, 4, 6

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
NA	Polyacrylate/ polyacrylamide blend	✓	2
66019-18-9	Polyacrylic acid, sodium bisulfite terminated	✓	3
25322-68-3	Polyethylene glycol	✓	1, 2, 3, 4, 7, 8
9004-98-2	Polyethylene glycol (9Z)-9-octadecenyl ether	✓	8
68187-85-9	Polyethylene glycol ester with tall oil fatty acid		1
9036-19-5	Polyethylene glycol mono(octylphenyl) ether	✓	1, 2, 3, 4, 8
9004-77-7	Polyethylene glycol monobutyl ether	✓	1, 4
68891-29-2	Polyethylene glycol mono-C8-10-alkyl ether sulfate ammonium	✓	1, 3, 4
9046-01-9	Polyethylene glycol tridecyl ether phosphate	✓	1, 3, 4
9002-98-6	Polyethyleneimine		4
25618-55-7	Polyglycerol	✓	2
9005-70-3	Polyoxyethylene sorbitan trioleate	✓	3
26027-38-3	Polyoxyethylene(10)nonylphenyl ether	✓	1, 2, 3, 4, 8
9046-10-0	Polyoxypropylenediamine	✓	1
68131-72-6	Polyphosphoric acids, esters with triethanolamine, sodium salts		1
68915-31-1	Polyphosphoric acids, sodium salts	✓	1, 4
25322-69-4	Polypropylene glycol	✓	1, 2, 4
68683-13-6	Polypropylene glycol glycerol triether, epichlorohydrin, bisphenol A polymer		1
9011-19-2	Polysiloxane		4
9005-64-5	Polysorbate 20	✓	8
9003-20-7	Polyvinyl acetate copolymer	✓	2
9002-89-5	Polyvinyl alcohol	✓	1, 2, 4
NA	Polyvinyl alcohol/polyvinyl acetate copolymer	✓	1
9002-85-1	Polyvinylidene chloride		8
65997-15-1	Portland cement		2, 4
127-08-2	Potassium acetate	✓	1, 3, 4
1327-44-2	Potassium aluminum silicate	✓	5
29638-69-5	Potassium antimonate	✓	1, 4
12712-38-8	Potassium borate	✓	3
20786-60-1	Potassium borate (1:x)	✓	1, 3
6381-79-9	Potassium carbonate sesquihydrate	✓	5

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
7447-40-7	Potassium chloride	✓	1, 2, 3, 4, 5, 6, 7
7778-50-9	Potassium dichromate	✓	4
1310-58-3	Potassium hydroxide	✓	1, 2, 3, 4, 6
7681-11-0	Potassium iodide	✓	1, 4
13709-94-9	Potassium metaborate	✓	1, 2, 3, 4, 8
143-18-0	Potassium oleate	✓	4
12136-45-7	Potassium oxide	✓	1, 4
7727-21-1	Potassium persulfate	✓	1, 2, 4
7778-80-5	Potassium sulfate	✓	2
74-98-6	Propane	✓	2, 5
2997-92-4	Propanimidamide,2,2''-aAzobis[(2-methyl-, amidinopropane) dihydrochloride	✓	1, 4
34590-94-8	Propanol, 1(or 2)-(2-methoxymethylethoxy)-	✓	1, 2, 3, 4
107-19-7	Propargyl alcohol	✓	1, 2, 3, 4, 5, 6, 7, 8
108-32-7	Propylene carbonate	✓	1, 4
15220-87-8	Propylene pentamer	✓	1
106-42-3	p-Xylene	✓	1, 4
68391-11-7	Pyridine, alkyl derivs.		1, 4
100765-57-9	Pyridinium, 1-(phenylmethyl)-, alkyl derivs., chlorides		4, 8
70914-44-2	Pyridinium, 1-(phenylmethyl)-, C7-8-alkyl derivs., chlorides	✓	6
289-95-2	Pyrimidine	✓	2
109-97-7	Pyrrole	✓	2
14808-60-7	Quartz	✓	1, 2, 3, 4, 5, 6, 8
308074-31-9	Quaternary ammonium compounds (2-ethylhexyl) hydrogenated tallow alkyl)dimethyl, methyl sulfates		8
68607-28-3	Quaternary ammonium compounds, (oxydi-2,1-ethanediyl)bis[coco alkyldimethyl, dichlorides		2, 3, 4, 8
68153-30-0	Quaternary ammonium compounds, benzylbis(hydrogenated tallow alkyl)methyl, salts with bentonite		2, 5, 6
68989-00-4	Quaternary ammonium compounds, benzyl-C10-16-alkyldimethyl, chlorides	✓	1, 4

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
68424-85-1	Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides	✓	1, 2, 4, 8
68391-01-5	Quaternary ammonium compounds, benzyl-C12-18-alkyldimethyl, chlorides	✓	8
61789-68-2	Quaternary ammonium compounds, benzylcoco alkylbis(hydroxyethyl), chlorides		1, 4
68953-58-2	Quaternary ammonium compounds, bis(hydrogenated tallow alkyl)dimethyl, salts with bentonite		2, 3, 4, 8
71011-27-3	Quaternary ammonium compounds, bis(hydrogenated tallow alkyl)dimethyl, salts with hectorite		2
68424-95-3	Quaternary ammonium compounds, di-C8-10-alkyldimethyl, chlorides	✓	2
61789-77-3	Quaternary ammonium compounds, dicoco alkyldimethyl, chlorides		1
68607-29-4	Quaternary ammonium compounds, pentamethyltallow alkyltrimethylenedi-, dichlorides		4
8030-78-2	Quaternary ammonium compounds, trimethyltallow alkyl, chlorides		1, 4
91-22-5	Quinoline	✓	2, 4
68514-29-4	Raffinates (petroleum)		5
64741-85-1	Raffinates, petroleum, sorption process		1, 2, 4, 8
64742-01-4	Residual oils, petroleum, solvent-refined		5
64741-67-9	Residues, petroleum, catalytic reformer fractionator		1, 4, 8
81-88-9	Rhodamine B	✓	4
8050-09-7	Rosin		1, 4
12060-08-1	Scandium oxide	✓	8
63800-37-3	Sepiolite		2
68611-44-9	Silane, dichlorodimethyl-, reaction products with silica		2
7631-86-9	Silica	✓	1, 2, 3, 4, 8
112926-00-8	Silica gel, cryst. -free		3, 4
112945-52-5	Silica, amorphous, fumed, cryst.-free	✓	1, 3, 4
60676-86-0	Silica, vitreous	✓	1, 4, 8
55465-40-2	Silicic acid, aluminum potassium sodium salt		4
68037-74-1	Siloxanes and silicones, di-Me, polymers with Me silsesquioxanes		4
67762-90-7	Siloxanes and Silicones, di-Me, reaction products with silica		4
63148-52-7	Siloxanes and silicones, dimethyl,		4

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
5324-84-5	Sodium 1-octanesulfonate	✓	3
2492-26-4	Sodium 2-mercaptobenzothiolate	✓	2
127-09-3	Sodium acetate	✓	1, 3, 4
532-32-1	Sodium benzoate	✓	3
144-55-8	Sodium bicarbonate	✓	1, 2, 3, 4, 7
7631-90-5	Sodium bisulfite	✓	1, 3, 4
1333-73-9	Sodium borate	✓	1, 4, 6, 7
7789-38-0	Sodium bromate	✓	1, 2, 4
7647-15-6	Sodium bromide	✓	1, 2, 3, 4, 7
1004542-84-0	Sodium bromosulfamate	✓	8
68610-44-6	Sodium caprylamphopropionate	✓	4
497-19-8	Sodium carbonate	✓	1, 2, 3, 4, 8
7775-09-9	Sodium chlorate	✓	1, 4
7647-14-5	Sodium chloride	✓	1, 2, 3, 4, 5, 8
7758-19-2	Sodium chlorite	✓	1, 2, 3, 4, 5, 8
3926-62-3	Sodium chloroacetate	✓	3
68608-68-4	Sodium cocaminopropionate		1
142-87-0	Sodium decyl sulfate	✓	1
527-07-1	Sodium D-gluconate	✓	4
126-96-5	Sodium diacetate	✓	1, 4
2893-78-9	Sodium dichloroisocyanurate	✓	2
151-21-3	Sodium dodecyl sulfate	✓	8
6381-77-7	Sodium erythorbate (1:1)	✓	1, 3, 4, 8
126-92-1	Sodium ethasulfate	✓	1
141-53-7	Sodium formate	✓	2, 8
7681-38-1	Sodium hydrogen sulfate	✓	4
1310-73-2	Sodium hydroxide	✓	1, 2, 3, 4, 7, 8
7681-52-9	Sodium hypochlorite	✓	1, 2, 3, 4, 8
7681-82-5	Sodium iodide	✓	4
8061-51-6	Sodium ligninsulfonate		2
18016-19-8	Sodium maleate (1:x)	✓	8
7681-57-4	Sodium metabisulfite	✓	1

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
7775-19-1	Sodium metaborate	✓	3, 4
16800-11-6	Sodium metaborate dihydrate	✓	1, 4
10555-76-7	Sodium metaborate tetrahydrate	✓	1, 4, 8
6834-92-0	Sodium metasilicate	✓	1, 2, 4
7631-99-4	Sodium nitrate	✓	2
7632-00-0	Sodium nitrite	✓	1, 2, 4
137-20-2	Sodium N-methyl-N-oleoyltaurate	✓	4
142-31-4	Sodium octyl sulfate	✓	1
1313-59-3	Sodium oxide	✓	1
11138-47-9	Sodium perborate	✓	4
10486-00-7	Sodium perborate tetrahydrate	✓	1, 4, 5, 8
7632-04-4	Sodium peroxoborate	✓	1
7775-27-1	Sodium persulfate	✓	1, 2, 3, 4, 7, 8
7632-05-5	Sodium phosphate	✓	1, 4
9084-06-4	Sodium polynaphthalenesulfonate	✓	2
7758-16-9	Sodium pyrophosphate	✓	1, 2, 4
54-21-7	Sodium salicylate	✓	1, 4
533-96-0	Sodium sesquicarbonate	✓	1, 2
1344-09-8	Sodium silicate	✓	1, 2, 4
9063-38-1	Sodium starch glycolate		2
7757-82-6	Sodium sulfate	✓	1, 2, 3, 4
7757-83-7	Sodium sulfite	✓	2, 4, 8
540-72-7	Sodium thiocyanate	✓	1, 4
7772-98-7	Sodium thiosulfate	✓	1, 2, 3, 4
10102-17-7	Sodium thiosulfate, pentahydrate	✓	1, 4
650-51-1	Sodium trichloroacetate	✓	1, 4
1300-72-7	Sodium xylenesulfonate	✓	1, 3, 4
10377-98-7	Sodium zirconium lactate	✓	1, 4
64742-88-7	Solvent naphtha (petroleum), medium aliph.		1, 2, 4
64742-96-7	Solvent naphtha, petroleum, heavy aliph.		2, 8
64742-94-5	Solvent naphtha, petroleum, heavy arom.		1, 2, 4, 5, 8
64742-95-6	Solvent naphtha, petroleum, light arom.		1, 2, 4
8007-43-0	Sorbitan, (9Z)-9-octadecenoate (2:3)	✓	4

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
1338-43-8	Sorbitan, mono-(9Z)-9-octadecenoate	✓	1, 2, 3, 4
9005-65-6	Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivis.	✓	3, 4
9005-67-8	Sorbitan, monooctadecenoate, poly(oxy-1,2-ethanediyl) derivis.	✓	3, 4
26266-58-0	Sorbitan, tri-(9Z)-9-octadecenoate	✓	8
10025-69-1	Stannous chloride dihydrate	✓	1, 4
9005-25-8	Starch		1, 2, 4
68131-87-3	Steam cracked distillate, cyclodiene dimer, dicyclopentadiene polymer		1
8052-41-3	Stoddard solvent		1, 3, 4
10476-85-4	Strontium chloride	✓	4
100-42-5	Styrene	✓	2
57-50-1	Sucrose	✓	1, 2, 3, 4
5329-14-6	Sulfamic acid	✓	1, 4
14808-79-8	Sulfate	✓	1, 4
68201-64-9	Sulfomethylated quebracho		2
68608-21-9	Sulfonic acids, C10-16-alkane, sodium salts	✓	6
68439-57-6	Sulfonic acids, C14-16-alkane hydroxy and C14-16-alkene, sodium salts		1, 3, 4
61789-85-3	Sulfonic acids, petroleum		1
68608-26-4	Sulfonic acids, petroleum, sodium salts		3
7446-09-5	Sulfur dioxide	✓	2, 4, 8
7664-93-9	Sulfuric acid	✓	1, 2, 4, 7
68955-19-1	Sulfuric acid, mono-C12-18-alkyl esters, sodium salts	✓	4
68187-17-7	Sulfuric acid, mono-C6-10-alkyl esters, ammonium salts	✓	1, 4, 8
14807-96-6	Talc		1, 3, 4, 6, 7
8002-26-4	Tall oil		4, 8
61791-36-4	Tall oil imidazoline		4
68092-28-4	Tall oil, compound with diethanolamine		1
65071-95-6	Tall oil, ethoxylated		4, 8
8016-81-7	Tall-oil pitch		4
61790-60-1	Tallow alkyl amines acetate		8
72480-70-7	Tar bases, quinoline derivatives, benzyl chloride-quaternized		1, 3, 4
68647-72-3	Terpenes and Terpenoids, sweet orange-oil		1, 3, 4, 8

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
8000-41-7	Terpineol	✓	1, 3
75-91-2	tert-Butyl hydroperoxide	✓	1, 4
614-45-9	tert-Butyl perbenzoate	✓	1
12068-35-8	Tetra-calcium-alumino-ferrite		1, 2, 4
629-59-4	Tetradecane	✓	8
139-08-2	Tetradecyldimethylbenzylammonium chloride	✓	1, 4, 8
112-60-7	Tetraethylene glycol	✓	1, 4
112-57-2	Tetraethylenepentamine	✓	1, 4
55566-30-8	Tetrakis(hydroxymethyl)phosphonium sulfate	✓	1, 2, 3, 4, 7
681-84-5	Tetramethyl orthosilicate	✓	1
75-57-0	Tetramethylammonium chloride	✓	1, 2, 3, 4, 7, 8
1762-95-4	Thiocyanic acid, ammonium salt	✓	2, 3, 4
68-11-1	Thioglycolic acid	✓	1, 2, 3, 4
62-56-6	Thiourea	✓	1, 2, 3, 4, 6
68527-49-1	Thiourea, polymer with formaldehyde and 1-phenylethanone	✓	1, 4, 8
68917-35-1	Thuja plicata donn ex. D. don leaf oil		3
7772-99-8	Tin(II) chloride	✓	1
13463-67-7	Titanium dioxide	✓	1, 2, 4
36673-16-2	Titanium(4+) 2-[bis(2-hydroxyethyl)amino]ethanolate propan-2-olate (1:2:2)	✓	1
74665-17-1	Titanium, iso-Pr alc. triethanolamine complexes	✓	1, 4
108-88-3	Toluene	✓	1, 3, 4
126-73-8	Tributyl phosphate	✓	1, 2, 4
81741-28-8	Tributyltetradecylphosphonium chloride	✓	1, 3, 4
7758-87-4	Tricalcium phosphate	✓	1, 4
12168-85-3	Tricalcium silicate	✓	1, 2, 4
87-90-1	Trichloroisocyanuric acid	✓	2
629-50-5	Tridecane	✓	8
102-71-6	Triethanolamine	✓	1, 2, 4
68299-02-5	Triethanolamine hydroxyacetate	✓	3
68131-71-5	Triethanolamine polyphosphate ester	✓	1, 4, 8
77-93-0	Triethyl citrate	✓	1, 4
78-40-0	Triethyl phosphate	✓	1, 4

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
112-27-6	Triethylene glycol	✓	1, 2, 3
112-24-3	Triethylenetetramine	✓	4
122-20-3	Triisopropanolamine	✓	1, 4
14002-32-5	Trimethanolamine	✓	3
121-43-7	Trimethyl borate	✓	8
25551-13-7	Trimethylbenzene	✓	1, 2, 4
7758-29-4	Triphosphoric acid, pentasodium salt	✓	1, 4
1317-95-9	Tripoli	✓	4
6100-05-6	Tripotassium citrate monohydrate	✓	4
25498-49-1	Tripropylene glycol monomethyl ether	✓	2
68-04-2	Trisodium citrate	✓	3
6132-04-3	Trisodium citrate dihydrate	✓	1, 4
150-38-9	Trisodium ethylenediaminetetraacetate	✓	1, 3
19019-43-3	Trisodium ethylenediaminetriacetate	✓	1, 4, 8
7601-54-9	Trisodium phosphate	✓	1, 2, 4
10101-89-0	Trisodium phosphate dodecahydrate	✓	1
77-86-1	Tromethamine	✓	3, 4
73049-73-7	Tryptone		8
1319-33-1	Ulexite		1, 2, 3, 8
1120-21-4	Undecane	✓	3, 8
57-13-6	Urea	✓	1, 2, 4, 8
1318-00-9	Vermiculite		2
24937-78-8	Vinyl acetate ethylene copolymer	✓	1, 4
25038-72-6	Vinylidene chloride/methylacrylate copolymer	✓	4
7732-18-5	Water	✓	2, 4, 8
8042-47-5	White mineral oil, petroleum		1, 2, 4
1330-20-7	Xylenes	✓	1, 2, 4
8013-01-2	Yeast extract		8
7440-66-6	Zinc	✓	2
3486-35-9	Zinc carbonate	✓	2
7646-85-7	Zinc chloride	✓	1, 2
1314-13-2	Zinc oxide	✓	1, 4
13746-89-9	Zirconium nitrate	✓	2, 6
62010-10-0	Zirconium oxide sulfate		1, 4

Table continued on next page

Table continued from previous page

CASRN	Chemical Name	IUPAC Name and Structure	Reference
7699-43-6	Zirconium oxychloride	✓	1, 2, 4
21959-01-3	Zirconium(IV) chloride tetrahydrofuran complex	✓	5
14644-61-2	Zirconium(IV) sulfate	✓	2, 6
197980-53-3	Zirconium, 1,1'-((2-((2-hydroxyethyl)(2-hydroxypropyl)amino)ethyl)imino)bis(2-propanol) complexes	✓	4
68909-34-2	Zirconium, acetate lactate oxo ammonium complexes		4, 8
174206-15-6	Zirconium, chloro hydroxy lactate oxo sodium complexes		4
113184-20-6	Zirconium, hydroxylactate sodium complexes		1, 4
101033-44-7	Zirconium,tetrakis[2-[bis(2-hydroxyethyl)amino-kN]ethanolato-kO]-	✓	1, 2, 4, 5

Table A-2 lists generic names of chemicals reported to be used in hydraulic fracturing fluids between 2005 and 2009. Generic chemical names provide limited information on the chemical, but are not specific enough to determine chemical structures. 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.

Table A-2. 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
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

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Table continued from previous page

Generic Chemical Name	Reference
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
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

Table continued on next page

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Generic Chemical Name	Reference
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
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

Table continued on next page

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Generic Chemical Name	Reference
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
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

Table continued on next page

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Generic Chemical Name	Reference
Epoxy	4
Epoxy resin	1, 4
Essential oils	1, 4
Ester Salt	2, 4
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 acids	1
Fatty acid, ethoxylate	4
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

Table continued on next page

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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
Metal salt solution	1
Mineral	1, 4
Mineral fiber	2
Mineral filler	1

Table continued on next page

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Generic Chemical Name	Reference
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
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

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Generic Chemical Name	Reference
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
Paraffinic naphthenic solvent	1
Paraffinic solvent	1, 4
Paraffin inhibitor	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
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

Table continued on next page

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Generic Chemical Name	Reference
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
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

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Generic Chemical Name	Reference
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
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

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Generic Chemical Name	Reference
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
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-3 contains a list of chemicals with CASRNs that have been detected in flowback and produced water (collectively referred to as "hydraulic fracturing wastewater"). The table identifies chemicals that are also reported to be used in hydraulic fracturing fluids (Table A-1).

Table A-3. List of CASRNs and names of chemicals detected in hydraulic fracturing wastewater. Chemicals also reportedly used in hydraulic fracturing fluids are marked with an "✓."

CASRN	Chemical Name	Also Listed in Table A 1	Reference
87-61-6	1,2,3-Trichlorobenzene		3, 9
120-82-1	1,2,4-Trichlorobenzene		9
95-63-6	1,2,4-Trimethylbenzene	✓	3, 9, 10
57-55-6	1,2-Propanediol	✓	3, 9
108-67-8	1,3,5-Trimethylbenzene	✓	3, 9, 10
123-91-1	1,4-Dioxane	✓	9, 10
105-67-9	2,4-Dimethylphenol		3, 9, 10
87-65-0	2,6-Dichlorophenol		3, 9
91-57-6	2-Methylnaphthalene		3, 9, 10
95-48-7	2-Methylphenol		3, 9, 10
79-31-2	2-Methylpropanoic acid		10
109-06-8	2-Methylpyridine		3, 9
503-74-2	3-Methylbutanoic acid		10
108-39-4	3-Methylphenol		3, 9, 10
106-44-5	4-Methylphenol		3, 9, 10
57-97-6	7,12-Dimethylbenz(a)anthracene		3, 9
64-19-7	Acetic acid	✓	3, 9, 10
67-64-1	Acetone	✓	3, 9, 10
98-86-2	Acetophenone	✓	3, 9
107-02-8	Acrolein	✓	9
107-13-1	Acrylonitrile		3, 9
309-00-2	Aldrin		3, 9
7429-90-5	Aluminum	✓	3, 9, 10
7664-41-7	Ammonia	✓	3, 9, 10
7440-36-0	Antimony		3, 9, 10
12672-29-6	Aroclor 1248		3, 9
7440-38-2	Arsenic	✓	3, 9, 10
7440-39-3	Barium		3, 9, 10
71-43-2	Benzene	✓	3, 9, 10
50-32-8	Benzo(a)pyrene		3, 9
205-99-2	Benzo(b)fluoranthene		3, 9
191-24-2	Benzo(g,h,i)perylene		3, 9, 10
207-08-9	Benzo(k)fluoranthene		3, 9
100-51-6	Benzyl alcohol		3, 9, 10

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CASRN	Chemical Name	Also Listed in Table A 1	Reference
7440-41-7	Beryllium		3, 9, 10
319-85-7	beta-1,2,3,4,5,6-Hexachlorocyclohexane		3, 9
111-44-4	Bis(2-chloroethyl) ether	✓	3, 9
7440-42-8	Boron		3, 9, 10
24959-67-9	Bromide (-1)		3, 9, 10
75-27-4	Bromodichloromethane		3
75-25-2	Bromoform		3, 9, 10
107-92-6	Butanoic acid		9, 10
104-51-8	Butylbenzene		9, 10
7440-43-9	Cadmium		3, 9, 10
10045-97-3	Caesium 137		3
7440-70-2	Calcium		3, 9, 10
124-38-9	Carbon dioxide	✓	3, 9, 10
75-15-0	Carbon disulfide		3, 9
16887-00-6	Chloride	✓	3, 9, 10
7782-50-5	Chlorine	✓	3, 10
124-48-1	Chlorodibromomethane		3
67-66-3	Chloroform		3, 9, 10
74-87-3	Chloromethane		3, 10
7440-47-3	Chromium		3, 9, 10
16065-83-1	Chromium (III), insoluble salts	✓	3
18540-29-9	Chromium (VI)	✓	3, 10
7440-48-4	Cobalt		3, 9, 10
7440-50-8	Copper	✓	3, 9, 10
98-82-8	Cumene	✓	3, 9
57-12-5	Cyanide, free		3, 9, 10
319-86-8	delta-Hexachlorocyclohexane		9
117-81-7	Di(2-ethylhexyl) phthalate	✓	3, 9, 10
53-70-3	Dibenz(a,h)anthracene		3, 9
84-74-2	Dibutyl phthalate		3, 9, 10
75-09-2	Dichloromethane		9, 10
60-57-1	Dieldrin		9
84-66-2	Diethyl phthalate		9
117-84-0	Dioctyl phthalate		9, 10
122-39-4	Diphenylamine		3, 9
959-98-8	Endosulfan I		3, 9
33213-65-9	Endosulfan II		3, 9
7421-93-4	Endrin aldehyde		3, 9

Table continued on next page

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CASRN	Chemical Name	Also Listed in Table A 1	Reference
100-41-4	Ethylbenzene	✓	3, 9, 10
107-21-1	Ethylene glycol	✓	3, 9
206-44-0	Fluoranthene		3, 9
86-73-7	Fluorene		3, 9, 10
16984-48-8	Fluoride		3, 9, 10
64-18-6	Formic acid	✓	10
76-44-8	Heptachlor		3, 9
1024-57-3	Heptachlor epoxide		3, 9
111-14-8	Heptanoic acid		10
142-62-1	Hexanoic acid		10
193-39-5	Indeno(1,2,3-cd)pyrene		3, 9
7439-89-6	Iron	✓	3, 9, 10
67-63-0	Isopropanol	✓	3, 9
7439-92-1	Lead	✓	3, 9, 10
58-89-9	Lindane		3, 9
7439-93-2	Lithium		3, 9, 10
7439-95-4	Magnesium		3, 9, 10
7439-96-5	Manganese		3, 9, 10
7439-97-6	Mercury		3, 9, 10
67-56-1	Methanol	✓	3, 9
74-83-9	Methyl bromide		3, 9
78-93-3	Methyl ethyl ketone		3, 9, 10
7439-98-7	Molybdenum		3, 9, 10
91-20-3	Naphthalene	✓	3, 9, 10
7440-02-0	Nickel		3, 9, 10
86-30-6	N-Nitrosodiphenylamine		3, 9
72-55-9	p,p'-DDE		3, 9
99-87-6	p-Cymene		9, 10
109-52-4	Pentanoic acid		10
85-01-8	Phenanthrene	✓	3, 9, 10
108-95-2	Phenol	✓	3, 9, 10
298-02-2	Phorate		9
7723-14-0	Phosphorus		3, 9
7440-09-7	Potassium		3, 9, 10
79-09-4	Propionic acid		10
103-65-1	Propylbenzene		9
129-00-0	Pyrene		9, 10
110-86-1	Pyridine		3, 9, 10

Table continued on next page

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CASRN	Chemical Name	Also Listed in Table A 1	Reference
13982-63-3	Radium 226		3, 10
7440-14-4	Radium 226,228		3
15262-20-1	Radium 228		3, 10
94-59-7	Safrole		3, 9
135-98-8	sec-Butylbenzene		9
7782-49-2	Selenium		3, 9, 10
7631-86-9	Silica	✓	10
7440-21-3	Silicon (elemental)		10
7440-22-4	Silver		3, 9, 10
7440-23-5	Sodium		3, 9, 10
7440-24-6	Strontium		3, 9, 10
14808-79-8	Sulfate	✓	3, 9, 10
14265-45-3	Sulfite		3
127-18-4	Tetrachloroethylene		3, 9
7440-28-0	Thallium and Compounds		3, 9, 10
7440-31-5	Tin		9, 10
7440-32-6	Titanium		3, 9, 10
108-88-3	Toluene	✓	3, 9, 10
7440-62-2	Vanadium		3, 10
1330-20-7	Xylenes	✓	3, 9, 10
7440-66-6	Zinc	✓	3, 9, 10
7440-67-7	Zirconium		3

Table A-4 contains a list of chemicals and properties that are detected in flowback and produced water (collectively referred to as "hydraulic fracturing wastewater").

Table A-4. List of chemicals and properties detected in hydraulic fracturing wastewater.

Chemical Name / Property	Reference
Alkalinity	3, 9, 10
Alkalinity, carbonate (as $CaCO_3$)	3, 9, 10
Alpha radiation	3
Aluminum, dissolved	3, 9
Barium strontium P.S.	3
Barium, dissolved	3, 9
Beta radiation	3
Bicarbonates (HCO_3)	3, 10
Biochemical oxygen demand	3, 9, 10
Cadmium, dissolved	3, 9
Calcium, dissolved	3, 9
Chemical oxygen demand	3, 9, 10
Chromium (VI), dissolved	3
Chromium, dissolved	3, 9
Cobalt, dissolved	3, 9
Coliform	3
Color	3
Conductivity	3, 9, 10
Hardness as $CaCO_3$	3, 9, 10
Heterotrophic plate count	3
Hexanoic acid	10
Iron, dissolved	3, 9
Lithium, dissolved	3, 9
Magnesium, dissolved	3, 9
Manganese, dissolved	3, 9
Nickel, dissolved	3, 9
Nitrate, as N	3, 9, 10
Nitrogen, total as N	3
Oil and grease	3, 9, 10
Petroleum hydrocarbons	3
pH	3, 9, 10
Phenols	3
Potassium, dissolved	3, 9
Salt	3
Scale inhibitor	3
Selenium, dissolved	3, 9
Silver, dissolved	3, 10
Sodium, dissolved	3, 10
Strontium, dissolved	3, 10
Surfactants	3
Total alkalinity	3, 9, 10
Total dissolved solids	3, 9, 10
Total Kjeldahl nitrogen	3, 9, 10
Total organic carbon	3, 9, 10
Total sulfide	9
Total suspended solids	3, 9, 10
Volatile acids	3, 9
Zinc, dissolved	3, 9

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Appendix B: Stakeholder Engagement[90]

B.1. Stakeholder Engagement Road Map for the EPA's Study on the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources

On March 18, 2010, at the request of the U.S. Congress, the EPA announced plans to develop a comprehensive research study on the potential impact of hydraulic fracturing on drinking water resources. The EPA believes a transparent, research-driven approach with significant stakeholder involvement can address questions about hydraulic fracturing and strengthen our clean energy future. The road map below outlines the EPA's plans to build upon its commitment to transparency and stakeholder engagement coordinated during the development of the Study Plan and will help inform the report of results.

Goals of Strengthened Stakeholder Engagement

- Increase technical engagement with the stakeholder community to ensure that the EPA has ongoing access to a broad range of expertise and data outside the agency.
- Improve public understanding of the goals and design of the study.
- Ensure that the EPA is current on changes in industry practices and technologies so the report of results reflects an up-to-date picture of hydraulic fracturing operations.
- Obtain timely and constructive feedback on projects undertaken as part of the study.

Increased Technical Engagement

In November 2012, the EPA held five roundtables focused on each stage of the water cycle:

- *Water acquisition.* This study takes steps to examine potential changes in the quantity of water available for drinking and potential changes in drinking water quality that result from acquisition for hydraulic fracturing. The EPA is aware that the use of recycling is rapidly growing and that this may affect the need to acquire water for hydraulic fracturing.
- *Chemical mixing.* The study examines the potential release of chemicals used in hydraulic fracturing to surface and ground water through onsite spills and/or leaks and compiles information on hydraulic fracturing fluids and chemicals from publicly available data, data provided by nine hydraulic fracturing service companies and other sources.
- *Flowback.* The study examines available data regarding release to surface or ground water through spills or leakage from onsite storage.
- *Water treatment and disposal.* The study examines the potential for contaminants to reach drinking water due to surface water discharge, the effectiveness of current wastewater treatment, and the potential formation of disinfection byproducts in drinking water treatment facilities.

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[90] The text and figure included in this appendix were taken from http://www.epa.gov/hfstudy/stakeholder-roadmap.html. Please see this website for updated information as it becomes available.

- *Well injection.* The study takes steps to examine the potential for release of hydraulic fracturing fluids to ground water due to inadequate well construction or operation, movement of hydraulic fracturing fluids from the target formation to drinking water aquifers through local man-made or natural features (e.g., other production or abandoned wells and existing faults or fractures).

Based on feedback from these roundtables, the EPA will host in-depth technical workshops to address specific issues in greater detail. These technical workshops will begin in February 2013 and continue as needed. Upon completion of the last technical workshop, the EPA will reconvene the original roundtables to review the work addressed in the technical workshop series.

Improve Public Understanding

To improve public understanding of the study, the EPA staff will increase the frequency of webinars. For instance, after the initial set of roundtables and each technical workshop, the EPA will host a webinar to report out to the public on these. The EPA will continue to provide regular electronic updates to its list of stakeholders.

In addition to the webinars, the EPA staff will regularly update its hydraulic fracturing study website with up-to-date materials and identify opportunities for briefings and updates on the study to stakeholders (e.g., annual or regional meetings of industry trade associations, annual meetings of environmental/public health groups, academic conferences, annual or regional meetings of water utilities, and tribal meetings).

The EPA has previously committed to the release in December 2012 of a progress report on the study. While the progress report will not make any final findings or conclusions, it will provide the public with an update on study activities and future work.

Ensure the EPA is Current on Industry Practices

To ensure that the EPA is up-to-date on evolving industry practices and technologies, the EPA will publish a *Federal Register* notice in late 2012 to create a docket where stakeholders can submit peer-reviewed data from ongoing or completed studies. This initial request will be followed up with requests in 2013 and 2014.

Obtain Timely Feedback

The EPA intends to receive timely feedback on the projects conducted as part of the study through the roundtables and technical workshops described above. In addition, the EPA's Science Advisory Board is forming a panel of independent experts who will provide advice and review under the auspices of the Science Advisory Board on the EPA's hydraulic fracturing research described in its 2012 Progress Report. The EPA plans to use such advice for the development of a report of results, estimated to be released in late 2014, which will also be reviewed by the Science Advisory Board. In addition, this panel may also provide advice on other technical documents and issues related to hydraulic fracturing upon further request by the EPA. The panel will provide opportunities for public comment in connection with these activities.

B.2 Stakeholder Road Map and Timeline

Increase technical engagement with the stakeholder community to ensure that the EPA has ongoing access to a broad range of expertise and data outside the agency.

Plan: The week of November 12, 2012, EPA held five roundtables focused on each stage of the water cycle, to be followed in Spring 2013 by a series of technical workshops on topics identified during the roundtables.

Implementation:

- Identify participants for meetings (September 2012):
    - The EPA consulted with industry, non-governmental organizations, states, and tribes through a series of one-on-one meetings in September to present the plan for the roundtables and ask for potential invitees with technical expertise. The EPA then selected invitees with appropriate technical backgrounds.
    - Roundtable participants numbered 15-20 in addition to the EPA staff.
- Kick-off (October 2012)
    - The EPA hosted a kick-off (virtual) meeting with technical representatives representing a broad range of stakeholders to lay out the context, goals, and logistics for the roundtables.
- Roundtables (November 14–16, 2012)
    - Each meeting was professionally facilitated.
    - All roundtables occurred in DC. These were half-day meetings.
- Workshops (February 2013 through April 2013)
- Second round of roundtables (Summer/Fall 2013)

Obtain timely and constructive feedback on projects undertaken as part of the study and ensure that the EPA is current on changes in industry practices and technologies so the report of results reflects an up-to-date picture of hydraulic fracturing operations.

Plan: Issue *Federal Register* notices in 2012, 2013, and 2014 requesting additional data and information to inform the study.[91] The notices will request peer-reviewed data and reports that can help answer the research questions, for example, the content of hydraulic fracturing flowback and produced water; the location of prior wastewater treatment pits, ponds, lagoons, and tanks; specific sources of water used for hydraulic fracturing; specific water quality requirements for use of water or reuse of waste water in hydraulic fracturing; partitioning of constituents into gas solid and liquid components (particularly the fate of metals, organics, and radionuclides).

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[91] The first *Federal Register* notice was published in November 2012 and is available at http://www.gpo.gov/fdsys/pkg/FR-2012-11-09/pdf/2012-27452.pdf.

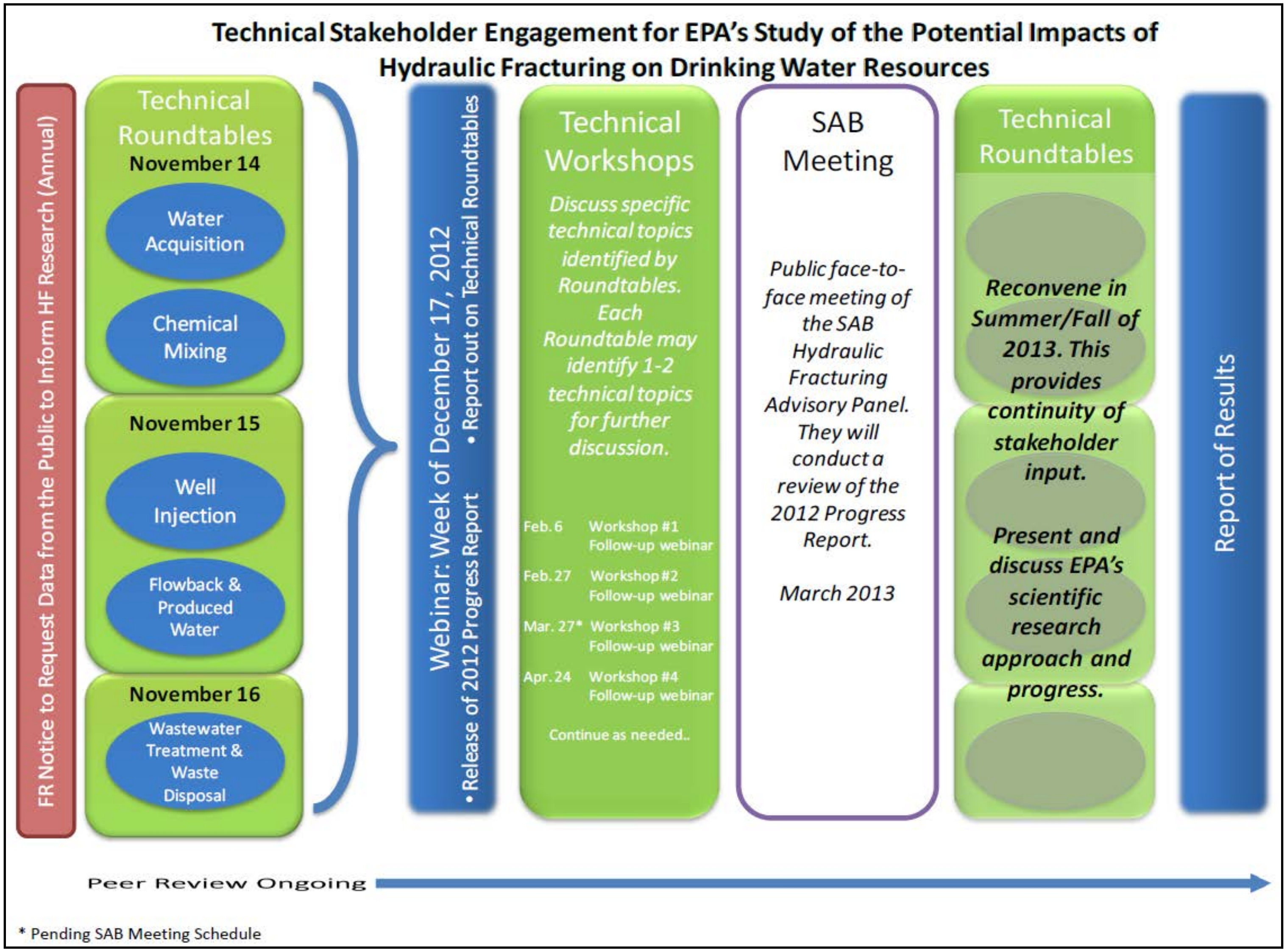
Implementation:

- Technical workshops on specific technical topics suggested by roundtable participants (begin February 2013)
- These sessions will flow from roundtable discussions. The EPA will convene experts to address specific issues of data collection, method or data interpretation (i.e., how to find more comprehensive/reliable spill data; how to get good data for the environmental justice analysis, etc.). The EPA will issue the first *Federal Register* notice in late 2012 to request peer-reviewed data and studies that can help answer the research questions. Additional *Federal Register* notices will request peer-reviewed information and will be published annually in 2013 and 2014.

Improve public understanding of the goals and design of the study.

Plan: In addition to the organized technical meetings, the EPA will seek opportunities (such as association or state organization meetings) to provide informal briefings and updates on the study to a diverse range of stakeholders, including states, non-governmental organizations, academia, and industry. The EPA will also increase the frequency of webinars, hosting them after each technical meeting to report out to the public on the discussion.

Implementation: The EPA will host monthly webinars following the initial set of roundtables and each technical workshop to inform the public of topics discussed. The EPA will develop and publish a calendar of events where presentations on the study will be made.



Discuss specific technical topics identified by Roundtables. Each Roundtable may identify 1-2 technical topics for further discussion.

Public face-to-face meeting of the SAB Hydraulic Fracturing Advisory Panel. They will conduct a review of the 2012 Progress Report.

Reconvene in Summer/Fall of 2013. This provides continuity of stakeholder input.

Present and discuss EPA's scientific research approach and progress.

Figure B-1. Timeline for technical roundtables and workshops. The goals of this enhanced engagement process are to improve public understanding of the study, ensure that the EPA is current on changes in industry practices and technologies so that the report of results reflects an up-to-date picture of hydraulic fracturing operations, and obtain timely and constructive feedback on ongoing research projects.

Appendix C: Summary of QAPPs

This appendix provides a quick reference table for QAPPs associated with the research projects that comprise the EPA's *Study of the Potential Impacts of Drinking Water Resources.* Current versions of the QAPPs are available at http://www.epa.gov/hfstudy/qapps.html.

Table C-1. QAPPs associated with the research projects discussed in this progress report.

Research Project	QAPP Title
Literature Review	QAPP for Hydraulic Fracturing Data and Literature Evaluation for the EPA's *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*
Spills Database Analysis	QAPP for Hydraulic Fracturing Surface Spills Data Analysis
Service Company Analysis	Final QAPP for the Evaluation of Information on Hydraulic Fracturing
	QAPP for Analysis of Data Received from Nine Hydraulic Fracturing Service Companies
Well File Review	QAPP for Hydraulic Fracturing
	National Hydraulic Fracturing Study Evaluation of Existing Production Well File Contents: QAPP
	Supplemental Programmatic QAPP for Work Assignment 4-58: National Hydraulic Fracturing Study Evaluation of Existing Production Well File Contents
FracFocus Analysis	Supplemental Programmatic QAPP for Work Assignment 4-58: National Hydraulic Fracturing Study Evaluation of Existing Production Well File Contents
	QAPP for Analysis of Data Extracted from FracFocus
Subsurface Migration Modeling	Analysis of Environmental Hazards Related to Hydrofracturing
Surface Water Modeling	QAPP for Surface Water Transport of Hydraulic Fracturing-Derived Waste Water
Water Availability Modeling	Data Collection/Mining for Hydraulic Fracturing Case Studies
	Modeling the Impact of Hydraulic Fracturing on Water Resources Based on Water Acquisition Scenarios
Source Apportionment Studies	QAPP for Hydraulic Fracturing Waste Water Source Apportionment Study
Wastewater Treatability Studies	Fate, Transport, and Characterization of Contaminants in Hydraulic Fracturing Water in Wastewater Treatment Processes
Br-DBP Precursor Studies	Formation of Disinfection By-Products from Hydraulic Fracturing Fluid Constituents: QAPP
Analytical Method Development	QAPP for the Chemical Characterization of Select Constituents Relevant to Hydraulic Fracturing
	QAPP for the Interlaboratory Verification and Validation of Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, 2-Butoxyethanol and 2-Methoxyethanol in Ground and Surface Waters by Liquid Chromatography/Tandem Mass Spectrometry

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Research Project	QAPP Title
Toxicity Assessment	QAPP: Health and Toxicity Theme, Hydraulic Fracturing Study
	QAPP for Chemical Information Quality Review and Physicochemical Property Calculations for Hydraulic Fracturing Chemical Lists
Las Animas and Huerfano Counties, Colorado	Hydraulic Fracturing Retrospective Case Study, Raton Basin, CO
Dunn County, North Dakota	Hydraulic Fracturing Retrospective Case Study, Bakken Shale, Killdeer and Dunn County, ND
Bradford County, Pennsylvania	Hydraulic Fracturing Retrospective Case Study, Bradford-Susquehanna Counties, PA
Washington County, Pennsylvania	Hydraulic Fracturing Retrospective Case Study, Marcellus Shale, Washington County, PA
Wise County, Texas	Hydraulic Fracturing Retrospective Case Study, Wise and Denton Cos., TX

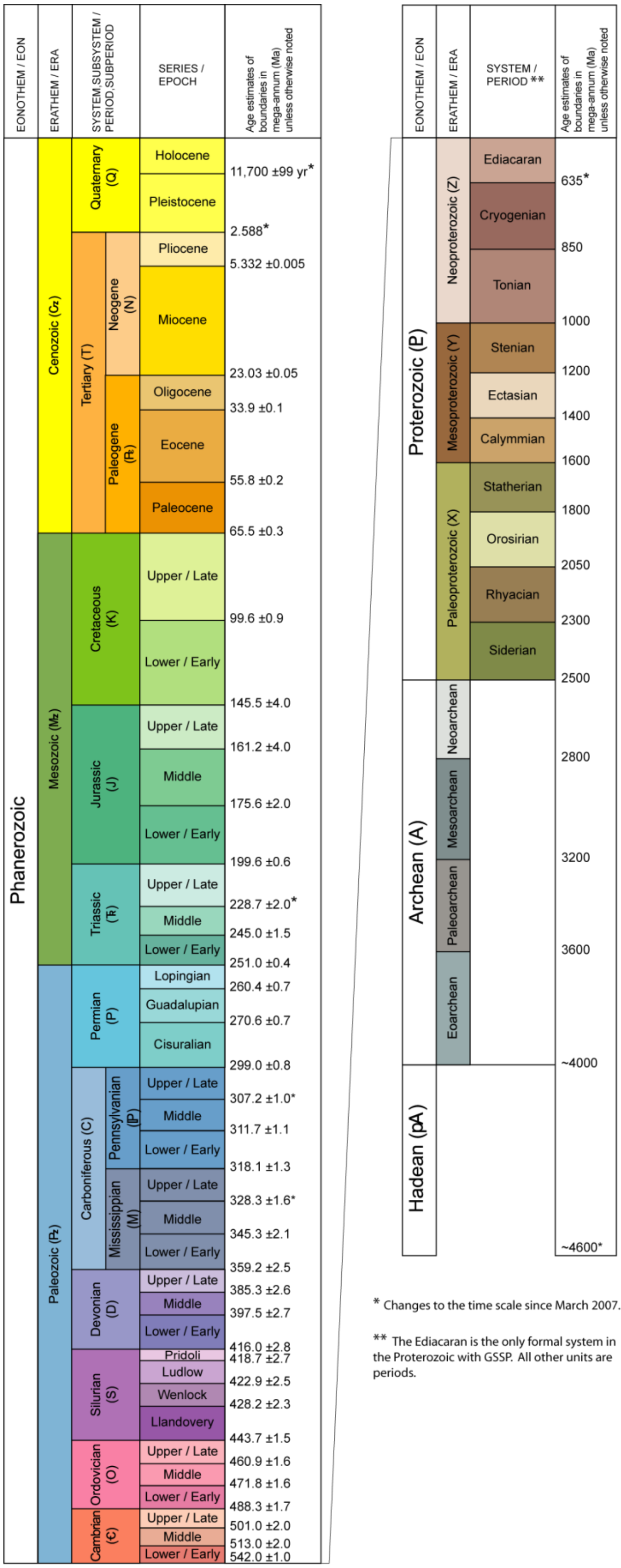
Appendix D: Divisions of Geologic Time

Figure E-1 is reproduced from a USGS fact sheet, “Divisions of Geologic Time: Major Chronostratigraphic and Geochronological Units.” A geologic timescale relates rock layers to time.

Chronstratigraphic units refer to specific rock layers while geochronological units refer to specific time periods.

Reference

US Geological Survey. 2010. Divisions of Geologic Time: Major Chronostratigraphic and Geochronological Units. Fact Sheet 2010-3059. US Geological Survey. Available at http://pubs.usgs.gov/fs/2010/3059/pdf/FS10-3059.pdf. Accessed November 30, 2012.



* Changes to the time scale since March 2007.

** The Ediacaran is the only formal system in the Proterozoic with GSSP. All other units are periods.

Figure D-1. Divisions of geologic time approved by the USGS Geologic Names Committee (2010).The chart shows major chronostratigraphic and geochronologic units.

Glossary

Acid mine drainage: Drainage of water from areas that have been mined for coal of other mineral ores. The water has a low pH because of its contact with sulfur-bearing material and is harmful to aquatic organisms. (2)

Adsorption: Adhesion of molecules of gas, liquid, or dissolved solids to a surface. (2)

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). (2)

Ambient water quality: Natural concentration of water quality constituents prior to mixing of either point or nonpoint source load of contaminants. Reference ambient concentration is used to indicate the concentration of a chemical that will not cause adverse impact to human health. (2)

Analysis of existing data: The process of gathering and summarizing existing data from various sources to provide current information on hydraulic fracturing activities.

Analyte: The element, ion, or compound that an analysis seeks to identify; the compound of interest. (2)

Annulus: Either the space between the casing of a well and the wellbore or the space between the tubing and casing of a well. (2)

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. (1)

Aquifer: An underground geological formation, or group of formations, containing water. A source of ground water for wells and springs. (2)

Baseline data: Initial information on a program or program components collected prior to receipt of services or participation activities. Often gathered through intake interviews and observations and used later for comparing measures that determine changes in a program. (2)

Case study: An approach often used in research to better understand real-world situations or events using a systematic process for the collection and analysis of data.

> **Prospective case study:** A study of sites where hydraulic fracturing will occur after the research is initiated. These case studies allow sampling and characterization of the site prior to, and after, water extraction, drilling, hydraulic fracturing fluid injection, flowback, and gas production. The data collected during prospective case studies will allow the EPA to evaluate any changes in water quality over time.
>
> **Retrospective case study:** A study of sites where hydraulic fracturing has occurred nearby, with a focus on sites with reported instances of drinking water resource contamination.

These studies will use existing data, sampling, and possibly modeling to determine whether reported impacts are due to hydraulic fracturing activities or other sources.

Casing: Pipe cemented in the well to seal off formation fluids and to keep the hole from caving in. (1)

Chemical Abstracts Service: Provides information on chemical properties and interactions. Every year, the Chemical Abstracts Service updates and writes new chemical abstracts on well over a million different chemicals, including each chemical's composition, structure, characteristics, and different names. Each abstract is accompanied by a registration number, or CASRN. (2)

Coalbed methane: Methane contained in coal seams. A coal seam is a layer or stratum of coal parallel to the rock stratification.

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. (2)

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. (2)

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. (5)

Discharge: Any emission (other than natural seepage), intentional or unintentional. Includes, but is not limited to, spilling, leaking, pumping, pouring, emitting, emptying or dumping. (2)

Disinfection byproduct (DBP): A compound formed by the reaction of a disinfectant such as chlorine with organic material in the water supply. (2)

Drinking water resource: Any body of water, ground or surface, that could currently, or in the future, serve as a source of drinking water for public or private water supplies.

DSSTox: The Distributed Structure-Searchable Toxicity Database Network, a project of the EPA's National Center for Computational Toxicology. The DSSTox website provides a public forum for publishing downloadable, structure-searchable, standardized chemical structure files associated with chemical inventories or toxicity datasets of environmental relevance. (2)

Effluent: Waste material being discharged into the environment, either treated or untreated. (2)

Environmental justice: The fair treatment of people of all races, cultures, incomes, and educational levels with respect to the development and enforcement of environmental laws, regulations, and policies. The fair distribution of environmental risks across socioeconomic and racial groups. (2)

Flowback: After the hydraulic fracturing procedure is completed and pressure is released, the direction of fluid flow reverses, and water and excess proppant flow up through the wellbore to the surface. The water that returns to the surface is commonly referred to as “flowback.” (3)

Fluid formulation: The entire suite of products and carrier fluid injected into a well during hydraulic fracturing.

Formation: A geological formation is a body of earth material with distinctive and characteristic properties and a degree of homogeneity in its physical properties. (2)

Formation water: Water that occurs naturally within the pores of rock. (5)

FracFocus: National registry for chemicals used in hydraulic fracturing, jointly developed by the Ground Water Protection Council and the Interstate Oil and Gas Compact Commission. Serves as an online repository where oil and gas well operators can upload information regarding the chemical compositions of hydraulic fracturing fluids used in specific oil and gas production wells. Also contains spatial information for well locations and information on well depth and water use.

Geographic information system (GIS): A computer system designed for storing, manipulating, analyzing, and displaying data in a geographic context, usually as maps. (2)

Gross α: The total radioactivity due to alpha particle emission as inferred from measurements on a dry sample. (2)

Gross β: The total radioactivity due to beta particle emission as inferred from measurements on a dry sample. (2)

Ground water: The supply of fresh water found beneath the Earth’s surface, usually in aquifers, which supply wells and springs. It provides a major source of drinking water. (2)

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. (5)

Hazardous air pollutants: Air pollutants that are not covered by ambient air quality standards but which, as defined in the Clean Air Act, may present a threat of adverse human health effects or adverse environmental effects. Although classified as air pollutants, they may also impact drinking water. (2)

Horizontal drilling: Drilling a portion of a well horizontally to expose more of the formation surface area to the wellbore. (1)

Hydraulic fracturing: The process of using high pressure to pump sand along with water and other fluids into subsurface rock formations in order to improve flow of oil and gas into a wellbore. (1)

> **Fluid:** Specially engineered fluids containing chemical additives and proppant that are pumped under high pressure into the well to create and hold open fractures in the formation.
>
> **Wastewater:** Flowback and produced water, where flowback is the fluid returned to the surface after hydraulic fracturing has occurred but before the well is placed into production, and produced water is the fluid returned to the surface after the well has been placed into production.
>
> **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. (2)

Hydrocarbon: An organic compound containing only hydrogen and carbon, often occurring in petroleum, natural gas, and coal. (2)

Immiscible: The chemical property where two or more liquids or phases do not readily dissolve in one another, such as soil and water. (2)

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. (2)

Laboratory studies: Targeted research conducted to better understand the ultimate fate and transport of chemical contaminants of concern. The contaminants of concern may be components of hydraulic fracturing fluids, naturally occurring substances released from the subsurface during hydraulic fracturing, or treated flowback and produced water that has been released.

Mass spectrometry: Method of chemical analysis in which the substance to be analyzed is heated and placed in a vacuum. The resulting vapor is exposed to a beam of electrons that causes ionization to occur, either of the molecules or their fragments. The ionized atoms are separated according to their mass and can be identified on that basis. (2)

Material Safety Data Sheet (MSDS): Form that contains brief information regarding chemical and physical hazards, health effects, proper handling, storage, and personal protection appropriate for use of a particular chemical in an occupational environment. (2)

Monte Carlo simulation: A technique used to estimate the most probable outcomes from a model with uncertain input data and to estimate the validity of the simulated model.

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. (2)

National Response Center (NRC): Communications center that receives reports of discharges or releases of hazardous substances into the environment. Run by the US Coast Guard, which relays information about such releases to the appropriate federal agency. (2)

Natural gas or **gas:** A naturally occurring mixture of hydrocarbon and non-hydrocarbon gases in porous formations beneath the Earth's surface, often in association with petroleum. The principal constituent of natural gas is methane. (5)

Natural organic matter (NOM): Complex organic compounds that are formed from decomposing plant animal and microbial material in soil and water. (2)

Offset wells: An existing wellbore close to a proposed well that provides information for planning the proposed well. (5)

Overburden: Material of any nature, consolidated or unconsolidated, that overlies a deposit of useful minerals or ores. (2)

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.

Permeability: Ability of rock to transmit fluid through pore spaces. (1)

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.

Play: A set of oil or gas accumulations sharing similar geologic, geographic properties, such as source rock, hydrocarbon type, and migration pathways. (1)

Porosity: Percentage of the rock volume that can be occupied by oil, gas or water. (1)

Produced water: After the drilling and fracturing of the well are completed, water is produced along with the natural gas. Some of this water is returned fracturing fluid and some is natural formation water. These produced waters move back through the wellhead with the gas. (4)

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.

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. (2)

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. (2)

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. (2)

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. (2)

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. (2)

Residuals: The solids generated or retained during the treatment of wastewater. (2)

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. (2)

Scenario evaluation: Exploration of realistic, hypothetical scenarios related to hydraulic fracturing activities using computer models. Used to identify conditions under which hydraulic fracturing activities may adversely impact drinking water resources.

Science Advisory Board: 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.

Service company: A company that assists well operators by providing specialty services, including hydraulic fracturing.

Shale: A fine-grained sedimentary rock composed mostly of consolidated clay or mud. Shale is the most frequently occurring sedimentary rock. (5)

Solubility: The amount of mass of a compound that will dissolve in a unit volume of solution. (2)

Sorption: The act of soaking up or attracting substances. (2)

Source water: Water withdrawn from surface or ground water, or purchased from suppliers, for hydraulic fracturing.

Spud (spud a well): To start the well drilling process by removing rock, dirt, and other sedimentary material with the drill bit.

Standard operating procedure (SOP): A written document that details the method of an operation, analysis, or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks. (2)

Statistical analysis: Analyzing collected data for the purposes of summarizing information to make it more usable and/or making generalizations about a population based on a sample drawn from that population. (2)

Surface water: All water naturally open to the atmosphere (rivers, lakes, reservoirs, ponds, streams, impoundments, seas, estuaries, etc.). (2)

Surfactant: Used during the hydraulic fracturing process to decrease liquid surface tension and improve fluid passage through the pipes.

Technical systems audit (TSA): A thorough, systematic, onsite, qualitative audit of facilities, equipment, personnel, training, procedures, record keeping, data validation, data management, and reporting aspects of a system. (2)

Tight sands: A geological formation consisting of a matrix of typically impermeable, non-porous tight sands.

Total dissolved solids (TDS): The quantity of dissolved material in a given volume of water. (2)

Toxicity reference value: A reference point (generally a dose or concentration) where exposures below that point are not likely to result in an adverse event/effect given a specific range of time.

Toxic Substances Control Act (TSCA): The act that controls the manufacture and sale of certain chemical substances. (2)

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. (5)

Underground Injection Control (UIC): The program under the Safe Drinking Water Act that regulates the use of wells to pump fluids into the ground. (2)

Underground injection control well: Units into which hazardous waste is permanently disposed of by injection 0.25 miles below an aquifer with an underground source of drinking water (as defined under the SDWA). (2)

Underground source of drinking water: An aquifer currently being used as a source of drinking water or containing a sufficient quantity of ground water to supply a public water system. USDWs have a total dissolved solids content of 10,000 milligrams per liter or less and are not aquifers exempted from protection under the Safe Drinking Water Act. (40 CFR 144.3) (2)

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. (2)

Viscosity: A measure of the internal friction of a fluid that provides resistance to shear within the fluid. (2)

Volatile: Readily vaporizable at a relatively low temperature. (2)

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. (2)

Water withdrawal: The process of taking water from a source and conveying it to a place for a particular type of use. (2)

Well files: Files that generally contain information regarding all activities conducted at an oil and gas production well. These files are created by oil and gas operators.

Well operator: A company that ultimately controls and operates oil and gas wells.

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