EPA/600/D-11/001/February 2011/www.epa.gov/research

United States
Environmental Protection
Agency

Draft Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources

United States Environmental Protection Agency
Office of Research and Development

EPA/600/D-11/001
February 2011

United States
Environmental Protection
Agency

Draft Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources

Office of Research and Development

U.S. Environmental Protection Agency

Washington, D.C.

February 7, 2011

This document is distributed solely for peer review under applicable information quality guidelines. It has not been formally disseminated by EPA. It does not represent and should not be construed to represent any Agency determination or policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

TABLE OF CONTENTS

List of Figures v
List of Tables v
List of Acronyms and Abbreviations vi
Executive Summary vii

1 Introduction and Purpose of Study 1
2 Process for Study Plan Development 2
2.1 Initial Science Advisory Board Review of the Study Plan Scope 2
2.2 Stakeholder Input 3
2.3 Research Prioritization 4
2.4 Next Steps 5
2.5 Interagency Cooperation 5
2.6 Quality Assurance 6
3 Overview of Unconventional Natural Gas Production 6
3.1 Site Selection and Preparation 10
3.2 Well Construction and Development 11
3.3 Hydraulic Fracturing 12
3.4 Well Production 13
3.5 Regulatory Framework 13
4 The Hydraulic Fracturing Water Lifecycle 13
5 Approach 15
5.1 Case Studies 15
5.2 Scenario Evaluation 16
5.3 Tools 16
6 Proposed Research 17
6.1 Water Acquisition: How might large volume water withdrawals from ground and surface water impact drinking water resources? 19
6.1.1 Background 19
6.1.2 What are the impacts on water availability? 20
6.1.3 What are the impacts on water quality? 21
6.1.4 Proposed Research Activities—Water Acquisition 21

6.1.4.1 Water Availability: Analysis of Existing Data, Prospective Case Studies, and Scenario Evaluation 21
6.1.4.2 Water Quality: Analysis of Existing Data and Prospective Case Studies 22
6.1.5 Potential Research Outcomes 23
6.2 Chemical Mixing: What are the possible impacts of releases of hydraulic fracturing fluids on drinking water resources? 23
6.2.1 Background 23
6.2.2 What is the composition of hydraulic fracturing fluids and what are the toxic effects of these constituents? 25
6.2.3 What factors may influence the likelihood of contamination of drinking water resources? 25
6.2.4 How effective are mitigation approaches in reducing impacts to drinking water resources? 25
6.2.5 Proposed Research Activities—Chemical Mixing 25
6.2.5.1 Chemical Identity and Toxicity: Analysis of Existing Data 25
6.2.5.2 Hydraulic Fracturing Fluid Release: Analysis of Existing Data and Case Studies 26
6.2.6 Potential Research Outcomes 27
6.3 Well Injection: What are the possible impacts of the injection and fracturing process on drinking water resources? 27
6.3.1 Background 27
6.3.1.1 Well Design and Construction 27
6.3.1.2 Injection of Hydraulic Fracturing Fluid 29
6.3.1.3 Naturally Occurring Substances 30
6.3.2 How effective are well construction practices at containing gases and fluids before, during, and after fracturing? 30
6.3.3 What are the potential impacts of pre-existing man-made or natural pathways/features on contaminant transport? 31
6.3.4 What chemical/physical/biological processes could impact the fate and transport of substances in the subsurface? 32
6.3.5 What are the toxic effects of naturally occurring substances? 32
6.3.6 Proposed Research Activities—Well Injection 32
6.3.6.1 Well Integrity: Analysis of Existing Data, Case Studies, and Scenario Evaluation 32
6.3.6.2 Impacts of Natural and Man-made Pathways: Case Studies and Scenario Evaluation 34

6.3.6.3 Physical/Chemical/Biological Processes Relevant to Hydraulic Fracturing: Laboratory Studies 35
6.3.7 Potential Research Outcomes 35
6.4 Flowback and Produced Water: What are the possible impacts of releases of flowback and produced water on drinking water resources? 35
6.4.1 Background 35
6.4.2 What is the composition and variability of flowback and produced water and what are the toxic effects of these constituents? 37
6.4.3 What factors may influence the likelihood of contamination of drinking water resources? 37
6.4.4 How effective are mitigation approaches in reducing impacts to drinking water resources? 38
6.4.5 Proposed Research Activities—Flowback and Produced Water 38
6.4.5.1 Composition and Variability of Flowback and Produced Water: Analysis of Existing Data and Prospective Case Studies 38
6.4.5.2 Flowback and Produced Water Release: Analysis of Existing Data, Retrospective Case Studies, and Scenario Evaluations 39
6.4.5.3 Flowback and Produced Water Management: Prospective Case Studies 39
6.4.6 Potential Research Outcomes 39
6.5 Wastewater Treatment and Waste Disposal: What are the possible impacts of inadequate treatment of hydraulic fracturing wastewaters on drinking water resources? 40
6.5.1 Background 40
6.5.2 How effective are treatment and disposal methods? 41
6.5.3 Proposed Research Activities—Wastewater Treatment and Waste Disposal 42
6.5.3.1 Effectiveness of Current Treatment Methods: Analysis of Existing Data, Laboratory Studies, and Prospective Case Studies 42
6.5.4 Potential Research Outcomes 42
7 Case Studies 42
7.1 Case Study Selection 42
7.2 Retrospective Case Studies 45
7.3 Prospective Case Studies 46
8 Characterization of Toxicity and Human Health Effects 47
9 Environmental Justice 49
10 Summary 49

11 Areas of Concern Outside the Scope of This Study 54
11.1 Routine Disposal of Hydraulic Fracturing Wastewaters in Class II Underground Injection Wells 55
11.2 Air Quality 55
11.3 Terrestrial and Aquatic Ecosystem Impacts 55
11.4 Seismic Risks 56
11.5 Public Safety Concerns 56
11.6 Occupational Risks 56
11.7 Economic Impacts 57

References 58
Appendix A: Proposed Research Summary 70
Appendix B: Stakeholder Comments 77
Appendix C: Information Request 80
Appendix D: Chemicals Identified in Hydraulic Fracturing Fluid and Flowback/Produced Water 83
Appendix E: Assessing Mechanical Integrity 99
Appendix F: Stakeholder-Nominated Case Studies 102
Appendix G: Field Sampling and Analytical Methods 111
Appendix H: Modeling 119
Glossary 123

LIST OF FIGURES

Figure 1. Fundamental research questions posed for each stage of the hydraulic fracturing water lifecycle ix

Figure 2. Natural gas production in the United States 7

Figure 3. Shale gas plays in the contiguous United States 8

Figure 4. Coalbed methane deposits in the contiguous United States 9

Figure 5. Major tight gas plays in the contiguous United States 10

Figure 6a. Illustration of horizontal well showing the water lifecycle in hydraulic fracturing 11

Figure 6b. Illustration of a vertical where hydraulic fracturing occurs near an underground source of drinking water 12

Figure 7. Water use in hydraulic fracturing 14

Figure 8. Well construction 28

Figure 9a. Summary of research projects proposed for the first three stages of the hydraulic fracturing water lifecycle 51

Figure 9b. Summary of research projects proposed for the last two stages of the hydraulic fracturing water lifecycle 52

LIST OF TABLES

Table 1. Relationship between case studies and scenario evaluations 15

Table 2. Hydraulic fracturing research questions 18

Table 3. Comparison of estimated water needs for hydraulic fracturing in different shale plays 19

Table 4. An example of the volumetric composition of hydraulic fracturing fluid 24

Table 5. Naturally occurring substances that may be found in gas-containing formations 30

Table 6. Decision criteria for selecting hydraulic fracturing sites for case studies 43

Table 7. Retrospective case study finalists 44

Table 8. Approach for conducting retrospective case studies 45

Table 9. Approach for conducting prospective case studies 47

LIST OF ACRONYMS AND ABBREVIATIONS

AOE	area of evaluation
API	American Petroleum Institute
DBP	disinfection byproducts
DOE	United States Department of Energy
EIA	United States Energy Information Administration
EPA	United States Environmental Protection Agency
g/mile	gram per mile
GIS	geospatial information systems
GWPC	Ground Water Protection Council
IOGCC	Interstate Oil and Gas Compact Commission
mcf/d	thousand cubic feet per day
mmcf/d	million cubic feet per day
NETL	National Energy Technology Laboratory
NGO	non-governmental organization
NIOSH	National Institute for Occupational Safety and Health
NPS	National Park Service
NYS dSGEIS	New York State Draft Supplemental Generic Environmental Impact Statement
ORD	Office of Research and Development
POTW	publicly owned treatment works
PPRTV	Provisional Peer Reviewed Toxicity Value
QA	quality assurance
QAPP	Quality Assurance Project Plan
QSAR	quantitative structure-activity relationship
SAB	Science Advisory Board
STAR	Science To Achieve Results
TDS	total dissolved solids
UIC	underground injection control
U.S.	United States
USACE	United States Army Corps of Engineers
USDW	underground source of drinking water
USGS	United States Geological Survey
VOC	volatile organic compound

EXECUTIVE SUMMARY

As natural gas production has increased, so have concerns about the potential environmental and human health impacts of hydraulic fracturing in the United States. Hydraulic fracturing, which involves the pressurized injection of water, chemical additives, and proppants into a geologic formation, induces fractures in the formation that stimulate the flow of natural gas or oil, thus increasing the volume of gas or oil that can be recovered from coalbeds, shales, and tight sands—the so-called "unconventional" reservoirs. Many concerns about hydraulic fracturing center on potential risks to drinking water resources, although other issues have been raised. In response to public concern, Congress directed the United States Environmental Protection Agency (EPA) to conduct research to examine the relationship between hydraulic fracturing and drinking water resources. This document presents the plan for the EPA study.

The overall purpose of this study is to understand the relationship between hydraulic fracturing and drinking water resources. More specifically, the study is designed to examine the conditions that may be associated with the potential contamination of drinking water resources, and to identify the factors that may lead to human exposure and risks. The scope of the proposed research includes the full lifecycle of water in hydraulic fracturing, from water acquisition through the mixing of chemicals and actual fracturing to the post-fracturing stage, including the management of flowback and produced water and its ultimate treatment and/or disposal. Figure 1 illustrates the hydraulic fracturing water lifecycle and the key research questions EPA will address through this study.

The research identified in this study plan has been designed to answer the questions listed in Figure 1 and will require a broad range of expertise, including petroleum engineering, fate and transport modeling, ground water hydrology, and toxicology. EPA will use case studies and generalized scenario evaluations as organizing constructs for the research identified in this plan.

Retrospective case studies will focus on investigating reported instances of drinking water resource contamination or other impacts in areas where hydraulic fracturing has already occurred. EPA will conduct retrospective case studies at three to five sites across the United States. The sites will be illustrative of the types of problems that have been reported to EPA during stakeholder meetings, and will provide EPA with information regarding key factors that may be associated with drinking water contamination. These studies will use existing data and possibly field sampling, modeling, and/or parallel laboratory investigations to determine the potential relationship between reported impacts and hydraulic fracturing activities.

Prospective case studies will involve sites where hydraulic fracturing will occur after the research is initiated. These case studies allow sampling and characterization of the site before, during, and after water extraction, drilling, hydraulic fracturing fluid injection, flowback, and gas production. EPA will work with industry and other stakeholders to conduct two to three prospective case studies in different regions of the United States. The data collected during prospective case studies will allow EPA to gain an understanding of hydraulic fracturing practices, evaluate changes in water quality over time, and assess the fate and transport of potential chemical contaminants.

Generalized scenario evaluations will allow EPA to explore hypothetical scenarios relating to hydraulic fracturing activities, and to identify scenarios under which hydraulic fracturing may adversely impact drinking water resources based on current understanding and available data.

To better understand potential human health effects, EPA plans to summarize the available data on the toxicity of chemicals used in or released by hydraulic fracturing, and to identify and prioritize data gaps for further investigation. The substances to be investigated include chemicals used in hydraulic fracturing fluids, their degradates and/or reaction products, and naturally occurring substances that may be released or mobilized as a result of hydraulic fracturing.

The research projects identified for this study are organized according to the hydraulic fracturing water lifecycle shown in Figure 1 and are summarized in Appendix A (p. 70). EPA is working with other federal agencies to collaborate on some aspects of the research described in this study plan. Additionally, EPA will announce requests for applications for extramural research projects related to this study as the study plan is finalized. These projects will be conducted through EPA's Science To Achieve Results (STAR) program.

All research activities associated with this study will be conducted in accordance with EPA's Quality Assurance Program for environmental data. EPA will provide periodic updates on the progress of various projects as the research is being conducted. The results of individual research projects will be made available after undergoing a quality assurance review. Early results may indicate the need for EPA to conduct further investigations to identify the key factors that may impact drinking water resources. It is expected that a report of interim research results will be completed in 2012. This interim report will contain a synthesis of EPA's research to date and will include results from retrospective case studies and initial results from scenario evaluations. However, certain portions of the work described here, including prospective case studies and work performed under STAR grants, are long-term projects that are not likely to be finished at that time. Additional reports of study findings will be published as these long-term projects progress, with a follow-up report on the study in 2014.

EPA recognizes that there are important potential research areas related to hydraulic fracturing other than those involving drinking water resources, including effects on air quality, aquatic and terrestrial ecosystem impacts, seismic risks, public safety concerns, occupational risks, and economic impacts. These topics are outside the scope of the current study, but should be examined in the future.

This draft study plan will be submitted to EPA's Science Advisory Board (SAB) for review before being finalized. Consistent with the operating procedures of the SAB, stakeholders and the public will have an opportunity to provide comments for the SAB to take into account during the review.

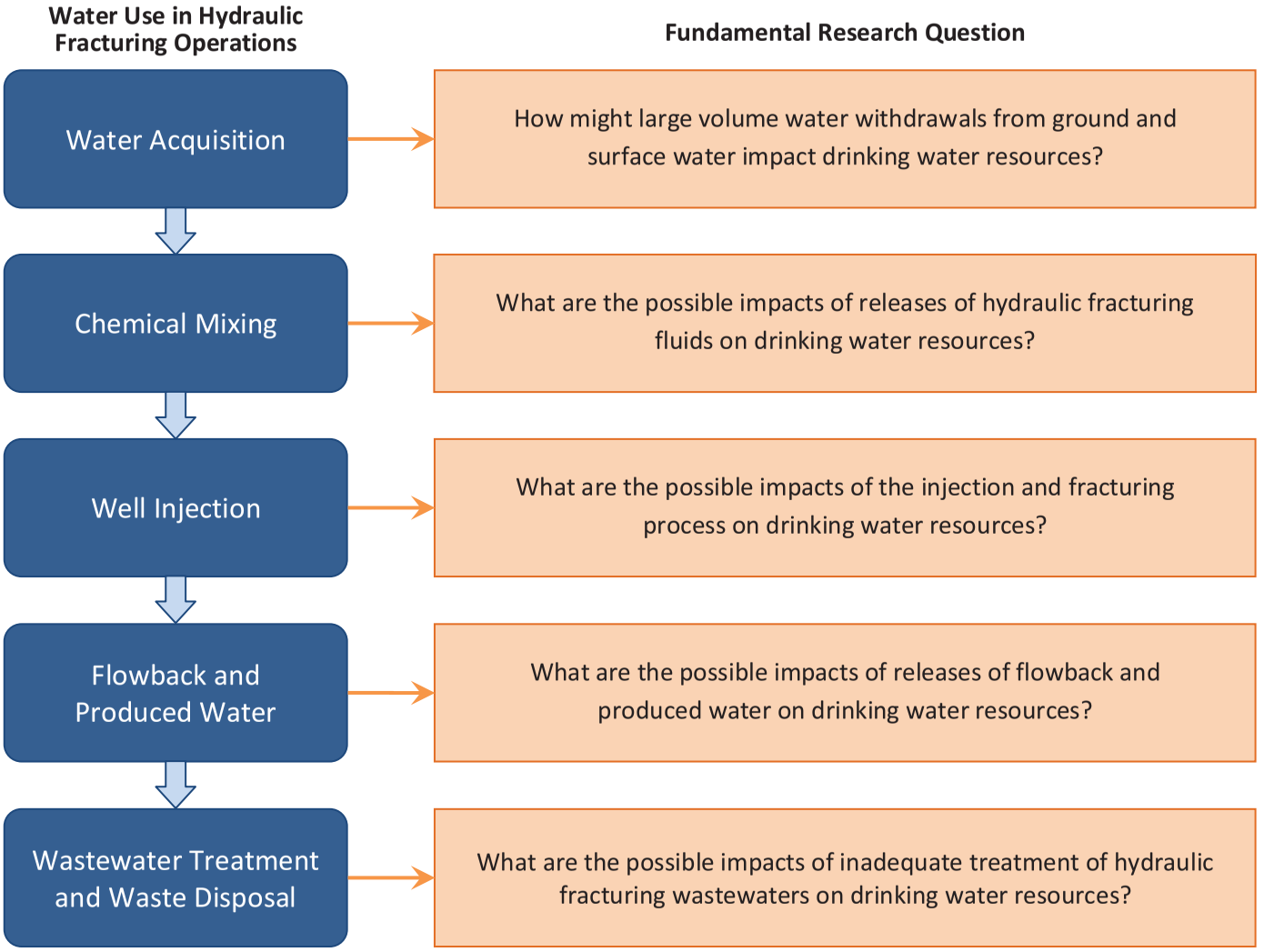


FIGURE 1. FUNDAMENTAL RESEARCH QUESTIONS POSED FOR EACH STAGE OF THE HYDRAULIC FRACTURING WATER LIFECYCLE

1 INTRODUCTION AND PURPOSE OF STUDY

Hydraulic fracturing is an important means of accessing one of the nation's most vital energy resources, natural gas. Advances in technology, along with economic and energy policy developments, have spurred a dramatic growth in the use of hydraulic fracturing across a wide range of geographic regions and geologic formations in the United States. 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 effects on drinking water resources. These concerns have intensified as hydraulic fracturing has spread from the South and West to other settings, such as the Marcellus Shale, which extends from the southern tier of New York through parts of Pennsylvania, West Virginia, eastern Ohio, and western Maryland.

In Fiscal Year 2010, the U.S. Congress' Appropriation Conference Committee directed EPA to conduct research to examine the relationship between hydraulic fracturing and drinking water resources:

> *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.*

This document presents a draft plan for EPA's research on hydraulic fracturing and drinking water resources and responds to both the request of Congress and concerns expressed by the public. For this study, EPA defines "drinking water resources" to be any body of water, ground or surface, that could currently, or in the future, produce an appropriate quantity and flow rate of water to serve as a source of drinking water for public or private water supplies. This includes both underground sources of drinking water (USDWs) and surface waters.

The overarching goal of this research is to answer the following questions:

- Can hydraulic fracturing impact drinking water resources?
- If so, what are the conditions associated with the potential impacts on drinking water resources due to hydraulic fracturing activities?

To answer these questions, EPA has identified a set of proposed research activities associated with each stage of the hydraulic fracturing water lifecycle, from water acquisition through the mixing of chemicals and actual fracturing to post-fracturing production, including the management of flowback and produced water and ultimate treatment and disposal. These research activities will identify potential sources and pathways of exposure and will provide information about the toxicity of contaminants of concern. This information can then be used to assess the potential risks to drinking water resources

from hydraulic fracturing activities. Ultimately, the results of this study will provide policymakers at all levels with sound scientific knowledge that can be used in decision-making processes.

The study plan is organized as follows:

- Chapter 2 details the process for developing the study plan and the criteria for prioritizing the proposed research.
- Chapter 3 provides a brief overview of the natural gas production process.
- Chapter 4 outlines the hydraulic fracturing water lifecycle and the research questions associated with each stage of the lifecycle.
- Chapter 5 briefly describes the research approach.
- Chapter 6 provides background information on each stage of the hydraulic fracturing water lifecycle, and proposes research specific to each stage.
- Chapter 7 summarizes EPA's case study approach, which is a central component of the research plan.
- Chapter 8 describes proposed studies to characterize the toxicity and potential human health effects of substances associated with hydraulic fracturing.
- Chapter 9 presents a brief discussion of hydraulic fracturing in the context of environmental justice.
- Chapter 10 provides a short summary of how the proposed studies will address the research questions posed for each stage of the water lifecycle.
- Chapter 11 identifies additional areas of concern relating to hydraulic fracturing that are outside the scope of this study plan.

2 Process for Study Plan Development

2.1 Initial Science Advisory Board Review of the Study Plan Scope

In early Fiscal Year 2010, EPA's Office of Research and Development (ORD) developed a document that presented a proposed scope and initial design of the study (USEPA, 2010a). The document was submitted to the EPA Science Advisory Board's (SAB's) Environmental Engineering Committee for review in March 2010. The SAB is a public advisory committee that provides a balanced, expert assessment of scientific matters relevant to EPA. In its response to EPA in June 2010 (USEPA, 2010c), the SAB recommended that (1) initial research be focused on potential impacts to drinking water resources with later research investigating more general impacts on water resources, (2) engagement with stakeholders occur throughout the research process, and (3) 5 to 10 in-depth case studies at "locations selected to represent the full range of regional variability of hydraulic fracturing across the nation" be part of the research plan.

The SAB cautioned EPA against studying all aspects of oil and gas production, stating that the study should "emphasize human health and environmental concerns specific to, or significantly influenced by, hydraulic fracturing rather than on concerns common to all oil and gas production activities." This

research plan, therefore, focuses on features of oil and gas production that are particular to—or closely associated with—hydraulic fracturing, and their impacts on drinking water resources.

2.2 Stakeholder Input

Stakeholder input has played, and will continue to play, an important role in the development of the hydraulic fracturing study plan and the research it will involve. EPA has implemented a strategy that engages stakeholders in dialogue and provides opportunities for input on the study scope and case study locations. The strategy also provides a means for exchanging information with experts on technical issues. EPA will continue to engage stakeholders as results from the study become available.

EPA has engaged stakeholders in the following ways:

Federal, state, and tribal partner consultations. Webinars were held with state partners in May 2010, with federal partners in June 2010, and with Indian tribes in August 2010. The state webinar included representatives from 21 states as well as representatives from the Association of State Drinking Water Administrators, the Association of State and Interstate Water Pollution Control Administrators, the Ground Water Protection Council (GWPC), and the Interstate Oil and Gas Compact Commission (IOGCC). The federal partners included the Bureau of Land Management, the U.S. Geological Survey (USGS), the U.S. Fish and Wildlife Service, the U.S. Forest Service, the U.S. Department of Energy (DOE), the U.S. Army Corps of Engineers (USACE), the National Park Service (NPS), and the Agency for Toxic Substances and Disease Registry. There were 36 registered participants for the tribal webinar representing 25 tribal governments; in addition, a meeting with the Haudenosaunee Environmental Task Force was held in August 2010 and included 20 representatives from the Onondaga, Mohawk, Tuscarora, Cayuga, and Tonawanda Seneca Nations. The purpose of these consultations was to discuss the study scope, data gaps, opportunities for sharing data and conducting joint studies, and current policies and practices for protecting drinking water resources.

Sector-specific meetings. Separate webinars were held in June 2010 with representatives from industry and non-governmental organizations (NGOs) to discuss the public engagement process, the scope of the study, coordination of data sharing, and other key issues. Overall, 176 people representing various natural gas production and service companies and industry associations participated in the webinars, as well as 64 people representing NGOs.

Informational public meetings. Public information meetings were held between July and September, 2010, in Fort Worth, Texas; Denver, Colorado; Canonsburg, Pennsylvania; and Binghamton, New York. At these meetings, EPA presented information on its reasons for studying hydraulic fracturing, an overview of what the study might include, and how stakeholders can be involved. Opportunities to present oral or written comments were provided, and EPA specifically asked for input on the following questions:

- What should be EPA's highest priorities?
- Where are the gaps in current knowledge?
- Are there data and information EPA should know about?

- Where do you recommend EPA conduct case studies?

Total attendance for all of the information public meetings exceeded 3,500 and more than 700 verbal comments were heard.

Summaries of all of the stakeholder meetings can be found at http://water.epa.gov/type/groundwater/uic/class2/hydraulicfracturing/wells_hydroout.cfm.

Other opportunities to comment. In addition to conducting the meetings listed above, EPA provided stakeholders with opportunities to submit electronic or written comments on the hydraulic fracturing study. EPA received over 5,000 comments, which are summarized in Appendix B.

2.3 Research Prioritization

In developing this proposed study plan, EPA considered the results of a review of the literature,[1] comments received from stakeholders, and input from meetings with interested parties, including other federal agencies, Indian tribes, state agencies, industry, and NGOs. EPA also considered recommendations from the initial SAB review of the study plan scope (USEPA, 2010c).

Based on stakeholder input and the expected growth in shale gas development, this study plan emphasizes hydraulic fracturing in shale formations. Portions of the proposed research, however, may provide information on hydraulic fracturing in coalbed methane reservoirs and tight sands, and EPA will pursue these research opportunities when possible.

As requested by Congress, EPA identified fundamental scientific research questions (summarized in Chapter 4) that will frame the research and help to evaluate the potential for hydraulic fracturing to impact drinking water resources. Following guidance from the SAB, EPA used a risk-based prioritization approach to identify research that addresses the most significant risks at each stage of the hydraulic fracturing water lifecycle. Other criteria considered in prioritizing proposed research activities include:

- *Relevance:* Only work that may directly inform an assessment of the potential impacts of hydraulic fracturing on drinking water resources was considered.
- *Precedence:* Work that needs to be completed before other work can be initiated received a higher priority.
- *Uniqueness of the contribution:* Relevant work already underway by others received a lower priority for investment by EPA.
- *Leverage:* Relevant work that EPA could leverage with co-investigators received a higher priority.

Application of the criteria listed above ensures that resources are provided for the areas that potentially pose the greatest risk to drinking water resources.

[1] The literature review includes information from more than 120 articles, reports, presentations, and other materials. Information resulting from this literature review is incorporated throughout this study plan.

2.4 NEXT STEPS

The next steps in the development and implementation of the study plan are:

- The draft study plan will be sent to the SAB for peer review and made available to the public in February 2011. The SAB will have an opportunity to hear verbal comments and read written comments from stakeholders and the public during their March 2011 public meeting to review the draft study plan. EPA will respond to comments from the SAB, and will adjust the study plan as appropriate.
- EPA will conduct the research described in this plan, and plans to announce requests for applications for extramural research projects in the early part of 2011 for research that is related to this study. Additionally, it is likely that other federal agencies will cooperate with EPA on some aspects of the research.
- The research projects will begin in the early part of 2011 after EPA receives and responds to comments from the SAB.
- Periodic updates will be provided on the progress of the research projects.
- A study report providing interim research results is expected to be completed in 2012 and will be made available to the public.
- Additional study results will be published as individual research projects are completed, with an additional report expected to be published in 2014.

2.5 INTERAGENCY COOPERATION

In a series of meetings, EPA consulted with several key state and federal agencies regarding research related to hydraulic fracturing. EPA met with representatives from DOE and DOE's National Energy Technology Laboratory (NETL), USGS, USACE, and IOGCC to learn about research that those agencies are involved in and to identify opportunities for collaboration and leverage. EPA also participated in a series of meetings in which a number of other federal agencies participated. As a result of those meetings, EPA has identified work underway by others that can inform its own study. EPA continues to discuss opportunities to collaborate on information gathering and research efforts with other agencies. In particular, the Agency plans to coordinate with DOE and USGS on existing and future research projects. Regular meetings between EPA and DOE will be set up to follow each agency's research on hydraulic fracturing and to exchange information among experts.

Federal agencies have also had an opportunity to provide comments on this draft study plan through an interagency review. EPA received comments from the Agency for Toxic Substances and Disease Registry, DOE, the Bureau of Land Management, USGS, the U.S. Fish and Wildlife Service, the Office of Management and Budget, the U.S. Energy Information Administration (EIA), the Occupational Safety and Health Administration, and the National Institute of Occupational Health and Safety. These comments have been reviewed and modifications to the study plan have been made where appropriate.

2.6 Quality Assurance

All EPA-funded research projects, both intramural and extramural, that generate or use environmental data to make conclusions or recommendations must comply with Agency Quality Assurance (QA) Program requirements (USEPA, 2002b). EPA recognizes the value of using a graded approach to QA such that QA requirements are based on the importance of the work to which the QA program applies. Given the significant national interest in the results of hydraulic fracturing related research, the following rigorous QA approach will be used:

- Research projects must comply with Agency requirements and guidance for quality assurance project plans (QAPPs), including the use of data quality objectives.
- Audits will be conducted as described in an audit plan and will include technical systems audits, audits of data quality, and data quality assessments.
- Performance evaluations of measurement systems will be conducted (if available).
- QA review of products[2] will occur.
- Reports must have a readily identifiable QA section.
- Research records will be managed according to EPA's record schedule for *Applied and Directed Scientific Research.*

All EPA 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. Given the cross-organizational nature of the proposed research, it is necessary to identify a Program Quality Assurance Manager who will coordinate the rigorous QA approach described above and oversee its implementation across all participating organizations. Typically, this person is associated with the organization that has the technical lead for the research program. The organizational complexity of the hydraulic fracturing research effort also demands that a quality management plan be written to define the QA-related policies, procedures, roles, responsibilities, and authorities for this research. The plan will document consistent QA procedures and practices that may otherwise vary between organizations.

3 Overview of Unconventional Natural Gas Production

Hydraulic fracturing is often used to stimulate the production of oil and gas from unconventional oil and gas deposits, which include shales, coalbeds, and tight sands.[3] Unconventional natural gas deposits generally contain a lower concentration of natural gas over broader areas that have a lower permeability than conventional gas reservoirs, which are typically porous and permeable and do not require additional stimulation for production (Vidas and Hugman, 2008). Similarly, hydraulic fracturing can make oil production from shale cost-effective.

[2] Applicable products may include reports, journal articles, symposium/conference papers, extended abstracts, computer products/software/models/databases, and scientific data.

[3] The use of hydraulic fracturing is not limited to natural gas production. It may also be used when drilling for oil (STRONGER, 2010), and has been used for other purposes, such as removing contaminants from soil and ground water at waste disposal sites, make geothermal wells more productive, and to complete water wells (Nemat-Nassar et al., 1983; New Hampshire Department of Environmental Services, 2010).

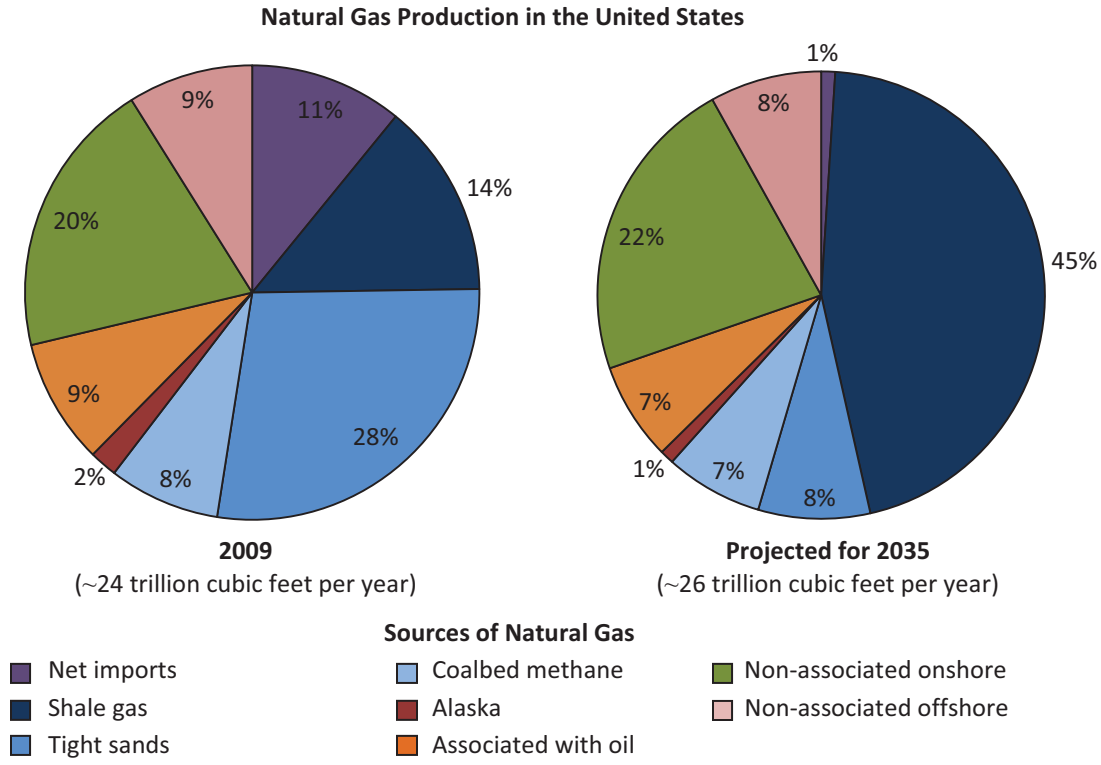
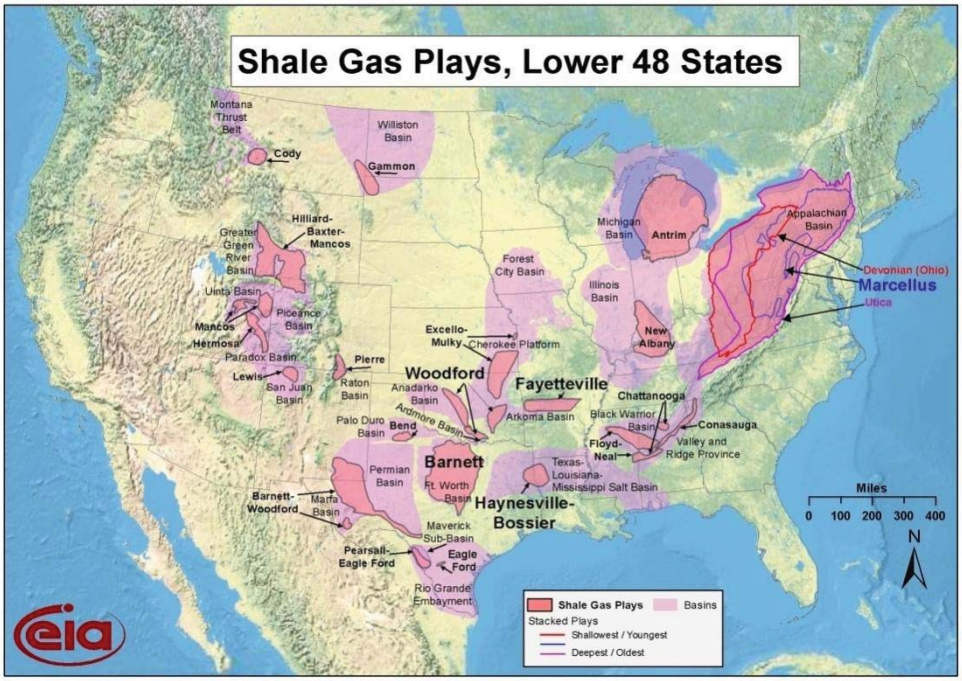


FIGURE 2. NATURAL GAS PRODUCTION IN THE UNITED STATES (DATA FROM USEIA, 2010)

Unconventional natural gas development has become an increasingly important source of natural gas in the United States in recent years. It accounted for 28 percent of total natural gas production in 1998 (Arthur et al., 2008). Figure 2 illustrates that this percentage has risen to 50 percent in 2009 and is projected to increase to 60 percent in 2035 (USEIA, 2010). This rise in hydraulic fracturing activities is also reflected in the number of drilling rigs operating in the United States; there were 603 horizontal gas rigs in June 2010, up 277 from the previous year (Baker Hughes, 2010). Most of these were involved in gas extraction via hydraulic fracturing.

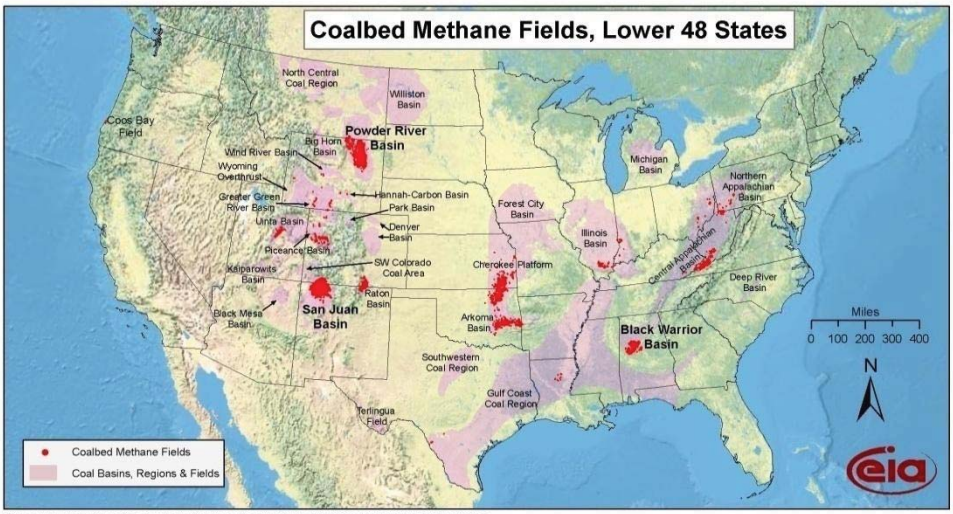


Source: Energy Information Administration based on data from various published studies.
Updated: March 10, 2010

FIGURE 3. SHALE GAS PLAYS IN THE CONTIGUOUS UNITED STATES

Shale gas extraction. Shale rock formations have become an important source of natural gas in the United States, and can be found in many locations across the country as shown in Figure 3. Depths for shale gas formations (commonly referring to as "plays") can range from 500 to 13,500 feet below the earth's surface (GWPC and ALL Consulting, 2009). At the end of 2009, the five most productive shale gas fields in the country—the Barnett, Haynesville, Fayetteville, Woodford, and Marcellus Shales—were producing 8.3 billion cubic feet of natural gas per day (Zoback et al., 2010). According to recent figures from EIA, shale gas constituted 14 percent of the total U.S. natural gas supply in 2009, and will constitute 45 percent of the U.S. gas supply in 2035 if current trends and policies persist (USEIA, 2010).

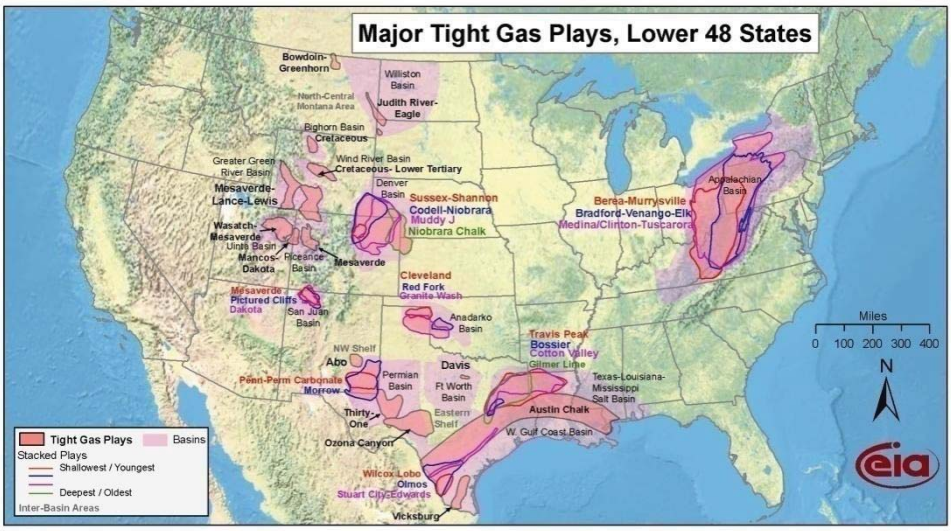
Oil production has similarly increased in oil-bearing shales following the increased use of hydraulic fracturing. Proven oil production from shales has concentrated primarily in the Williston Basin in North Dakota, although oil production is increasing in the Eagle Ford Shale in Texas and the Niobrara Shale in Colorado, Nebraska, and Wyoming (USEIA, 2010; OilShaleGas.com, 2010).



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

FIGURE 4. COALBED METHANE DEPOSITS IN THE CONTIGUOUS UNITED STATES

Production of coalbed methane. Coalbed methane is formed as part of the geological process of coal generation and is contained in varying quantities within all coal. Depths of coalbed methane formations range from 450 feet to greater than 10,000 feet (Rogers et al., 2007; National Research Council, 2010). At greater depths, however, the permeability decreases and production is lower. Below 7,000 feet, efficient production of coalbed methane can be challenging from a cost-effectiveness perspective (Rogers et al., 2007). Figure displays coalbed methane reservoirs in the contiguous United States. In 1984, there were very few coalbed methane wells in the United States; by 1990, there were almost 8,000, and in 2000, there were almost 14,000 (USEPA, 2004). In 2009, natural gas production from coalbed methane reservoirs made up 8 percent of the total U.S. natural gas production; this percentage would remain relatively constant over the next 20 years if current trends and policies persist (USEIA, 2010). Production of gas from coalbeds almost always requires hydraulic fracturing (USEPA, 2004), and many existing coalbed methane wells that have not been fractured are now being considered for hydraulic fracturing.



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

FIGURE 5. MAJOR TIGHT GAS PLAYS IN THE CONTIGUOUS UNITED STATES

Tight sands. Tight sands (gas-bearing, fine-grained sandstones or carbonates with a low permeability) accounted for 28 percent of total gas production in the United States in 2009 (USEIA, 2010), but may account for as much as 35 percent of the nation's recoverable gas reserves (Oil and Gas Investor, 2005). Figure 5 shows the locations of tight gas plays in the United States. Typical depths of tight sand formations range from 1,200 to 20,000 feet across the United States (Prouty, 2001). Almost all tight sand reservoirs require hydraulic fracturing to release gas unless natural fractures are present.

The following sections provide an overview of unconventional natural gas production, including site selection and preparation, well construction and development, hydraulic fracturing, and natural gas production. The current regulatory framework that governs hydraulic fracturing activities is briefly described in Section 3.5.

3.1 Site Selection and Preparation

The hydraulic fracturing process begins with exploring possible well sites, followed by selecting and preparing an appropriate site. In general, appropriate sites are those that are considered most likely to yield substantial quantities of natural gas at minimum cost. Other factors, however, may be considered in the selection process. These include proximity to buildings and other infrastructure, geologic considerations, and proximity to natural gas pipelines or the feasibility of installing new pipelines (Chesapeake Energy, 2009). Laws and regulations may also influence site selection. For example, applicants applying for a Marcellus Shale natural gas permit in Pennsylvania must provide information about proximity to coal seams and distances from surface waters and water supplies (PADEP, 2010a).

During site preparation, an area is cleared to provide space to accommodate one or more wellheads; pits for holding water, used drilling fluids, and other materials; and space for trucks and other equipment. At a typical shale gas production site, a 3- to 5-acre space is needed in addition to access

roads for transporting materials to and from the well site. If not already present, both the site and access roads need to be built or improved to support heavy equipment.

3.2 Well Construction and Development

Current practices in drilling for natural gas include drilling vertical, horizontal, and directional (S-shaped) wells. Figure 6 depicts two different well completions, one in a typical deep shale gas-bearing formation like the Marcellus Shale (6a) and one in a shallower environment (6b) often encountered where coalbed methane or tight sand gas production takes place. The figures demonstrate a significant difference in the challenges posed for protecting underground drinking water resources. The deep shale gas environment shown in Figure 6a typically has several thousand feet of rock formation separating underground drinking water resources, while Figure 6b shows that gas production can take place at shallow depths that also contain underground sources of drinking water. The water well in Figure 6b illustrates the relative depths of a gas well and a water well.

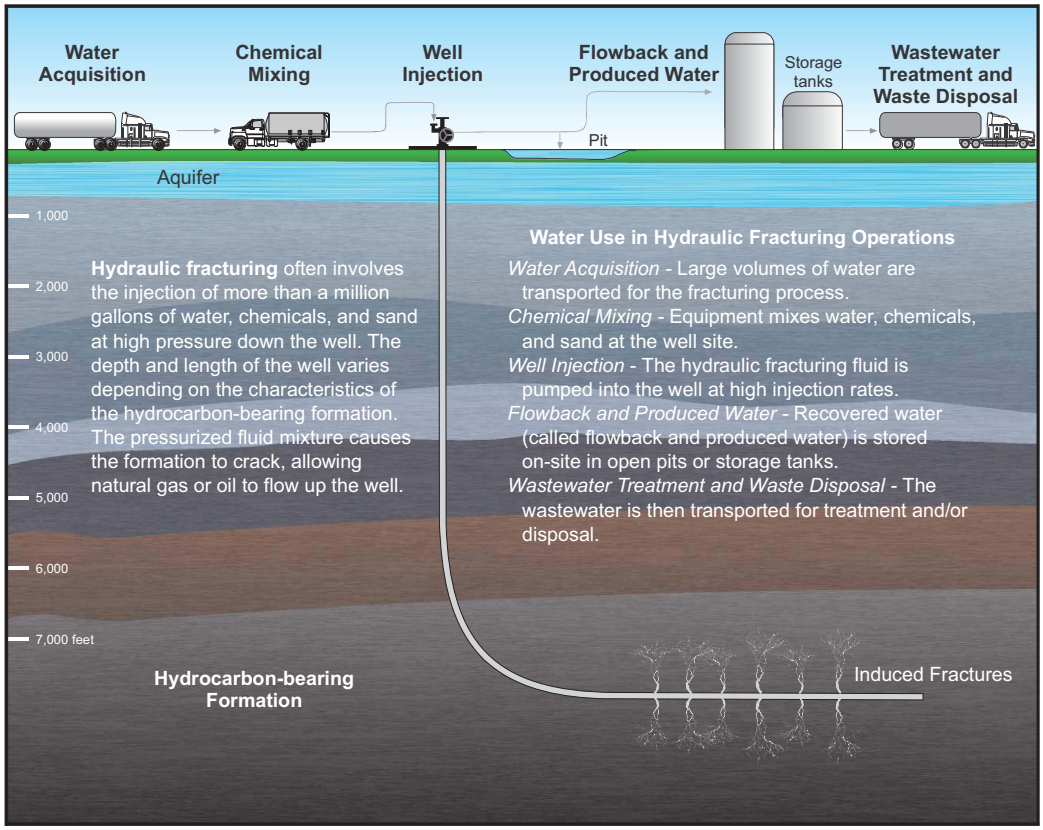


FIGURE 6a. ILLUSTRATION OF A HORIZONTAL WELL SHOWING THE WATER LIFECYCLE IN HYDRAULIC FRACTURING

Figure 6a depicts a horizontal well, which is composed of both vertical and horizontal legs. The depth and length of the well varies with the location and properties of the gas-containing formation. In unconventional cases, the well can extend more than a mile below the ground surface (Chesapeake Energy, 2010) while the "toe" of the horizontal leg can be almost 2 miles from the vertical leg (Zoback et al., 2010). Horizontal drilling provides more exposure to a formation than a vertical well does;

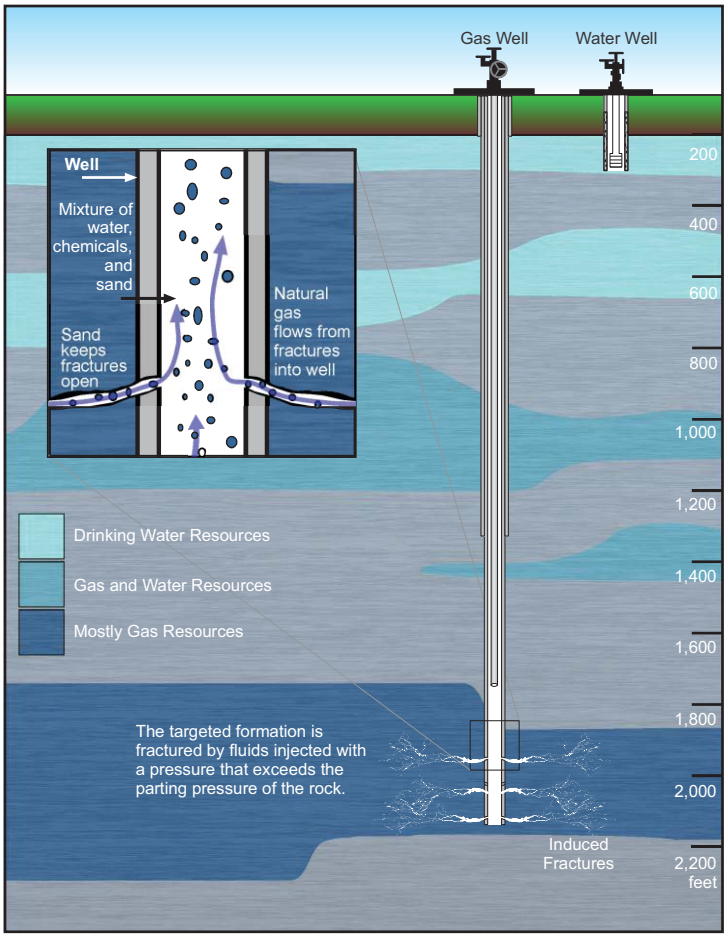


FIGURE 6b. ILLUSTRATION OF A VERTICAL WELL WHERE HYDRAULIC FRACTURING OCCURS NEAR AN UNDERGROUND SOURCE OF DRINKING WATER

therefore, it increases recovery of natural gas and makes drilling more economical. It may also have the advantage of limiting environmental disturbances on the surface because fewer wells are needed to access the natural gas resources in a particular area (GWPC and ALL Consulting, 2009).

The technique of multilateral drilling is becoming more prevalent in gas production in the Marcellus Shale region (Kargbo et al., 2010) and elsewhere. In multilateral drilling, two or more horizontal production holes are drilled from a single surface location (Ruszka, 2007) to create an arrangement resembling an upside-down tree, with the vertical portion of the well as the "trunk," and multiple "branches" extending out from it in different directions and at different depths.

In all wells, casing and cement are installed to contain the contents of the well in an effort to prevent contamination of the surrounding subsurface formations, especially USDWs. The high injection pressures associated with the hydraulic fracturing process, and the increased potential for aquifer contamination due to the close proximity of the aquifer to the well, make cementing and casing activities a crucial step in protecting ground water. The process of constructing a well is described in greater detail later in the study plan.

3.3 Hydraulic Fracturing

After the well is constructed and perforated, the targeted formation (shale, coalbed, or tight sands) is hydraulically fractured to stimulate natural gas production. As shown in Figure 6a, the hydraulic fracturing process requires large volumes of water that must be transported to the well site. Once on-site, the water is mixed with chemicals and a propping agent (called a proppant) such as sand, bauxite, or ceramic beads. The resulting hydraulic fracturing fluid is pumped down the well under high pressures, causing the targeted formation to fracture. As the injection pressure is reduced, the fluid is returned to the surface, leaving the proppant behind to keep the fractures open. The inset in Figure 6b illustrates how the resulting fractures create pathways in otherwise impermeable gas-containing formations, resulting in gas flow to the well for production. A portion of the injected fracturing fluid

(water, chemical additives, and proppant), as well as naturally occurring substances released from the targeted formation, is then returned to the surface as flowback and produced water. These wastewaters are stored on-site in tanks or pits before being transported for treatment, disposal, land application, and/or discharge.

3.4 Well Production

Natural gas production rates can vary between basins as well as within a basin, depending on geologic factors and completion techniques. For example, the average well production rates for coalbed methane formations range from 50 to 500 thousand cubic feet per day (mcf/d) across the United States with maximum production rates reaching 20 million cubic feet per day (mmcf/d) in the San Juan basin and 1 mmcf/d in the Raton Basin (Rogers et al., 2007). The New York State Draft Supplemental Generic Environmental Impact Statement (NYS dSGEIS) for the Marcellus Shale cites industry estimates that a typical well will initially produce 2.8 mmcf/d; the production rate will decrease to 550 mcf/d after 5 years and 225 mcf/d after 10 years, after which it will drop approximately 3 percent a year (NYSDEC, 2009). A study of actual production rates in the Barnett Shale found that the average well produces about 800 mmcf during its lifetime, which averages about 7.5 years (Berman, 2009).

Refracturing is possible once an oil or gas well begins to approach the point where it is no longer cost-effectively producing hydrocarbons. Zoback et al. (2010) maintain that shale gas wells are rarely refractured. Berman (2009), however, claims that wells may be refractured once they are no longer profitable. The NYS dSGEIS estimates that wells may be refractured after roughly five years of service (NYSDEC, 2009).

3.5 Regulatory Framework

Hydraulic fracturing for oil and gas production wells is typically addressed by state oil and gas boards or equivalent state natural resource agencies. However, EPA retains authority to address many issues related to hydraulic fracturing under its environmental statutes. The major statutes include the Clean Air Act; the Resource Conservation and Recovery Act; the Clean Water Act; the Safe Drinking Water Act; the Comprehensive Environmental Response, Compensation and Liability Act; the Toxic Substances Control Act; and the National Environmental Policy Act. EPA does not expect to address the efficacy of the regulatory framework as part of this investigation. However, EPA may assess existing state regulations in a separate effort.

4 The Hydraulic Fracturing Water Lifecycle

Figure 7 illustrates the key stages of the hydraulic fracturing water lifecycle—from water acquisition to wastewater treatment and disposal—and the potential drinking water issues associated with each stage.

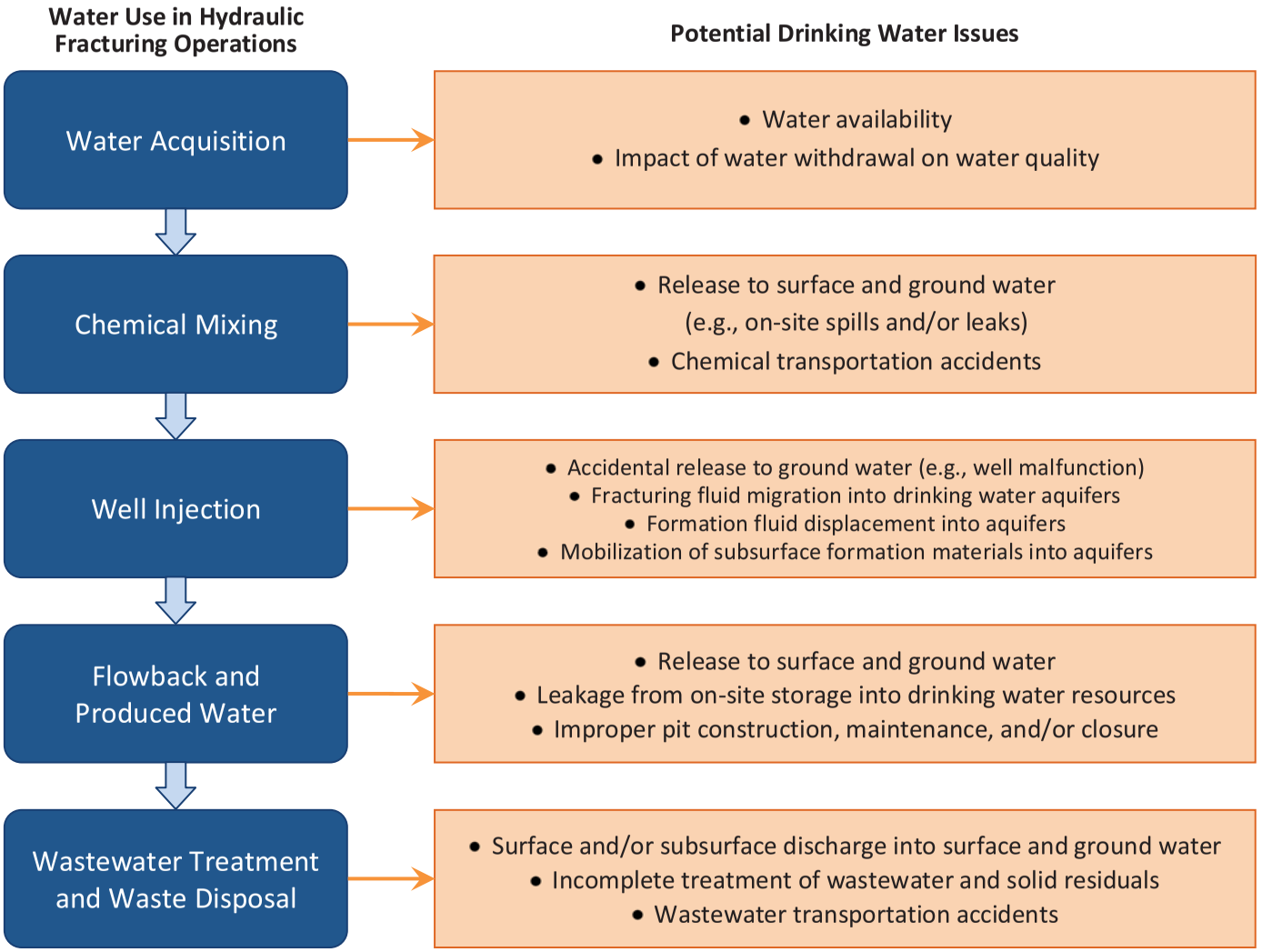


FIGURE 7. WATER USE IN HYDRAULIC FRACTURING OPERATIONS

Summarized below are the fundamental research questions EPA has identified for each stage of the hydraulic fracturing water lifecycle.

- *Water acquisition:* How might large volume water withdrawals from ground and surface water impact drinking water resources?
- *Chemical mixing:* What are the possible impacts of releases 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 releases 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?

The next chapter outlines the research approach and activities needed to answer these questions.

5 APPROACH

The highly complex nature of the problems to be studied will 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 areas. EPA will need to take a transdisciplinary research approach that integrates various types of expertise from inside and outside the EPA.

Case studies and *generalized scenario evaluations* provide organizing constructs for the research that will be used to address the key questions associated with each of the five water cycle stages of hydraulic fracturing. Table 1 shows the objectives for the case studies, both retrospective and prospective, and the scenario evaluations. Each of these approaches is briefly described below.

TABLE 1. RELATIONSHIP BETWEEN CASE STUDIES AND SCENARIO EVALUATIONS

Activity	Objectives
Case studies	
Retrospective	Perform a forensic analysis of sites with reported contamination to understand the underlying mechanisms and potential impacts on drinking water resources
Prospective	Develop understanding of hydraulic fracturing processes and their potential impacts on drinking water resources
Scenario evaluation	Assess the potential for hydraulic fracturing to impact drinking water resources based on knowledge developed

5.1 CASE STUDIES

Case studies are widely used to conduct in-depth investigations of complex topics and provide a systematic framework for investigating the relationship among relevant factors. In conjunction with other elements of the research program, case studies can help to determine whether drinking water resources are impacted by hydraulic fracturing, the extent and possible causes of any impacts, and what management practices are, or may be, used to avoid or mitigate such impacts. Additionally, case studies

may provide data and model inputs to assess the fate and transport of fluids and contaminants in different regions and geologic settings.

Retrospective case studies are focused on investigating reported instances of drinking water resource contamination in areas where hydraulic fracturing events have already occurred. The goal is to determine whether or not the reported impacts are due to hydraulic fracturing activities. These studies will use existing data and will include environmental field sampling, modeling, and/or parallel laboratory investigations.

Prospective case studies involve sites where hydraulic fracturing will be implemented after the research is initiated. These cases allow sampling and characterization of the site prior to, during, and after drilling, water extraction, injection of the fracturing fluid, flowback, and production. At each step in the process, data will be collected to characterize both the pre- and post-fracturing conditions at the site. This progressive data collection will allow EPA to evaluate changes in water availability and quality, as well as other factors, over time to gain a better understanding of the impacts of hydraulic fracturing on drinking water resources. Prospective case studies can also provide data with which models of hydraulic fracturing and associated processes, such as fate and transport of chemical contaminants, can be evaluated and improved.

Retrospective and prospective case studies are discussed further in Chapter 7.

5.2 Scenario Evaluation

The objective of this approach is to explore realistic, hypothetical scenarios across the hydraulic fracturing water lifecycle that may result in adverse impacts to drinking water resources based on current understanding and available data. The scenarios will include a reference case involving typical management and engineering practices in representative geologic settings. Typical management and engineering practices will be based on what EPA learns from case studies as well as the minimum requirements imposed by state regulatory agencies. Potential modes of failure, both in terms of engineering controls and geologic characteristics, will be introduced and modeled to represent various states of system vulnerability. The scenario evaluations will produce insights into site-specific and regional vulnerabilities.

The proposed applications of scenario evaluation will be described in detail for each stage of the hydraulic fracturing water lifecycle in the next chapter.

5.3 Tools

Various combinations of the following four general tools or activities will be used to conduct the case studies and scenario evaluations:

Existing data evaluation. Various existing data support the proposed hydraulic fracturing research study, including mapped data, surface water discharge data, chemical data, and site data. These data are available from a variety of sources, such as state regulatory agencies, federal agencies, industry, and public sources. To support this study, EPA has specifically requested data from nine hydraulic fracturing

service companies. As detailed in Appendix C, EPA asked for data on the chemical composition of fluids used in the fracturing process, the health and environmental impacts of the chemicals, standard operating procedures, and locations where fracturing has been conducted or is planned. The hydraulic fracturing service companies have claimed this data to be confidential business information.

Field monitoring. EPA will collect field samples during both retrospective and prospective case studies to look for the migration of chemical and gas contaminants into drinking water resources as a result of hydraulic fracturing activities. Direct studies of field sites can also assess the behavior of chemicals in the environment by characterizing the flow and transport of chemicals through heterogeneous media on a scale that is not represented in the laboratory.

Laboratory-scale experimentation/analysis. Laboratory studies will be necessary to develop and refine analytical methods needed to analyze samples collected during field monitoring activities. For hydraulic fracturing-related chemicals without extensive study, laboratory experimentation may be needed to determine the processes that control the transport and ultimate fate of the chemicals, including sorption and biodegradation.

Modeling. Modeling is a tool for integrating diverse phenomena to enhance understanding of environmental exposures. When sufficiently tested, models can also allow alternate hypothesis testing, which can help to determine the plausibility of contamination of drinking water resources due to hydraulic fracturing activities. Models may also be able to identify the factors that are the most important in understanding hydraulic fracturing impacts on drinking water resources.

6 PROPOSED RESEARCH

This chapter is organized by the hydraulic fracturing water lifecycle depicted in Figure 7 and the associated fundamental research questions outlined in Chapter 4. Each section of this chapter provides relevant background information on a water cycle stage, as well as identifying a series of more specific questions that need to be researched in order to answer one of these fundamental questions. These secondary research questions are listed in Table 2. Proposed research activities and potential research outcomes are outlined at the end of the discussion of each stage of the water lifecycle.

TABLE 2. HYDRAULIC FRACTURING RESEARCH QUESTIONS

Water Lifecycle Stage	Fundamental Research Question	Secondary Research Questions
Water acquisition	How might large volume water withdrawals from ground and surface water impact drinking water resources?	• What are the impacts on water availability? • What are the impacts on water quality?
Chemical mixing	What are the possible impacts of accidental releases of hydraulic fracturing fluids on drinking water resources?	• What is the composition of hydraulic fracturing fluids and what are the toxic effects of these constituents? • What factors may influence the likelihood of contamination of drinking water resources? • How effective are mitigation approaches in reducing impacts to drinking water resources?
Well injection	What are the possible impacts of the injection and fracturing process on drinking water resources?	• How effective are well construction practices at containing gases and fluids before, during, and after fracturing? • What are the potential impacts of pre-existing artificial or natural pathways/features on contaminant transport? • What chemical/physical/biological processes could impact the fate and transport of substances in the subsurface? • What are the toxic effects of naturally occurring substances?
Flowback and produced water	What are the possible impacts of accidental releases of flowback and produced water on drinking water resources?	• What is the composition and variability of flowback and produced water and what are the toxic effects of these constituents? • What factors may influence the likelihood of contamination of drinking water resources? • How effective are mitigation approaches in reducing impacts to drinking water resources?
Wastewater treatment and waste disposal	What are the possible impacts of inadequate treatment of hydraulic fracturing wastewaters on drinking water resources?	• How effective are treatment and disposal methods?

A summary of the research outlined in this chapter can be found in Appendix A.

6.1 WATER ACQUISITION: HOW MIGHT LARGE VOLUME WATER WITHDRAWALS FROM GROUND AND SURFACE WATER IMPACT DRINKING WATER RESOURCES?

6.1.1 BACKGROUND

The amount of water needed in the hydraulic fracturing process depends on the type of formation (coalbed, shale, or tight sands) and the fracturing operations (e.g., well depth and length, fracturing fluid properties, and fracture job design). Water requirements for hydraulic fracturing in coalbed methane range from 50,000 to 350,000 gallons per well (Holditch, 1990 and 1993; Jeu et al., 1988; Palmer et al., 1991 and 1993). The water usage in shale gas plays is significantly larger: 2 to 4 million gallons of water are typically needed per well (API, 2010a; GWPC and ALL Consulting, 2009; Satterfield et al., 2008). Table 3 shows how the total volume of water used in fracturing varies depending on the depth and porosity of the shale gas play.

TABLE 3. COMPARISON OF ESTIMATED WATER NEEDS FOR HYDRAULIC FRACTURING IN DIFFERENT SHALE PLAYS

Shale Play	Formation Depth (ft)	Porosity (%)	Organic Content (%)	Freshwater Depth (ft)	Fracturing Water (gallons/well)
Barnett	6,500-8,500	4-5	4.5	1,200	2,300,000
Fayetteville	1,000-7,000	2-8	4-10	500	2,900,000
Haynesville	10,500-13,500	8-9	0.5-4	400	2,700,000
Marcellus	4,000-8,500	10	3-12	850	3,800,000

Data are from GWPC and ALL Consulting, 2009.

EPA estimates that approximately 35,000 wells are fractured each year across the United States. Assuming that the majority of these wells are horizontal wells, the annual water requirement may range from 70 to 140 billion gallons. This is equivalent to the total amount of water used each year in roughly 40 to 80 cities with a population of 50,000 or about 1 to 2 cities of 2.5 million people. In the Barnett Shale area, the annual estimates of total water used by gas producers range from 2.6 to 5.3 billion gallons per year from 2005 through 2007 (Bene et al., 2007, as cited in Galusky, 2007). During the projected peak shale gas production in 2010, the total water used for gas production in the Barnett Shale was estimated to be 9.5 billion gallons. This represents 1.7 percent of the estimated total freshwater demand by all users within the Barnett Shale area (554 billion gallons) (Galusky, 2007).

To meet these large volume requirements, source water is typically stored in 20,000-gallon portable steel ("frac") tanks located at the well site (GWPC, 2009; ICF International, 2009a; Veil, 2007). Source water can also be stored in impoundment pits on-site or in a centralized location that services multiple sites. This storage practice is used, for example, in the Barnett and Fayetteville Shale plays, where source water may be stored in large, lined impoundments ranging in capacity from 8 million gallons for 4 to 20 gas wells to 163 million gallons for 1,200 to 2,000 gas wells (Satterfield et al., 2008). The water used to fill tanks or impoundments may come from either ground or surface water, depending on the region in which the fracturing takes place. The transportation of source water to the well site depends on site-specific conditions. In many areas, trucks generally transport the source water to the well site. In the long term, where topography allows, a network of pipelines may be installed to transfer source water between the source and the impoundments or tanks.

Whether the withdrawal of this much water from local surface or ground water sources has a significant impact may vary from one part of the country to another and from one time of the year to another. In arid North Dakota, the projected need of 5.5 billion gallons of water per year to release oil and gas from the Bakken Shale has prompted serious concerns by stakeholders (Kellman and Schneider, 2010). On the other hand, in less arid parts of the country (e.g., the Barnett Shale area), the impact of water withdrawals may be less significant. In the Marcellus Shale area, stakeholder concerns have focused on large volume, high rate water withdrawals from small streams in the headwaters of watersheds supplying drinking water (Maclin et al., 2009; Myers, 2009) rather than on overall water use.

One way to offset the large water requirements for hydraulic fracturing is to recycle the flowback produced in the fracturing process. Estimates for the amount of fracturing fluid that is recovered during the first two weeks after a fracture range from 10 to 40 percent of the original fluid injected (Ewing, 2008; Vidic, 2010). This water may be treated and reused by adding additional chemicals as well as fresh water to compose a new fracturing solution. There are, however, challenges associated with reusing flowback due to the high concentrations of total dissolved solids (TDS) and other dissolved constituents found in flowback (Bryant et al., 2010). Acid mine drainage, which has a lower TDS concentration, has also been suggested as possible source water for hydraulic fracturing (Vidic, 2010).

API has published general guidance on best practices for water management associated with hydraulic fracturing (API, 2010a). Such practices include proactive communication with local water agencies and planning for a potential well drilling program on a basin-wide basis. API also recommends a detailed evaluation of the amount and quality of water required in addition to the identification and evaluation of potential water sources. Other literature describes current and proposed practices for on-site water management at some shale gas plays (Satterfield et al., 2008; Horn, 2009; Veil, 2007 and 2010).

6.1.2 What are the impacts on water availability?

Large volume water withdrawals for hydraulic fracturing are unique in that much of the water used for the fracturing process may not be recovered after injection. The impact from large volume water withdrawals varies not only with geographic area, but also with the quantity, quality, and sources of the water used. The removal of large volumes of water could stress drinking water supplies, especially in drier regions where aquifer or surface water recharge is limited. This could lead to lowering of water tables or dewatering of drinking water aquifers, decreased stream flows, and reduced volumes of water in surface water reservoirs. These activities could impact the availability of water for drinking and other uses in areas where hydraulic fracturing is occurring. The lowering of water levels in aquifers can necessitate the lowering of pumps or the deepening or replacement of wells, as has been reported near Shreveport, Louisiana, in the area of the Haynesville Shale (personal communication from Gary M. Hanson, Director, Red River Watershed Management Institute, Louisiana State University in Shreveport, to EPA's Robert Puls).

As the intensity of hydraulic fracturing activities increases within individual watersheds and geologic basins, it is important to understand the net impacts on water resources and identify opportunities to optimize water management strategies.

6.1.3 What are the impacts on water quality?

The lowering of water levels in aquifers may also affect water quality by exposing naturally occurring minerals to an oxygen-rich environment. This may cause chemical changes to the minerals that can affect solubility and mobility and may cause salination of the water and other chemical contaminations. Bacterial growth may be stimulated by lowered water tables, causing taste and odor problems. Depletion of aquifers may also cause an upwelling of lower quality water from deeper within an aquifer. In some cases, changes in water levels may interact with well construction in such a way as to cause an increase in siltation or cloudiness of the produced water. Large volume water withdrawals from ground water can also lead to subsidence and/or destabilization of the geology.

Withdrawals of large quantities of water from surface water resources (e.g., streams) may have significant impacts on the hydrology and hydrodynamics of these resources. Such withdrawals from streams can alter the flow regime by changing their flow depth, velocity, and temperature (Zorn et al., 2008). Additionally, removal of significant volumes of water may reduce the dilution effect and increase the concentration of contaminants in surface water resources (Pennsylvania State University, 2010). Furthermore, it is important to recognize that ground water and surface water are hydraulically connected (Winter et al., 1998); any changes in the quantity and quality of the surface water will affect ground water and vice versa.

6.1.4 Proposed Research Activities—Water Acquisition

6.1.4.1 Water Availability: Analysis of Existing Data, Prospective Case Studies, and Scenario Evaluation

Analysis of existing data. In cooperation with USACE, USGS, state environmental agencies, state oil and gas associations, river basin commissions, and others, EPA will compile data on water use and the hydrology of selected study areas. These data will include ground water levels, surface water flows, and water quality as well as data on hydraulic fracturing operations, such as the location of wells and the recorded water used during fracturing. EPA has chosen potential study areas that represent both arid and humid areas of the country, restricting its selection to areas for which sufficient data are available. Current potential study areas include: (1) the Bakken Shale in North Dakota, (2) the Barnett Shale in Texas, (3) Garfield County/Piceance Basin in Colorado, and (4) the Susquehanna River Basin/Marcellus Shale in Pennsylvania.

Simple water balance and geospatial information system (GIS) analysis will be conducted using the existing data. The collected data will be compiled in conjunction with hydrological trends over the same period of time. Control areas that have similar baseline water demands and have no oil and gas development will be compared to areas with intense hydraulic fracturing activity to isolate and identify the impacts of hydraulic fracturing on water availability. A critical analysis of trends in water flows and water usage patterns in areas impacted by hydraulic fracturing activities will be conducted to determine whether water withdrawals for hydraulic fracturing activities alter ground and surface water flows. Data collection will support the assessment of the impacts of hydraulic fracturing on water availability at various spatial scales (e.g., site, watershed, basin, and play) and temporal scales (e.g., days, months, and years).

Prospective case studies. EPA will conduct prospective case studies that will monitor all aspects of the hydraulic fracturing water lifecycle illustrated in Figure . These prospective case studies will collect data to evaluate potential impacts on water availability due to large volume water withdrawals, and will assess management practices related to water acquisition. Additionally, the assessment of site-scale water use on the hydrologic cycle will allow EPA to test the models used in the scenario evaluations described below.

Scenario evaluation. Scenario evaluations will assess the environmental futures and impacts of hydraulic fracturing operations at various spatial and temporal scales in the selected study areas using the existing data described above. The scenarios will include at least two futures: (1) average annual conditions in 10 years based on the full exploitation of non-conventional natural gas and (2) average annual conditions in 10 years based on sustainable water use in hydraulic fracturing operations. Both scenarios will build on predictions for land use and climate (e.g., drought, average, and wet). EPA will take advantage of the future scenario work constructed for the EPA Region 3 Chesapeake Bay Program (for 2030) and the EPA ORD Futures Midwest Landscape Program (for 2022). The spatial scales of analysis will reflect both environmental boundaries (e.g., site, watershed, river basin, and geologic play) and political boundaries (e.g., city/municipality, county, state, and EPA Region).

These assessments will consider typical water requirements for hydraulic fracturing activities and will also account for estimated demands for water from other human needs (e.g., drinking water, agriculture, and energy), adjusted for future populations. The sustainability analysis will reflect minimum river flow requirements and aquifer drawdown for drought, average, and wet precipitation years, and will allow a determination of the number of typical hydraulic fracturing operations that could be sustained for the relevant formation (e.g., Marcellus Shale) and future scenario. Appropriate physics-based watershed and ground water models will be used for representation of the water balance and hydrologic cycle, as discussed in Appendix H.

6.1.4.2 Water Quality: Analysis of Existing Data and Prospective Case Studies

Analysis of existing data. EPA will use the data collected in collaboration with USACE, USGS, and others to analyze changes in water quality in areas impacted by hydraulic fracturing, and to determine if any changes are due to water withdrawals for hydraulic fracturing. Water quality trends will also be evaluated to determine the potential for using routine monitoring data in identifying water resource vulnerabilities.

Prospective case studies. These case studies will allow EPA to collect data on the quality of ground and surface waters that may be used for hydraulic fracturing before and after water is removed for hydraulic fracturing purposes. The resulting data will be analyzed to determine if there are any changes in water quality, and if these changes are due to the large volume water withdrawals associated with hydraulic fracturing.

6.1.5 Potential Research Outcomes

The research outlined above will allow EPA to:

- Identify possible impacts on water availability and quality associated with large volume water withdrawals for hydraulic fracturing.
- Determine the cumulative effects of large volume water withdrawals within a watershed and aquifer.
- Develop metrics that can be used to evaluate the vulnerability of water resources.
- Provide an assessment of current water resource management practices related to hydraulic fracturing.

6.2 Chemical Mixing: What are the possible impacts of releases of hydraulic fracturing fluids on drinking water resources?

6.2.1 Background

Most hydraulic fracturing fluids are water-based fluids that serve two purposes: to create pressure to propagate the fracture and to carry the proppant into the fracture. Proppants are solid materials that are used to keep the fractures open after pressure is reduced in the well. The most common proppant is sand (Carter et al., 1996), although resin-coated sand, bauxite, and ceramics have also been used (Arthur et al., 2008; Palisch et al., 2008). Most, if not all, water-based fracturing techniques use proppants. There are, however, some fracturing techniques that do not use proppants. For example, nitrogen gas is commonly used to fracture coalbeds and does not require the use of proppants (Rowan, 2009).

In addition to proppants and water, hydraulic fracturing fluids contain chemical additives. The types and concentrations of proppants and chemical additives vary depending on the conditions of the specific well being fractured, and are selected to create a fracturing fluid tailored to the properties of the formation and the needs of the project. In many cases, reservoir properties are entered into modeling programs that simulate fractures (see Castle et al., 2005, and Hossain and Rahman, 2008, for commercial software available for fracture design). The fracturing models are then used to reverse engineer the requirements for fluid composition, pump rates, and proppant concentrations. In shale gas plays, for example, the fracturing fluid is predominantly water and sand, with added chemicals depending upon the characteristics of the source water and the shale play formation being fractured (GWPC and ALL Consulting, 2009).

Table 4 lists the volumetric composition of a fluid used in a fracturing operation in the Fayetteville Shale as an example of additive types and concentrations (GWPC and ALL Consulting, 2009; API, 2010b). A list of publicly known chemical additives found in hydraulic fracturing fluids is provided in Appendix D.

TABLE 4. AN EXAMPLE OF THE VOLUMETRIC COMPOSITION OF HYDRAULIC FRACTURING FLUID

Component/ Additive Type	Example Compound(s)	Purpose	Percent Composition (by Volume)	Volume of Chemical (Gallons)[a]
Water		Deliver proppant	90	2,700,000
Proppant	Silica, quartz sand	Keep fractures open to allow gas flow out	9.51	285,300
Acid	Hydrochloric acid	Dissolve minerals, initiate cracks in the rock	0.123	3,690
Friction reducer	Polyacrylamide, mineral oil	Minimize friction between fluid and the pipe	0.088	2,640
Surfactant	Isopropanol	Increase the viscosity of the fluid	0.085	2,550
Potassium chloride		Create a brine carrier fluid	0.06	1,800
Gelling agent	Guar gum, hydroxyethyl cellulose	Thickens the fluid to suspend the proppant	0.056	1,680
Scale inhibitor	Ethylene glycol	Prevent scale deposits in the pipe	0.043	1,290
pH adjusting agent	Sodium or potassium carbonate	Maintain the effectiveness of other components	0.011	330
Breaker	Ammonium persulfate	Allow delayed breakdown of the gel	0.01	300
Crosslinker	Borate salts	Maintain fluid viscosity as temperature increases	0.007	210
Iron control	Citric acid	Prevent precipitation of metal oxides	0.004	120
Corrosion inhibitor	N,n-dimethyl formamide	Prevent pipe corrosion	0.002	60
Biocide	Glutaraldehyde	Eliminate bacteria	0.001	30

Data are from GWPC and ALL Consulting, 2009, and API, 2010b. Note that the example compounds are not necessarily the compounds used in this fracturing operation in the Fayetteville Shale. [a] Based on 3 million gallons of fluid used.

In the case outlined in Table 4, the total concentration of chemical additives was 0.49 percent. Table 4 also calculates the volume of each additive based on a total fracturing fluid volume of 3 million gallons, and shows that the total volume of chemical additives is 14,700 gallons. In general, however, the overall concentration of chemical additives in fracturing fluids used in shale gas plays ranges from 0.5 to 2 percent by volume with water and proppant comprising the remainder (GWPC and ALL Consulting, 2009), indicating that 15,000 to 60,000 gallons of the total fracturing fluid consist of chemical additives (assuming a total fluid volume of 3 million gallons).

The chemical additives are typically stored in tanks on-site and blended with water and the proppant prior to injection. Flow, pressure, density, temperature, and viscosity can be measured before and after mixing (Pearson, 1989). High pressure pumps then send the mixture from the blender into the well (Arthur et al., 2008). In some cases, special on-site equipment is used to measure the properties of the mixed chemicals *in situ* to ensure proper quality control (Hall and Larkin, 1989).

6.2.2 What is the composition of hydraulic fracturing fluids and what are the toxic effects of these constituents?

In 2010, EPA compiled a list of chemicals that were publicly known to be used in hydraulic fracturing (Table D1 in Appendix D). The chemicals identified in Table D1, however, do not represent the entire set of chemicals used in hydraulic fracturing activities. EPA also lacks information regarding the frequency, quantity, and concentrations of the chemicals used, which is important when considering the toxic effects of hydraulic fracturing fluid additives. In January 2011, Congressmen Waxman and Markey and Congresswoman DeGette notified EPA that they found that "between 2005 and 2009, oil and gas service companies injected 32.2 million gallons of diesel fuel or hydraulic fracturing fluids containing diesel fuel in wells in 19 states" (Waxman et. al, 2011). Stakeholder meetings and media reports have emphasized the public's concern regarding the identity and toxicity of chemicals used in hydraulic fracturing.

Much of the information regarding the identity and concentration of chemicals used in hydraulic fracturing fluids is considered by the industry to be proprietary and, therefore, confidential. This makes identifying the toxicity and human health effects associated with these chemicals difficult. Table 4 illustrates that the chemicals used in hydraulic fracturing fluids can have a range of toxicities. For example, sand, polyacrylamide, guar gum, and hydroxyethyl cellulose are relatively benign materials. Acids and bases present an irritant response upon dermal or inhalation exposure, but more acute responses are possible. On the other hand, chronic toxicity has been associated with some identified chemicals, such as ethylene glycol, glutaraldehyde, and n,n-dimethyl formamide (TOXNET, 2011). An approach for assessing the toxicity and human health effects of fracturing fluid additives is outlined in Chapter 8.

6.2.3 What factors may influence the likelihood of contamination of drinking water resources?

Large hydraulic fracturing operations require extensive quantities of supplies, equipment, water, and vehicles, which could create risks of accidental releases, such as spills or leaks. Surface spills or releases can occur as a result of tank ruptures, equipment or surface impoundment failures, overfills, vandalism, accidents, ground fires, or improper operations. Released fluids might flow into a nearby surface water body or infiltrate into the soil and near-surface ground water, potentially reaching drinking water aquifers (NYSDEC, 2009).

6.2.4 How effective are mitigation approaches in reducing impacts to drinking water resources?

API provides a description of general practices relating to the transportation, storage, and handling of source water and other fluids prior to fracturing (API, 2010a). However, the extent to which these practices are followed in the industry or what other practices may be used is unclear.

6.2.5 Proposed Research Activities—Chemical Mixing

6.2.5.1 Chemical Identity and Toxicity: Analysis of Existing Data

In September 2010, EPA issued information requests to nine hydraulic fracturing service companies seeking information on the identity and quantity of chemicals used in hydraulic fracturing fluid in the

past five years (Appendix C). This information will provide EPA with a better understanding of the common compositions of hydraulic fracturing fluids (e.g., identity of components, concentrations, and frequency of use) and the factors that influence these compositions. By asking for data from the past five years, EPA expects to obtain information on chemicals that are currently used as well as those that are no longer used in hydraulic fracturing operations, but could be present in areas where retrospective case studies will be conducted. The data collected from this request will also be compared to the list of publicly known hydraulic fracturing chemical additives to determine the accuracy and completeness of the list of chemicals given in Table D1.

The chemical list from the nine companies will be combined with the list of publicly known chemical additives to provide EPA with a comprehensive list of chemicals used in hydraulic fracturing operations. The resulting list of chemical additives will be used in two ways: First, EPA will work to determine the toxicity and estimated human health effects associated with hydraulic fracturing fluid chemical additives using methods described later in Chapter 8. Secondly, this list of chemicals will allow EPA to identify existing analytical methods—or develop new methods—to detect fracturing fluids and their degradation products in drinking water resources. EPA expects to identify a short list of 10 to 20 chemical indicators to track the fate and transport of hydraulic fracturing fluids through the environment. The criteria for selecting these indicators will include, but are not limited to, (1) the frequency of occurrence in fracturing fluids, (2) the toxicity of the chemical, (3) the fate and transport of the chemical (e.g., mobility in the environment), and (4) the availability of detection methods.

6.2.5.2 Hydraulic Fracturing Fluid Release: Analysis of Existing Data and Case Studies

Analysis of existing data. The tanks, valves, and pipes used to store and mix hydraulic fracturing fluid (i.e., water, proppant, and chemical additives) are subject to spills, releases, or leaks (subsequently, the term "release" will refer to a leak, spill, or release). Releases, in general, are not restricted to hydraulic fracturing operations, and can occur under a variety of conditions. Because these are common types of problems, there already exists a body of scientific literature that describes how a chemical solution released on the ground can infiltrate the subsurface and/or run off to a surface water body. EPA will use the list of hydraulic fracturing fluid chemical additives generated through the research proposed in Section 6.2.5.1 to identify individual chemicals and classes of chemicals for review in the existing scientific literature. EPA will then identify relevant existing research on the fate and transport of hydraulic fracturing fluid additives. The relevant research will be summarized to determine the known impacts of spills of fracturing fluid on drinking water resources and to identify existing knowledge gaps related to surface spills of hydraulic fracturing fluid chemical additives.

Retrospective case studies. Some of the candidate case study sites (listed in Appendix F) have reported accidental releases from chemical tanks, supply lines, or leaking valves. It is expected that at least one of the case studies chosen will allow EPA to investigate the impacts of accidental releases on drinking water resources.

Prospective case studies. Prospective case studies will monitor and assess current chemical management practices, and will identify potential areas of concern related to on-site chemical mixing of hydraulic fracturing fluid. EPA will also collect information on the effectiveness of current management

practices used to contain or mitigate the impacts of spills and/or leaks of fracturing fluid on drinking water resources.

6.2.6 Potential Research Outcomes

Through the above research activities, EPA will:

- Summarize available data on the identity and frequency of use of various hydraulic fracturing chemicals, the concentrations at which the chemicals are typically injected, and the total amounts used.
- Identify the toxicity of chemical additives, and apply tools to prioritize data gaps and identify chemicals for further assessment.
- Identify a set of chemical indicators associated with hydraulic fracturing fluids and associated analytical methods.
- Determine the likelihood that surface spills will result in the contamination of drinking water resources.
- Assess current management practices related to on-site chemical storage and mixing.

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

6.3.1 Background

Ideally, the successful injection of hydraulic fracturing fluid results in natural gas production without contamination of USDWs, and is necessarily dependent upon the mechanical integrity of the well and the fluid design. The fluid design is determined by the subsurface properties and the oil/gas service field operator. Mechanical integrity is determined by well design and construction, which is regulated by the states. Requirements for well construction vary from state to state, but many states incorporate standards such as those published by API (2009). It is useful, therefore, to provide a brief summary of well construction, which is adapted from the well construction and integrity guidelines published by API (2009).

6.3.1.1 Well Design and Construction

According to API (2009), the goal of well design is to "ensure the environmentally sound, safe production of hydrocarbons by containing them inside the well, protecting ground water resources, isolating the production formations from other formations, and by proper execution of hydraulic fractures and other stimulation operations." Thus, proper well construction is essential for isolating the production zone from USDWs, and includes drilling a hole, installing a steel pipe (casing), and cementing the pipe in place. These activities are repeated multiple times throughout the drilling event until the well is complete.

Drilling. Various techniques can be used to drill wells. For example, air or water can be used to drill wells in coalbed methane formations and other fragile formations (Rogers et al., 2007). In most cases, however, a drilling string—composed of a drill bit, drill collars, and a drill pipe—is used to drill the well. During the drilling process, a drilling fluid such as compressed air or a water- or oil-based liquid ("mud")

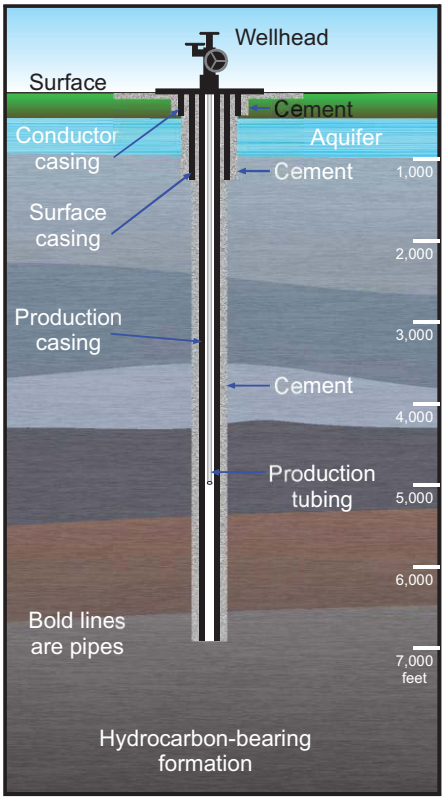


FIGURE 8. WELL CONSTRUCTION

is circulated down the drilling string. Water-based liquids typically contain a mixture of water, barite, clay, and chemical additives (OilGasGlossary.com, 2010). This fluid serves multiple purposes, including cooling the drill bit, lubricating the drilling assembly, removing the formation cuttings, maintaining the pressure control of the well, and stabilizing the hole being drilled. Once removed from the wellbore, both drilling liquids and drill cuttings must be treated, recycled and/or disposed of.

Casing. Casings are steel pipes that line the borehole and serve to isolate the geologic formation from the materials and equipment in the well. The casing also prevents the borehole from caving in, confines the injected/produced fluid to the wellbore and the intended production zone, and provides a method of pressure control. Thus, the casing must be capable of withstanding the external and internal pressures encountered during the installation, cementing, fracturing, and operation of the well. Because fluid is confined within the casing, the possibility of contamination of zones adjacent to the well is greatly diminished.

Figure 8 illustrates the different types of casings that may be used in well construction: conductor, surface, intermediate (if necessary), and production. Each casing serves a unique purpose. Ideally, the surface casing should extend below the base of the deepest USDW and be cemented to the surface. This casing isolates the USDWs and provides protection from contamination during drilling, completion, and operation of the well. Note that the shallow portions of the well may have multiple layers of casing and cement, isolating the production area from the surrounding formation. For each casing, a hole is drilled and the casing is installed and cemented into place.

Casings should be positioned in the center of the borehole using casing centralizers, which attach to the outside of the casing. A centralized casing improves the likelihood that it will be completely surrounded by cement during the cementing process, leading to the effective isolation of the well from USDWs.

Cementing. Once the casing is inserted in the borehole, it is cemented into place by pumping a cement slurry down the casing and up the annular space between the formation and the outside of the casing. The principal functions of the cement (for vertical wells or the vertical portion of a horizontal well) are to be of suitable quality (during and after setting) to act as a barrier to migration of fluids up the wellbore behind the casing and to mechanically support the casing. To accomplish these functions, the proper cement must be used for the conditions encountered in the borehole. Additionally, placement of the cement and the type of cement used in the well must be carefully planned and executed to ensure that the cement functions effectively.

The presence of the cement sheath around each casing and the effectiveness of the cement in preventing fluid movement are the major factors in establishing and maintaining the mechanical integrity of the well. Even a correctly constructed well can fail over time due to downhole stresses and corrosion (Bellabarba et al., 2008). Therefore, ongoing mechanical integrity testing of the well is recommended; many states require that wells be tested periodically (GWPC, 2009).

6.3.1.2 Injection of Hydraulic Fracturing Fluid

Before the injection of hydraulic fracturing fluid, the production casing is perforated using explosive charges. The perforations allow the injected fluid to enter, and thus fracture, the target formation. Wells may be fractured either in a single stage or in multiple stages as determined by the total length of the injection zone. Vertical wells can be fractured in a single stage or multiple stages while horizontal wells typically require multiple stages due to the overall length of the horizontal leg (GWPC and ALL Consulting, 2009). In a multi-stage fracture of a horizontal well, the fracturing operation typically begins with the stage furthest from the wellhead until the entire length of the horizontal leg has been fractured.

The actual fracturing process within each stage consists of a series of injections using different volumes and compositions of fracturing fluids (GWPC and ALL Consulting, 2009). Sometimes a small amount of fluid is pumped into the well before the actual fracturing begins. This "mini-frac" may be used to help determine reservoir properties and to enable better fracture design (API, 2009). In the first stage of the fracture job, fracturing fluid (typically without proppant) is pumped down the well at high pressures to initiate the fracture. The fracture initiation pressure will depend on the depth and the mechanical properties of the formation. A combination of fracturing fluid and proppant is then pumped in, often in slugs of varying sizes and concentrations. After the combination is pumped, a water flush is used to begin flushing out the fracturing fluid (Arthur et al., 2008).

API recommends that several parameters be continuously monitored during the actual hydraulic fracturing process, including surface injection pressure, slurry rate, proppant concentration, fluid rate, and proppant rate (API, 2009). Monitoring the surface injection pressure is particularly important for two reasons: (1) it ensures that the pressure exerted on equipment does not exceed the tolerance of the weakest components, and (2) unexpected or unusual pressure changes may be indicative of a problem that requires prompt attention (API, 2009).

Models can also be used during the fracturing process to make real-time adjustments to the fracture design (Armstrong et al., 1995). Additionally, microseismic monitors and tiltmeters may be used during fracturing to plot the positions of the fractures (Warpinski et al., 1998 and 2001; Cipolla and Wright, 2000), although this is done primarily when a new area is being developed or new techniques are being used (API, 2009). Microseismic monitoring is used in about three percent of fracturing jobs (Zoback et al., 2010).

6.3.1.3 NATURALLY OCCURRING SUBSTANCES

Hydraulic fracturing may affect the mobility of naturally occurring substances in the subsurface, particularly in the hydrocarbon-containing formation. These substances, described in Table 5, include formation fluid, gases, trace elements, naturally occurring radioactive material, and organic material.

TABLE 5. NATURALLY OCCURRING SUBSTANCES THAT MAY BE FOUND IN HYDROCARBON-CONTAINING FORMATIONS

Type of Contaminant	Example(s)
Formation fluid	Brine[a]
Gases	Natural gas[b] (e.g., methane, ethane), carbon dioxide, hydrogen sulfide, nitrogen, helium
Trace elements	Mercury, lead, arsenic[c]
Naturally occurring radioactive material	Radium, thorium, uranium[c]
Organic material	Organic acids, polycyclic aromatic hydrocarbons, volatile and semi-volatile organic compounds

[a] Piggot and Elsworth, 1996.
[b] Zoback et al., 2010.
[c] Harper, 2008; Leventhal and Hosterman, 1982; Tuttle et al., 2009; Vejahati et al., 2010.

Some or all of these substances may find a pathway to USDWs as a result of hydraulic fracturing activities. For example, if fractures extend beyond the target formation and reach aquifers, or if the casing or cement around a wellbore fails under the pressures exerted during hydraulic fracturing, these potential contaminants could migrate into drinking water supplies. Some of these substances may be liberated from the formation via complex biogeochemical reactions with chemical additives found in hydraulic fracturing fluid (Falk et al., 2006; Long and Angino, 1982). These reactions are discussed in more detail in Section 6.3.4.

6.3.2 HOW EFFECTIVE ARE WELL CONSTRUCTION PRACTICES AT CONTAINING GASES AND FLUIDS BEFORE, DURING, AND AFTER FRACTURING?

In researching information sources for this study plan, EPA found evidence showing that improper well construction or improperly sealed wells may provide subsurface pathways for ground water pollution by allowing contaminant migration to sources of drinking water (PADEP, 2010b; McMahon et al., 2011; State of Colorado Oil and Gas Conservation Commission, 2009a, 2009b, and 2009c; USEPA, 2010b). Based on these findings, EPA believes that well mechanical integrity will likely be an important factor in preventing contamination of drinking water resources from hydraulic fracturing activities.

In addition to concerns related to improper well construction and well abandonment processes, there are concerns about the repeated fracturing of a well over its lifetime. Hydraulic fracturing can be repeated as necessary to maintain the flow of gas or hydrocarbons to the well. The near- and long-term effects of repeated pressure treatments on well components (e.g., casing, cement) are not well understood. While EPA recognizes that fracturing or refracturing existing wells may pose a risk to drinking water resources, EPA has not been able to identify potential partners for a case study,

therefore, this practice is not considered in the current study. The issues of well age and maintenance, however, are important and warrant more study.

6.3.3 What are the potential impacts of pre-existing man-made or natural pathways/features on contaminant transport?

Although hydraulic fracture design and control have been researched extensively, predicted and actual fracture lengths still differ frequently (Daneshy, 2003; Warpinski et al., 1998). Hence, it is difficult to accurately predict and control the location and length of fractures. If hydraulic fractures combine with pre-existing faults or fractures that lead to aquifers or directly extend into aquifers, injection could lead to the contamination of drinking water supplies by fracturing fluid, natural gas, and/or naturally occurring substances (see Table 5).

During the fracturing process, some fracturing fluid may flow from the created fractures to other areas within the gas-containing formation in a phenomenon known as "fluid leakoff." In the case of leakoff, the fluid may flow into the micropore or pore spaces within the formation, existing natural factures in the formation, or small fractures opened into the formation by the pressure in the induced fracture (API, 2009; Economides et al., 2007). Fluid leakoff during hydraulic fracturing can exceed 70 percent of the injected volume if not controlled properly (Glenn et al., 1985), and may result in fluid migrating into drinking water aquifers (Hess, 2010; Subra, 2010; Bielo, 2010; URS Corporation, 2009). Additionally, the fracturing process may change the fine scale structure of the rock and alter the fluid flow properties of the formation (Yang et al., 2004).

The risk posed by fluid leakoff to drinking water resources will depend on the distance to those resources and the geochemical and transport processes that are occurring in the intermediate strata. A common assumption in shale gas formations is that natural barriers in the rock strata that act as seals for the gas in the target formation also act as barriers to the vertical migration of fracturing fluids (GWPC and ALL Consulting, 2009). In contrast to shale gas, coalbed methane reservoirs are mostly shallow and may also be underground resources of drinking water. In this instance, hydraulic fracturing may be occurring in or near an USDW, raising concerns about the contamination of shallow water supplies with hydraulic fracturing fluids (Pashin, 2007). Some states have regulations addressing hydraulic fracturing of this type of reservoir (GWPC and ALL Consulting, 2009).

In addition to natural faults or fractures, it is important to consider the proximity of artificial penetrations such as drinking water wells, exploratory wells, production wells, abandoned wells (plugged and unplugged), injection wells, and underground mines. If such penetrations intersect the injection zone in the vicinity of a hydraulically fractured well, they may serve as conduits for contaminants to reach USDWs. Several instances of natural gas migrations have been noted. A 2004 EPA report on coalbed methane indicated that methane migration in the San Juan Basin was mitigated once abandoned and improperly sealed wells were plugged. The same report found that in some cases in Colorado, poorly constructed, sealed, or cemented wells used for a variety of purposes could provide conduits for methane migration into shallow USDWs (USEPA, 2004).

6.3.4 What chemical/physical/biological processes could impact the fate and transport of substances in the subsurface?

There are numerous chemical/physical/biological processes that may alter the fate and transport of substances in the subsurface as the result of hydraulic fracturing. These processes could increase or decrease the mobility of these substances, depending on their properties and the complex interactions of all processes occurring in the subsurface. For example, several of the chemicals used in fracturing fluid (e.g., acids and carbonates) are known to mobilize naturally occurring substances out of rocks and soils by changing the pH or reduction-oxidation (redox) conditions in the subsurface. Conversely, a change in the redox conditions in the subsurface may also decrease the mobility of naturally occurring substances (Eby, 2004; Sparks, 1995; Sposito, 1989; Stumm and Morgan, 1996; Walther, 2009).

Along with chemical mechanisms, biological processes can change the mobility of fracturing fluid additives and naturally occurring substances. Many microbes, for example, are known to produce siderophores, which can mobilize metals from the surrounding matrix (Gadd, 2004). Microbes may also reduce the mobility of substances by binding to metals or organic substances, leading to the localized sequestration of fracturing fluid additives or naturally occurring substances (Gadd, 2004; McLean and Beveridge, 2002; Southam, 2000).

Physical processes can also increase the mobility of naturally occurring substances. For example, hydraulic fracturing itself is a physical process that may increase the mobility of methane into the surrounding media (GWPC and ALL Consulting, 2009). In the formation, methane is trapped inside the matrix and is not mobile because the pores within the formation are too small or are unconnected. When the rock is fractured, the connection between the pores increases, allowing methane to flow into the fracture and wellbore.

6.3.5 What are the toxic effects of naturally occurring substances?

As discussed above, multiple pathways may exist that allow contaminants to reach drinking water resources. The toxic effects of chemical additives in hydraulic fracturing fluid were briefly discussed in Section 6.2.2. Table 5 and Table D3 in Appendix D provide examples of naturally occurring substances that may contaminate drinking water resources. The toxicity of these substances varies considerably. For example, naturally occurring metals, though they are essential nutrients, exert various forms of toxicity even at low concentrations. Natural gases can also have adverse consequences stemming from their toxicity as well as their physical characteristics (e.g., some are very explosive). Research to summarize and explore these effects is described in Chapter 8.

6.3.6 Proposed Research Activities—Well Injection

6.3.6.1 Well Integrity: Analysis of Existing Data, Case Studies, and Scenario Evaluation

Analysis of existing data: well files. As part of the voluntary request for information sent by EPA to nine hydraulic fracturing service companies (see Appendix C), EPA asked for the locations of sites where hydraulic fracturing operations have occurred within the past year. From this potential list of thousands of hydraulic fracturing sites, EPA will select a representative sample of sites and request the complete well files for these sites. Well files generally contain information regarding all activities conducted at the

site, including any instances of well failure. EPA will analyze the well files to assess the typical causes, frequency, and severity of well failures.

Retrospective case studies. While conducting retrospective case studies, EPA will assess the mechanical integrity of relevant wells (e.g., existing and historical production wells) near the reported area of drinking water contamination. To do this, EPA will review existing well construction and mechanical integrity data and/or collect new data using the tools described in Appendix E. By investigating well construction and mechanical integrity at sites with reported drinking water contamination, EPA will work to determine if well failure was responsible for the reported contamination and whether original well integrity tests were effective in identifying problems.

Prospective case studies. EPA will assess well construction and mechanical integrity at prospective case study sites by:

- Assessing the integrity of wells with respect to casing and cement placement using available logging tools and pressure tests conducted before hydraulic fracturing.
- Repeating mechanical integrity assessments on wells following hydraulic fracturing treatments to evaluate changes related to the high pressures used in the fracturing.
- Sampling the pressure within, and the fluid from, well components (e.g., annular spaces behind the production casing) before and after hydraulic fracturing operations.

During prospective case studies, EPA will also identify what, if any, mechanisms are used to monitor mechanical integrity after the hydraulic fracturing event has taken place.

Scenario evaluation. Computer modeling provides a scientific approach to test potential impacts of hydraulic fracturing well injection scenarios on drinking water resources. The models will include engineering and geological aspects, which will be informed by existing data and laboratory experiments. Models of the engineering systems will include the design and geometry of the vertical and horizontal wells in addition to information on the casing and cementing materials. Models of the geology will include the expected geometry of aquifers and aquitards/aquicludes, the permeability of the formations, and the geometry and nature of boundary conditions (e.g., closed and open basins, recharge/discharge).

Once built, the models will be used to explore the influence of pressure response and contaminant transport under conceptual models representing expected fracturing conditions as well as potential modes of failure. For example, it is suspected that breakdowns in the well casing or cement may provide a high permeability pathway between the well casing and the borehole wall, which may lead to contamination of a drinking water aquifer. In this case, it will be informative to compare typical well construction and testing practices to unexpected situations that might affect drinking water resources.

6.3.6.2 Impacts of Natural and Man-made Pathways: Case Studies and Scenario Evaluation

Retrospective case studies. In cases of suspected drinking water contamination, EPA will investigate the role of natural and/or artificial pathways in leading to the possible contamination through geophysical testing, field sample analysis, and modeling. This investigation will determine the role of existing natural or artificial pathways in providing conduits for the migration of fracturing fluid, natural gas and/or naturally occurring substances to drinking water resources.

EPA will also review the data collected on the hydraulic fracturing process itself, including data gathered to calculate the fracture pressure gradients in the injection zone and confining layers; data resulting from fracture modeling, microseismic fracture mapping and tiltmeter analysis; and any other data used to determine fracture location, length, and height. A critical assessment of these data will allow EPA to determine if fractures created during hydraulic fracturing were localized to the injection zone or possibly intersected existing faults or fractures, leading to the reported contamination.

Prospective case studies. The prospective case studies will give EPA a better understanding of the processes and tools used to determine fracture location, length, and height. Additionally, EPA will assess the impacts of natural and man-made pathways on the fate and transport of chemical contaminants to drinking water resources by measuring water quality before, during, and after injection. EPA is currently exploring the possibility of using chemical tracers to track the fate and transport of injected fracturing fluids. The tracers may be used to determine if fracturing fluid migrates from the targeted formation to a USDW via existing natural or man-made pathways.

Scenario evaluation. The physics-based computer modeling tools described above allow for the exploration of scenarios in which, for example, the fracturing of the target formation unintentionally extends outside of the target zone and potentially creates new pathways for pressure and fluid leakage. It is also suspected that abandoned wells and natural fractures and fault zones may provide pathways for any fluids that leave the target injection zone. In these studies, the injection pulses will be distinguished by their near-field, short-term impacts (fate and transport of injection fluids) as well as their far-field and long-term impacts (including the displacement of native brines or existing gas pockets). These studies will allow the exploration of the potential impacts of fracturing on drinking water resources with regard to variances in geology and well construction, and will help to inform the retrospective and prospective case studies.

Data and information provided by these studies will allow EPA to identify and predict the area of evaluation (AOE) around a hydraulic fracturing site. The AOE includes the subsurface zone that is potentially impacted by hydraulic fracturing activities and is projected as an area at the land surface. Within this area, drinking water resources could be affected by the migration of hydraulic fracturing fluids and liberated gases outside the injection zone, as well as the displacement of native brines within the subsurface. Maps of the AOEs for multiple injection operations can be overlaid on regional maps to evaluate cumulative impacts, and, when compared to regional maps of areas contributing recharge to drinking water wells (source water areas), to evaluate regional vulnerability. The AOE may also be used to support contaminant fate and transport hypothesis testing in retrospective case studies.

6.3.6.3 Physical/Chemical/Biological Processes Relevant to Hydraulic Fracturing: Laboratory Studies

Laboratory studies will be conducted to evaluate which characteristics of gas-bearing formations and fracturing conditions (e.g., temperature and pressure) are most important in determining the potential impact of hydraulic fracturing on drinking water resources. Chemical degradation, biogeochemical reactions, and weathering reactions will be studied by pressurizing subsamples of cores, cuttings, or aquifer material in temperature-controlled reaction vessels. The subsamples will then be exposed to hydraulic fracturing fluids using either a batch or continuous flow system to simulate subsurface reactions. After specific exposure conditions, samples will be drawn for chemical, mineralogical, and microbiological characterization. This approach will enable the evaluation of degradation products as well as constituents that may be mobilized from the solid phase due to biogeochemical reactions.

The laboratory studies will also help to identify possible components in flowback and produced water. Once identified, the list of possible components can be used to identify or develop analytical methods needed for detecting these components. Additionally, the list of possible flowback and produced water components can be used to determine the toxicity and human health effects of naturally occurring substances that may be released during hydraulic fracturing operations using the methods outlined in Chapter 8.

6.3.7 Potential Research Outcomes

The research opportunities outlined above will allow EPA to:

- Determine the frequency and severity of well failures, as well as the factors that contribute to them.
- Identify the key conditions that increase or decrease the likelihood of the interaction of existing pathways with hydraulic fractures.
- Evaluate water quality before, during, and after injection.
- Determine the identity, mobility, and fate of potential contaminants, including fracturing fluid additives and/or naturally occurring substances (e.g., formation fluid, gases, trace elements, radionuclides, organic material) and their toxic effects.
- Develop analytical methods for detecting chemicals associated with hydraulic fracturing events.

6.4 Flowback and Produced Water: What are the possible impacts of releases of flowback and produced water on drinking water resources?

6.4.1 Background

After the fracturing event, the pressure is decreased and the direction of fluid flow is reversed, allowing fracturing fluid and naturally occurring substances to flow out of the wellbore to the surface; this mixture of fluids is called “flowback.” Generally, the flowback period in shale gas reservoirs is several weeks (URS Corporation, 2009), while the flowback period in coalbed methane reservoirs appears to be longer (Rogers et al., 2007).

Estimates of the amount of fracturing fluid recovered as flowback in shale gas operations vary from as low as 25 percent to high as 70 to 75 percent (Pickett, 2009; Veil, 2010; Horn, 2009). Other estimates specifically for the Marcellus Shale project a fracture fluid recovery rate of 10 to 30 percent (Arthur et al., 2008). Less information is available, however, for coalbed methane reservoirs. Palmer et al. (1991) estimated a 61 percent fracturing fluid recovery rate over a 19-day period based on sampling from a single well in the Black Warrior Basin. A recent GWPC report states that none of the 27 oil and natural gas producing states in the United States requires the volume of flowback to be reported to state agencies (GWPC, 2009).

The initial flow rate at which the flowback exits the well can be relatively high (e.g., > 100,000 gallons per day) for the first few days. However, this flow diminishes rapidly with time, ultimately dropping to the normal rate of produced water flow from a natural gas well (e.g., 50 gallons per day) (Chesapeake Energy, 2010; Hayes, 2009b). While there is no clear transition between flowback and produced water, produced water is generally considered to be the fluid that exits the well during oil or gas production (API, 2010a; Clark and Veil, 2009). Like flowback, produced water also contains fracturing fluid and naturally occurring materials, including oil and/or gas. Produced water, however, is generated throughout the well's lifetime.

The physical and chemical properties of flowback and produced water vary with fracturing fluid composition, geographic location, and geological formation (Veil et al., 2004). In general, analyses of flowback from various reports show that concentrations of TDS can range from 5,000 mg/L (Horn, 2009) to more than 100,000 mg/L (Hayes, 2009a), and may even reach 200,000 mg/L (Gaudlip and Paugh, 2008; Keister, 2009; Vidic, 2010). These high values can be reached in a matter of two weeks.

Along with high TDS values, flowback can have high concentrations of major ions (e.g., barium, bromide, calcium, chloride, iron, magnesium, sodium, strontium, bicarbonate), with concentrations of calcium and strontium sometimes reported to be as high as thousands of milligrams per liter (Vidic, 2010). Flowback may also contain radionuclides (Zoback et al., 2010) as well as volatile organic compounds (VOC), including benzene, toluene, xylenes, and acetone (URS Corporation, 2009). A list of chemicals identified in flowback and produced water can be found in Table D2 in Appendix D. Additionally, flowback has been reported to have pH values ranging from 5 to 8 (Hayes, 2009a). A limited time series monitoring program of post-fracturing flowback fluids in the Marcellus Shale indicated increased concentrations through time of TDS, chloride, barium, and calcium; water hardness; and levels of radioactivity (URS Corporation, 2009).

Flowback and produced water from hydraulic fracturing operations are held in storage tanks and waste impoundment pits prior to or during treatment, recycling, and disposal (GWPC, 2009). Impoundments may be temporary (e.g., reserve pits for storage) or long-term (e.g., evaporation pits used for treatment). In areas of New York overlying the Marcellus Shale, regulators are reviewing double-lined centralized impoundments ranging in capacity from 1 to 16 million gallons for the storage of flowback that serve well pads within a 4-square-mile area (ICF International, 2009b**;** NYSDEC, 2009). The transportation of flowback and produced water for disposal depends on site-specific conditions. In the

Marcellus Shale, for example, if the disposal area is not located nearby, flowback and produced water are trucked to disposal facilities (ICF International, 2009a).

The storage of flowback and produced water in tanks or impoundment pits is regulated in many oil and gas producing states (GWPC, 2009). According to the GWPC, 81 percent of these states require tanks for the storage of flowback and produced water to be surrounded by a containment dike. Five states, however, require that materials used to construct storage tanks be compatible and of sufficient strength to hold flowback and produced water. If flowback and produced water is contained in pits, 18 of the 27 states studied require a permit for the pit while 23 states require liners in pits and 16 limit the duration of their use. For example, New York limits the duration fluids can be stored in pits on-site to 45 days after the fracturing treatment (unless reuse has been approved). When liners are used, some states require interstitial monitoring for leaks while others do not.

6.4.2 What is the composition and variability of flowback and produced water and what are the toxic effects of these constituents?

Much of the existing data on the composition of flowback and produced water focuses on the detection of major ions in additional to pH and TDS measurements. For example, data provided by the USGS produced water database indicates that the distribution of major ions, pH, and TDS levels is not only variable on a national scale (e.g., between geologic basins), but also on the local scale (e.g., within one basin) (USGS, 2002). However, less is known about the composition and variability of flowback and produced water with respect to the chemical additives found in hydraulic fracturing fluid or radioactive materials. A recent report by the Gas Technology Institute offers a fairly extensive analysis of the constituents found in flowback in several wells in the Marcellus Shale (Hayes, 2009b). Veil (2004) also provides data for several organic compounds in produced water. It is unclear, however, how the chemical composition of flowback varies on both the national and local scales.

A thorough understanding of how the composition of flowback and produced water varies at both the local and national scales could lead to improved predictions of the identity and toxicity of chemical additives and naturally occurring substances in flowback and produced water. The toxicity of these substances is discussed above in Sections 6.2.2 and 6.3.5.

6.4.3 What factors may influence the likelihood of contamination of drinking water resources?

There may be opportunities for the contamination of drinking water resources both below and above ground. If the mechanical integrity of the well has been compromised, flowback and produced water traveling up the wellbore may have direct access to local aquifers, leading to the contamination of drinking water resources. Once above ground, flowback and produced water are stored on-site in storage tanks and waste impoundment pits, and then may be transported off-site for treatment and/or disposal. There is a potential for releases, leaks, and/or spills associated with the storage and transportation of flowback and produced water, which could lead to contamination of shallow drinking water aquifers and surface water bodies. There are also concerns associated with the design, construction, operation, and closure of waste impoundment pits.

6.4.4 How effective are mitigation approaches in reducing impacts to drinking water resources?

Standard management practices for the industry recommend that spills be cleaned up and disposed of, or reused, to protect human health and the environment. If applicable, these efforts should be pursued in compliance with existing federal and state regulations (USEPA, 2002a). As in the case of accidental releases associated with chemical mixing, it is unclear what practices are used on-site to prevent, contain, or mitigate accidental releases of flowback and produced water. EPA is interested in gathering information relating to the current on-site management practices that are used to prevent and/or contain accidental releases of flowback and produced water to drinking water resources.

6.4.5 Proposed Research Activities—Flowback and Produced Water

6.4.5.1 Composition and Variability of Flowback and Produced Water: Analysis of Existing Data and Prospective Case Studies

Analysis of existing data. EPA requested data on the amounts and management of flowback and produced water in the information request sent to the nine hydraulic fracturing service companies (Appendix C). As noted above, a comprehensive chemical analysis of flowback at several wells in the Marcellus Shale is available (Hayes, 2009b) as well as information on potential constituents in produced water (Veil et al., 2004). In addition, the New York State Department of Environmental Conservation reported on the constituents in samples of flowback and produced water (NYSDEC, 2009). These and other data EPA can locate will be used to enhance our current understanding of the composition and variability of flowback and produced water, which will allow EPA to identify or develop analytical methods needed to detect potential chemicals of concern (e.g., fracturing fluid additives, metals, and radionuclides) in hydraulic fracturing wastewaters. These data will also be used to identify the toxic effects of hydraulic fracturing wastewaters, as described in Chapter 8.

Prospective case studies. EPA will monitor current management practices associated with flowback and produced water, and will also draw samples as part of the full water lifecycle monitoring at sites. At the case study sites, flowback and produced water will be sampled periodically following the completion of the injection of hydraulic fracturing fluids into the formation. Samples will be analyzed for the presence of fracturing fluid chemicals and naturally occurring substances found in formation samples analyzed prior to fracturing. This will allow EPA to study the composition and variability of flowback and produced water over a given period of time.

The analysis of flowback and produced water collected during prospective case studies will be done in coordination with DOE NETL. NETL is currently studying the fate and biogeochemistry of radionuclides and VOCs that may appear in flowback and produced water during unconventional oil and natural gas development projects. In addition, DOE NETL has an ongoing project to identify the isotopic signature of Marcellus flowback and produced water. The objective of this project is to determine if stable isotopes can be used to identify Marcellus flowback and produced water when commingled with surface waters or shallow ground water (such as in a surface spill or casing leak scenario); if successful, this is also a technique that EPA may use in retrospective case studies.

6.4.5.2 Flowback and Produced Water Release: Analysis of Existing Data, Retrospective Case Studies, and Scenario Evaluations

Analysis of existing data. There is a chance for flowback and produced water to be released once at the surface, either due to failure at the pipeline or failure of the waste pit or storage tank. Chemical spills and wastewater leakage from waste pits have been studied extensively for other types of wastes. EPA will take advantage of the existing scientific literature by reviewing it for situations that may be similar to hydraulic fracturing operations. To accomplish this, EPA will use the list of constituents identified in flowback and produced water to determine chemicals and classes of chemicals for review in the existing literature. The relevant research will be summarized to determine the fate and transport of flowback and produced water constituents. This literature review will allow EPA to summarize the known impacts of releases of flowback and produced water on drinking water resources and to identify existing knowledge gaps related to surface releases of flowback and produced water.

Retrospective case studies. There are several candidate sites where surface releases of flowback and/or produced water have occurred from spills, blowouts, and leaking pits. Case studies will examine the extent of the impacts, if any, from these releases on surface and ground water resources.

Scenario evaluation. Computer modeling will provide a scientific approach for testing the potential impacts of hydraulic fracturing flowback and produced water on drinking water resources. The conceptual model for representative geology remains the same as in the case of injected fluids, but the reservoir production and engineering changes from injection to extraction. An important exposure pathway to consider is the long-term movement of injected chemicals, formation fluids, and/or transformation products of the mixture up an improperly cemented section of the borehole or casing. Again, it will be informative to compare the typical management practices to unexpected situations that may lead to impacts of flowback and produced water on drinking water resources.

6.4.5.3 Flowback and Produced Water Management: Prospective Case Studies

Prospective case studies. EPA will collect data on the on-site handling of flowback and produced water, including the monitoring of storage pits and the potential for leakage of flowback and produced water to the subsurface from lined and unlined pits. When surface pits or storage tanks are used on-site, EPA will sample their contents. When the pits are closed and abandoned, core samples will be taken beneath the pits to confirm adequate containment of wastes. Information will also be collected on the ways in which wastewater is transported for treatment or disposal and on the efficacy of various forms of on-site treatment (e.g., biocides) in reducing levels of key contaminants.

6.4.6 Potential Research Outcomes

Through the research activities outlined, EPA will:

- Compile information on the identity, quantity, and toxicity of flowback and produced water components.
- Develop analytical methods to identify and quantify flowback and produced water components.
- Provide a prioritized list of components requiring future studies relating to toxicity and human health effects.

- Determine the likelihood that surface spills will result in the contamination of drinking water resources.
- Evaluate risks posed to drinking water resources by current methods for on-site management of wastes produced by hydraulic fracturing.

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

6.5.1 Background

Flowback and produced water can be managed through disposal or treatment, which may then be followed by discharge to surface water bodies or reuse. Land disposal and discharge to surface waters without treatment pose environmental and legal problems. Underground injection is the primary method for disposal in all the major gas shale plays, except the Marcellus Shale (Horn, 2009; Veil, 2007 and 2010). Underground injection, however, can be problematic because of insufficient capacity and the costs of trucking the wastewater to an injection site (Gaudlip and Paugh, 2008; Veil, 2010).

In shale gas areas near population centers (e.g., the Marcellus Shale), wastewater treatment at publicly owned treatment works (POTWs) or commercial industrial treatment facilities may be an option for some operations. Many commercial wastewater treatment facilities are designed to treat the known constituents in flowback or produced water. POTWs, however, are not designed to treat hydraulic fracturing wastewaters; large quantities of sodium and chloride are detrimental to digesters and can result in high TDS concentrations in the effluent (Veil, 2010; West Virginia Water Research Institute, 2010). This high TDS water can be corrosive and harm drinking water treatment facilities downstream from POTWs. Additionally, POTWs are not generally equipped to treat fluids that contain radionuclides, which may be released from the formation during hydraulic fracturing. Elevated levels of bromide, a constituent of flowback in many areas, can also create problems for POTWs. Wastewater plants using chlorination as a treatment process will produce more brominated disinfection byproducts, which have significant health concerns associated with them. When POTWs are used, there may be strict limits on the volumes permitted, such as those found in Pennsylvania where the disposal of production waters at POTWs is limited to less than 1 percent of the POTW's average daily flow (Pennsylvania Environmental Quality Board, 2009).

A primary goal of treatment for shale gas flowback is to meet current water quality standards, which largely focus on TDS levels. Some treatment options include reverse osmosis systems, distillation, filtration, and precipitation processes (West Virginia Water Research Institute, 2010). Reverse osmosis systems, which have been adapted for use with oilfield wastewater, are viable for influents with TDS concentrations of about 40,000 to 50,000 mg/L (e.g., Stepan et al., 2010), making them unsuitable for some extremely concentrated flowback waters. Thermal distillation systems such as mechanical vapor recompression evaporation have been developed (e.g., Veil, 2008). Thermal and reverse osmosis systems are both subject to fouling from organic compounds, necessitating some form of pretreatment. Horn (2009) describes a treatment train using settling and filtration, followed by an advanced oxidation

process to remove organics. This sequence prepares the water for salt separation (such as by reverse osmosis).

As noted earlier, recycling of flowback for use in fracturing other wells is becoming increasingly common and is facilitated by developments in on-site treatment to prepare the flowback for reuse. Researchers at Texas A&M, for example, are developing a mobile treatment system that is being pilot tested in the Barnett Shale (Pickett, 2009). Water treated on site may also be used for irrigation or livestock (Horn, 2009) in addition to fracturing other wells. Given the logistical and financial benefits to be gained from treatment of flowback water, continued developments in on-site treatment technologies are expected.

Regulations and practices for management and disposal of hydraulic fracturing wastes vary by region and state, and are influenced by the stage of infrastructure development as well as geology, climate, and formation composition.

6.5.2 How effective are treatment and disposal methods?

Treatment, disposal, and reuse of flowback and produced water from hydraulic fracturing activities are important because of the contaminants present in these waters and their potential for adverse health impacts on populations and ecosystems. While recycling and reuse is also an effective approach for dealing with these waters, and at the same time conserves fresh water resources, ultimately there will still be a need to treat and properly dispose of the final concentrated volumes from a given area of operation. The separation and appropriate disposal of the toxic constituents is the most protective approach for reducing potential adverse health impacts. However, much is unknown about the efficacy of current treatment processes for adequately removing certain flowback and produced water constituents, such as fracturing fluid additives and radionuclides. Additionally, the chemical composition and concentration of solid residuals created by wastewater treatment plants that treat hydraulic fracturing wastewaters—and their subsequent disposal—warrants more study.

In particular, bromide and chloride can have significant impacts to downstream drinking water utilities. Hydraulic fracturing streams can have very high levels of both, and other waters such as wastewater and river water may offer only limited ability to dilute these constituents by blending. The presence of bromide in source waters to drinking water systems that chlorinate will produce a greater amount of brominated disinfection byproducts (DBPs), which have been shown to have greater health impacts than chlorinated DBPs. Also, because of their inherent higher molecular weight, brominated DBPs will result in higher concentrations (by weight) than their chlorinated counterparts (e.g., bromoform versus chloroform), potentially causing a drinking water utility to exceed the current DBP regulatory limits. Meanwhile, higher levels of chloride in drinking waters can impact lead and copper corrosion, resulting in higher lead levels in consumer tap water and an increase in pitting incidences in copper premise plumbing. This project will evaluate management practices for chloride and bromide in hydraulic fracturing wastewaters, along with evaluating potential impacts to drinking water utilities and their consumers.

6.5.3 Proposed Research Activities—Wastewater Treatment and Waste Disposal

6.5.3.1 Effectiveness of Current Treatment Methods: Analysis of Existing Data, Laboratory Studies, and Prospective Case Studies

Analysis of existing data. Important work on the treatment of flowback and produced water has been completed by DOE NETL. To optimize resources, EPA will compile the lessons learned and identify research gaps for: (1) the impacts of the direct discharge of these waters in community wastewater systems, (2) the effectiveness of pretreatment of these waters for ultimate discharge into a wastewater treatment plant or for direct land application, and (3) the effectiveness of treatment of these waters for reuse in the hydraulic fracturing industry and other industries, including agriculture. Specific emphasis will be placed on inorganic and organic contaminants, with the latter being an area that has the least historical information, and hence the greatest opportunity for advancement in treatment.

Laboratory studies. EPA will conduct bench-scale studies to investigate if hydraulic fracturing fluid additives, constituents from underground formations released, or degradation products of fracturing fluid additives are precursors to DBPs, such as trihalomethanes, haloacetic acids, or nitrosamines. EPA will also evaluate at the bench and pilot scale whether other constituents such as elevated chloride levels result in unintended problems (e.g., increased drinking water distribution system corrosion). The results from these studies will inform the prospective case studies discussed below.

Prospective case studies. EPA will collect data on the efficacy of the treatment and disposal of hydraulic fracturing wastewaters in prospective case studies by sampling both pre- and post-treatment wastewaters. It is expected that such studies will include on-site treatment, use of wastewater treatment plants, recycling, and underground injection control wells. These studies are anticipated to provide data on the chemical composition and concentrations found in treated hydraulic fracturing wastewaters and in the resulting solid residuals.

6.5.4 Potential Research Outcomes

This research will allow EPA to:

- Evaluate current treatment and disposal methods of flowback and produced water resulting from hydraulic fracturing activities.
- Assess the short- and long-term effects resulting from inadequate treatment of hydraulic fracturing wastewaters.

7 Case Studies

This chapter of the study plan describes the rationale for case study selection as well as the approaches used in both retrospective and prospective case studies.

7.1 Case Study Selection

EPA invited stakeholders nationwide to nominate potential case studies through informational public meetings and the submission of electronic or written comments. Appendix F contains a list of potential

case study sites that were nominated by stakeholders. Of the 48 nominations, EPA intends to select five to eight sites for inclusion in the study. This will include three to five retrospective case study sites, which will focus on cases involving possible drinking water contamination due to hydraulic fracturing operations. The remaining two to three sites will be prospective case studies where EPA will monitor key aspects of the hydraulic fracturing process. The final location and number of case studies will be chosen based on the types of distinct information a given case study would be able to provide.

Table 6 outlines the systematic approach used to identify and prioritize potential retrospective and prospective case study sites.

TABLE 6. DECISION CRITERIA FOR SELECTING HYDRAULIC FRACTURING SITES FOR CASE STUDIES

Selection Step	Inputs Needed	Decision Criteria
Nomination	• Planned, active, or historical hydraulic fracturing activities • Local drinking water resources • Community at risk • Site location, description, history • Site attributes (e.g., physical, geology, hydrology) • Operating and monitoring data, including well construction and surface management activities • Rationale for inclusion	• Proximity of population and drinking water supplies • Magnitude of activity (e.g., density of wells) • Evidence of impaired water quality (retrospective only) • Health and environmental concerns (retrospective only) • Knowledge gap that could be filled by a case study
Prioritization	• Available data on chemical use, site operations, health and environmental concerns • Site access for monitoring wells, sampling, and geophysical testing • Potential to collaborate with other groups (e.g., federal, state, or interstate agencies; industry; non-governmental organizations, communities; and citizens)	• Geographic and geologic diversity • Diversity of suspected impacts to drinking water resources • Population at risk • Site status (planned, active, or completed) • Unique geological or hydrological features • Characteristics of water resources (e.g., proximity to site, ground water levels, surface water and ground water interactions, unique attributes) • Multiple nominations from diverse stakeholders • Land use (e.g., urban, suburban, rural, agricultural)

The criteria shown in Table 6 were used to determine the finalists for both retrospective and prospective case studies, and represent the highest-priority case study sites that EPA would like to conduct as part of this study. The finalists for both retrospective and prospective case study sites were chosen to represent a wide range of conditions that reflect the spectrum of impacts that may result from hydraulic fracturing activities. These case studies are intended to provide enough detail to determine the extent to which conclusions can be generalized at local, regional, and national scales.

Table 7 lists the finalists for retrospective case studies, highlighting the areas to be investigated and the potential outcomes expected for each site. The potential case study sites listed in Table 7 are illustrative of the types of situations that may be encountered during hydraulic fracturing activities and represent a

range of locations. In some of these cases, hydraulic fracturing occurred more than a year ago, while in others, the wells were fractured less than a year ago. EPA expects to be able to coordinate with other federal and state agencies as well as landowners to conduct these studies, as listed in Appendix F.

TABLE 7. RETROSPECTIVE CASE STUDY FINALISTS

Location	Areas to be Investigated	Potential Outcomes
Bakken Shale—Killdeer and Dunn County, ND	• Production well failure during hydraulic fracturing • Suspected drinking water aquifer contamination • Possible soil and surface water contamination	• Identify sources of well failure • Determine if drinking water resources are contaminated and to what extent
Barnett Shale—Wise and Denton Counties, TX	• Possible drinking water well contamination • Spills and runoff leading to suspected drinking water well contamination	• Determine if private water wells are contaminated • Obtain information about the likelihood of transport of contaminants via spills, leaks, and runoff
Marcellus Shale—Bradford and Susquehanna Counties, PA	• Ground water and drinking water well contamination • Suspected surface water contamination from a spill of fracturing fluids • Methane contamination of multiple drinking water wells	• Determine if drinking water wells are contaminated • Determine source of methane in private wells • Transferable results due to common types of impacts
Marcellus Shale—Wetzel County, WV; Green/ Washington Counties, PA	• Changes in water quality in drinking water, suspected contamination • Stray gas in wells, spills	• Determine if drinking water wells are contaminated • Determine if surface spills affect surface and ground water • If contamination exists, determine potential source of contaminants in drinking water
Raton Basin—Los Animas County, CO	• Potential drinking water well contamination (methane and other contaminants) in an area with intense concentration of gas wells in shallow surficial aquifer (coalbed methane)	• Determine source of methane • Identify presence/source of contamination in drinking water wells

Prospective case studies will be made possible by partnering with federal and state agencies, landowners, and industry, as highlighted in Appendix F. Potential sites for these case studies include:

- The Bakken Shale in Berthold Indian Reservation, North Dakota.
- The Barnett Shale in Flower Mound/Bartonville, Texas.
- The Marcellus Shale in Green County, Pennsylvania, or another location yet to be determined.
- The Niobrara Shale in Laramie County, Wyoming.

For each case study (retrospective and prospective), EPA will write and approve a QAPP before the start of any new data collection, as described in Section 2.6. As discussed in the following sections, EPA will use a tiered approach for both retrospective and prospective case studies; after each tiered activity, EPA

will write a short summary of findings from field investigations before moving to the next activity. Upon completion of each case study, a report summarizing key findings will be produced, peer-reviewed, and published. The data will also be presented in a 2012 interim report and a 2014 report of results.

EPA will perform extensive sampling of relevant environmental media as part of both retrospective and prospective case studies. Appendix G provides details on field sampling, monitoring, and analytical methods.

7.2 Retrospective Case Studies

As described briefly in Section 5.1, retrospective case studies are focused on investigating reported instances of drinking water contamination in areas where hydraulic fracturing events have already occurred. Table 7 lists five finalists for the retrospective case studies. EPA will choose three to five of these for further investigation. Each case study will address one or more of the research questions proposed in Table 2.

The goal of each retrospective case study is to assess whether or not the reported contamination is due to hydraulic fracturing activities. These studies will seek to use existing data and may include additional environmental field sampling, modeling, and/or parallel laboratory investigations. Using in-house personnel as well as contractors, EPA expects to complete key aspects of these case studies in 2012. However, it should be noted that field studies are subject to a wide range of complex issues (e.g., site access and stakeholder support) that must be addressed in order to complete such a study, which may affect the completion date of these studies.

As shown in Table 8, retrospective case studies will be conducted in a tiered fashion to develop integrated data on site history and characteristics, water resources, contaminant migration pathways and exposure routes, and diagnostic tools to evaluate risks.

TABLE 8. APPROACH FOR CONDUCTING RETROSPECTIVE CASE STUDIES

Tier	Goal	Critical Path
1	Verify potential issue	• Evaluate existing data and information • Conduct site visit • Survey stakeholders and interested parties
2	Screen to determine approach for detailed investigations	• Conduct additional sampling: sample wells, taps, surface water, and other fluids associated with hydraulic fracturing activities (e.g., chemical tanks, holding ponds, produced water) • Develop site conceptual model and alternative exposure hypotheses
3	Evaluate potential sources of contamination	• Conduct geophysical testing • Perform mechanical integrity testing • Install new monitoring wells • Develop, calibrate, and test flow and transport model(s)
4	Detailed investigations	• Conduct comprehensive chemical characterization • Evaluate alternate hypotheses using the calibrated model(s)

Retrospective case studies will begin with verifying the potential issue (Tier 1) by evaluating existing data, conducting site visits, and interviewing stakeholders. EPA will then conduct initial screening activities to determine what future efforts may be required for a detailed investigation of the reported drinking water contamination. A major focus of these initial screening activities will be to identify potential evidence of drinking water contamination and to develop hypotheses describing possible sources of the reported contamination, including hydraulic fracturing operations as well as non-fracturing activities. With the exposure hypotheses in mind, additional testing will be conducted to evaluate the potential sources of contamination (see Appendix G for additional information), which will lead to an evaluation of the validity of the exposure hypotheses.

The data collected during retrospective case studies may be used to assess the risks posed to drinking water resources as a result of hydraulic fracturing activities. Because of this possibility, EPA will collect information on: (1) the toxicity of chemicals associated with hydraulic fracturing, (2) the spatial distribution of chemical concentrations and the locations of drinking water wells, (3) how many people are served by the potentially impacted wells, and (4) how the chemical concentrations vary over time.

7.3 Prospective Case Studies

Prospective case studies will be performed at sites where hydraulic fracturing will occur, and are made possible by partnering with oil and natural gas companies and other stakeholders. These case studies will be focused on the entire water lifecycle illustrated in Figure and will: (1) provide data that will be used to inform our current understanding of processes associated with hydraulic fracturing events; and (2) evaluate current water management practices during each stage of the water lifecycle.

Because of the need to enlist the support and collaboration of a wide array of stakeholders in these efforts, the prospective case studies will most likely not begin until mid- to late 2011. Some preliminary results could be available for the 2012 interim reports, but case studies of this type will likely be completed 12 months from the start dates.

Prospective case studies will be conducted in a tiered fashion, as outlined in Table 9, and will include field sampling, monitoring, modeling, and parallel laboratory investigations to explore the research questions summarized in Table 2.

TABLE 9. APPROACH FOR CONDUCTING PROSPECTIVE CASE STUDIES

Field Sampling Phases	Critical Path
Baseline characterization of the production well site and areas of concern	• Sample all available existing wells, catalogue depth to drinking water aquifers, gather well logs • Sample any adjoining surface water bodies • Sample source water • Install and sample a minimum of three new monitoring wells • Sample soil gas • Perform geophysical characterization • Review site geology • Develop site conceptual model • Develop and calibrate flow system model
Production well construction	• Test mechanical integrity • Resample all wells (new and existing), surface water, and soil gas • Survey, record, and evaluate on-site management practices (e.g., pad construction)
Hydraulic fracturing of the production well	• Sample fracturing fluids • Resample all wells, surface water, and soil gas • Sample flowback • Evaluate on-site management practices (e.g., fluids management) • Calibrate hydraulic fracturing model • Assess model results through testing of calibrated model
Gas production	• Resample all wells, surface water, and soil gas • Survey, record, and evaluate on-site management practices • Calibrate hydraulic fracturing model • Assess model results through testing of calibrated model • Sample produced water

While conducting the prospective case studies, EPA will obtain water quality, geologic, seismic, and other data before, during, and immediately after fracturing, as discussed in Appendix G. Similarly, monitoring will be continued during a follow-up period of approximately one year after hydraulic fracturing has been completed. The sampling includes the opportunity for comprehensive baseline characterization and opportunities to monitor flowback and produced water, including the storage and treatment of these wastewaters. The data collected can then be used to test whether hydraulic fracturing models accurately simulate changes in the formation caused by fracturing activities. Modeling details for prospective case studies are discussed further in Appendix H.

8 CHARACTERIZATION OF TOXICITY AND HUMAN HEALTH EFFECTS

In almost all stages of the hydraulic fracturing water lifecycle, there is potential for fracturing fluids and/or naturally occurring substances to be introduced into drinking water resources. As highlighted throughout Chapter 6, EPA is concerned with assessing the toxicity and potential human health effects associated with these possible drinking water contaminants. In order to do this, EPA will first obtain an inventory of the chemicals associated with hydraulic fracturing activities (and their estimated concentrations of occurrence), including chemicals used in hydraulic fracturing fluid and naturally

occurring substances that may be released from subsurface formations during the hydraulic fracturing process. EPA will also need to identify the relevant reaction and degradation products of these substances, which may have different toxicity and human health effects than their parent compounds, in addition to the fate and transport characteristics of the chemicals. The aggregation of these data is described in Chapter 6.

Based on the number of chemicals currently known to be used in hydraulic fracturing operations, EPA anticipates that there are several hundred potential drinking water contaminants. Therefore, EPA expects to develop a prioritized list of chemicals and, where estimates of toxicity are not otherwise available, to conduct additional testing or quantitative health assessments for certain high-priority chemicals. In the first phase of this work, EPA will conduct an initial screen for known toxicity and human health effects information (including existing toxicity values such as reference doses and cancer slope factors) by searching existing databases.[4] At this stage, chemicals will be grouped into one of three categories: high priority for chemicals that are potentially of concern, low priority for chemicals that are likely to be of little concern, and unknown priority for chemicals with an unknown level of concern. These groupings will likely be based on known toxicity or human health effects, reported occurrence levels, and the potential need for metabolism information.

Chemicals with an unknown level of concern are those for which no toxicity information is available. For these chemicals, a quantitative structure-activity relationship (QSAR) analysis may be conducted to obtain comparative toxicity information. A QSAR analysis uses mathematical models to predict measures of toxicity from physical characteristics of the structure of the chemicals; it will allow EPA to designate these chemicals as either high- or low-priority.

The second phase of this work will focus on additional testing and/or assessment of high-priority chemicals. High-priority chemicals may be subjected to a battery of tests used in the ToxCast program, a high-throughput screening tool that can identify toxic responses (Judson et al., 2010a and 2010b; Reif et al., 2010). ToxCast may also be used to establish the level of toxicity or dose-response relationships for chemicals where some existing information on toxicity or mode of action is available. For chemicals that QSAR analysis and high-throughput screening identify as having a high priority for assessing risk in a semi-quantitative or quantitative mode, EPA will initially apply computational modeling (e.g., ToxPi and computation dose-response analysis) to determine a relative estimate of toxicity. Based on these assessments, additional testing of the highest-priority chemicals may be conducted using medium-throughput cellular and alternative animal models (e.g., *C. elegans,* zebra fish, and stress response cellular assays) together with targeted laboratory animal assays. The latter will be targeted to the specific mode of action indicated by high- and medium-throughput assays and computational modeling.

[4] These databases include the Aggregated Computational Toxicology Resources (ACToR) database, the Distributed Structure-Searchable Toxicity (DSSTox) database, the Exposure Forecaster Database (ExpoCastDB), Health and Environmental Research Online (HERO), the Integrated Risk Information System (IRIS), the High Production Volume Information System (HPVIS), the Toxicity Forecaster Database (ToxCastDB), and the Toxicity Reference Database (ToxRefDB).

EPA may also develop chemical-specific Provisional Peer Reviewed Toxicity Values (PPRTVs) for high-priority chemicals for which there are no existing toxicity values. PPRTVs summarize the available scientific information about the adverse effects of a chemical and the quality of the evidence, then ultimately derive toxicity values, such as reference doses and cancer slope factors, that can be used in conjunction with exposure and other information to develop a risk assessment.

In addition to single chemical assessments, further information may be obtained for mixtures of chemicals based on which components occur most frequently together and their relevant proportions as identified from exposure information. EPA may also assess how changes in source water characteristics impact treated drinking water and associated disinfection by products.

The overall level of effort for these characterizations will depend on the amount of information currently available in databases, the number of high-priority chemicals that warrant a more quantitative risk assessment, and results from other study areas that identify and characterize priority contaminant sources and exposures. EPA anticipates that the initial database search and ranking of high-, low-, and unknown-priority chemicals will be completed for the 2012 interim report. Additional work using QSAR analysis and high-throughput screening tools is expected to be available in the 2014 report. The development of chemical-specific PPRTVs for high-priority chemicals is also expected to be available in 2014.

Information developed from this effort to characterize the toxicity and health effects of chemicals will be an important component of understanding the overall risk posed by hydraulic fracturing chemicals that may be present in drinking water resources. When combined with exposure and other relevant data, this information will help EPA characterize the potential public health impacts of hydraulic fracturing on drinking water resources.

9 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. Achieving environmental justice is an Agency-wide priority (USEPA, 2010d), and is therefore considered in this study plan. There are concerns that hydraulic fracturing may adversely affect some communities that may be more likely to be exposed to harmful chemical contaminants as a result of fracturing activities, particularly through contaminated drinking water resources. Stakeholders have raised concerns about the environmental justice implications of gas drilling operations, noting that people with a lower socioeconomic status may be more likely to consent to drilling arrangements because they may not have the resources to engage with policymakers and agencies to affect alternatives. Additionally, drilling agreements are between landowners and well operators, implying that tenants and neighbors may have little or no input in the decision-making process.

To address these concerns, EPA will combine the data collected on the location of well sites within the United States with demographic information (e.g., income and race) to screen whether hydraulic fracturing disproportionately impacts some citizens and to identify areas for further study.

10 SUMMARY

The research outlined in this study plan will address all stages of the hydraulic fracturing water lifecycle shown in Figure 7 and the research questions posed in Table 2. EPA will conduct the research using case studies and generalized scenario evaluations, which will rely on data produced by a combination of the tools listed in Section 5.3. A comprehensive program of quality assurance will be developed for all aspects of the proposed research. Figure 9 summarizes the research activities for each stage of the hydraulic fracturing water lifecycle, and also provides anticipated timelines for research results. Brief summaries of how the research activities proposed in Chapter 6 will answer the fundamental research questions appear below.

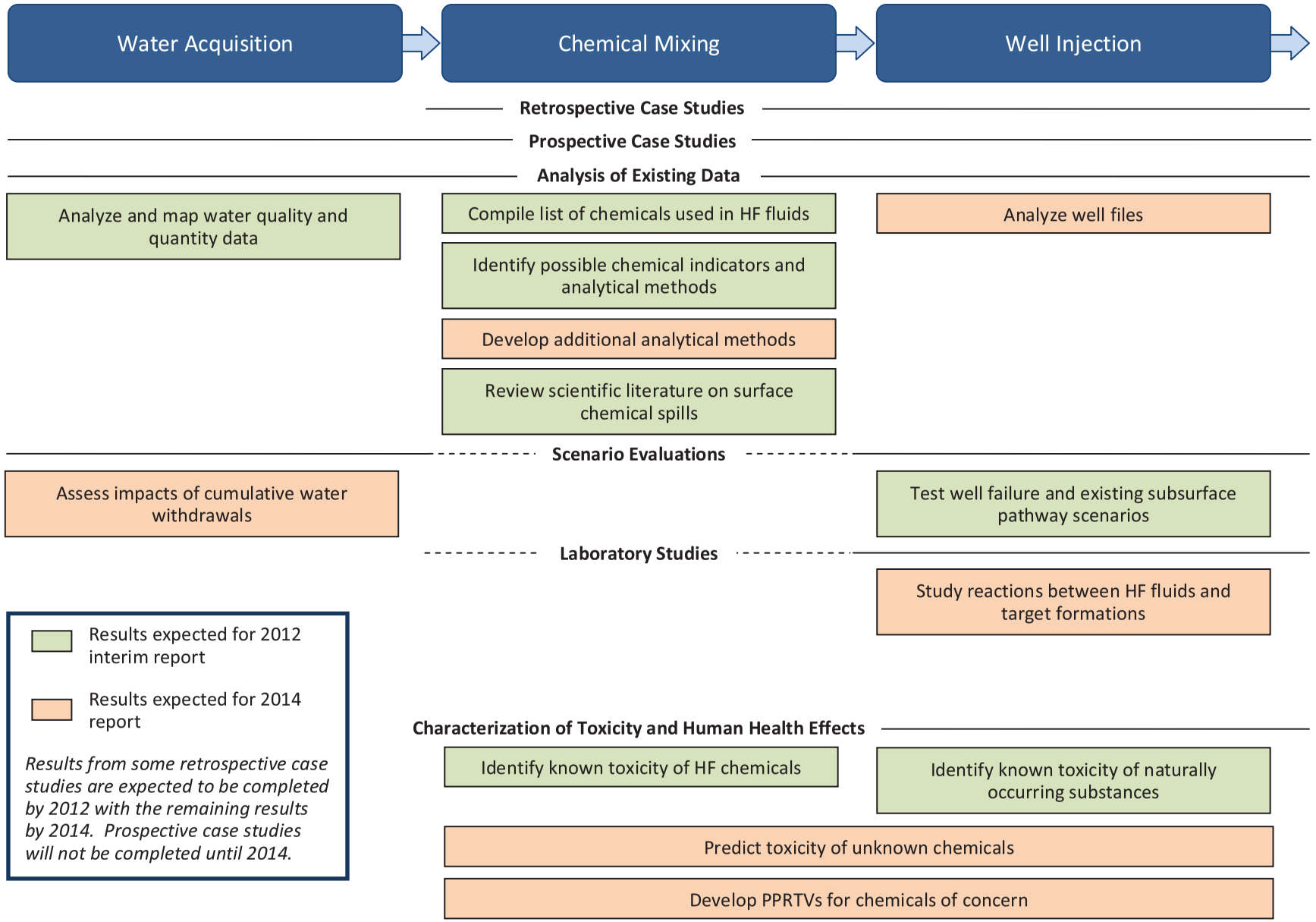


FIGURE 9a. SUMMARY OF RESEARCH PROJECTS PROPOSED FOR THE FIRST THREE STAGES OF THE HYDRAULIC FRACTURING WATER LIFECYCLE

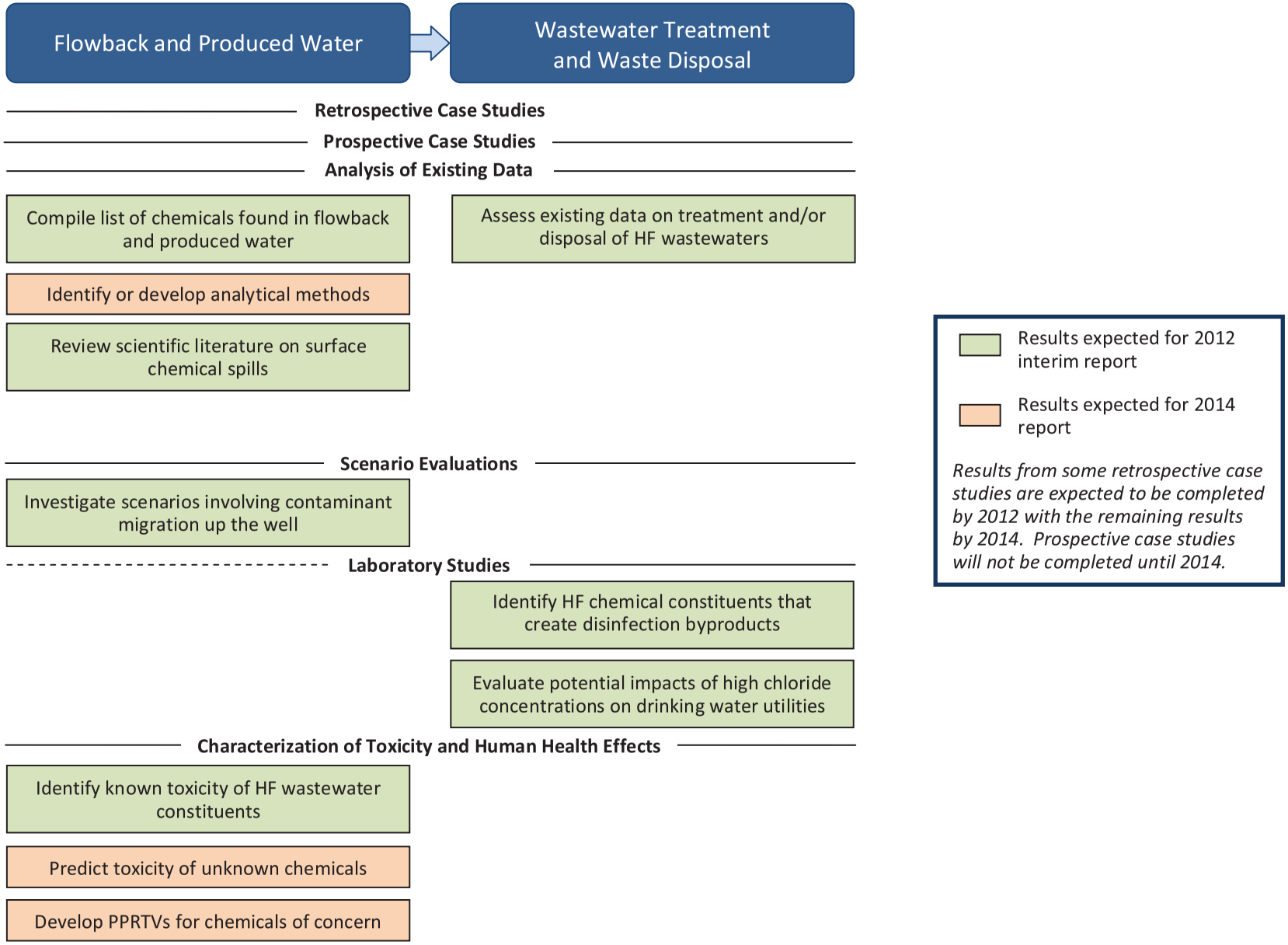


FIGURE 9b. SUMMARY OF RESEARCH PROJECTS PROPOSED FOR THE LAST TWO STAGES OF THE HYDRAULIC FRACTURING WATER LIFECYCLE

Water acquisition: How might large volume water withdrawals from ground and surface water impact drinking water resources? By analyzing both existing data as well as data from prospective case studies, EPA expects to be able to identify the potential impacts of large volume water withdrawals from hydraulic fracturing operations on drinking water resources. The data will also be used in scenario evaluations, which will simulate the cumulative effects of large volume water withdrawals under a variety of conditions and locations, allowing EPA to better understand how these withdrawals may impact different regions.

Chemical mixing: What are the possible impacts of releases on of hydraulic fracturing fluids on drinking water resources? To address this question, EPA will first compile a list of chemicals used in hydraulic fracturing fluids from public sources and the data collected from nine hydraulic fracturing service companies. The resulting list will be used to inform a variety of proposed research projects: (1) the identification of fracturing fluid chemical indicators and corresponding analytical methods needed for the detection of these compounds, (2) a review of the scientific literature pertaining to surface chemical releases, and (3) the identification of toxic and human health effects associated with hydraulic fracturing fluid chemical additives. Case studies will necessarily rely on the results of one or more of these research projects. Retrospective case studies will identify what, if any, impacts a reported spill of fracturing fluid had on nearby drinking water resources. To accomplish this, the case studies may need to use the analytical methods identified for hydraulic fracturing fluid additives that may be identified through the information gathered from the hydraulic fracturing service companies and may also use information provided by the scientific literature review of surface chemical spills as well as the results of the toxicity assessments. Meanwhile, prospective case studies will monitor current chemical management practices related to hydraulic fracturing fluids and will mostly likely track the fate and transport of potential chemical indicators related to fracturing fluids using the identified analytical methods.

Well injection: What are the possible impacts of the injection and fracturing process on drinking water resources? Data from case studies and scenario evaluations will be analyzed to determine the impacts of the injection and fracturing process on drinking water resources. Case studies will be based on a combination of field monitoring and modeling data to determine the impacts of well construction and mechanical integrity as well as existing natural and artificial pathways on contaminant transport to drinking water resources. Scenario evaluations will use data obtained during case studies and will investigate the roles of various injection and geological conditions on drinking water resource contamination. The case studies and scenario evaluations will be informed by data on the constituents of hydraulic fracturing fluids, laboratory studies of chemical/biological/physical processes between those constituents and the fractured formation, and an analysis of well files. The laboratory studies will identify degradates and reaction products of hydraulic fracturing fluid chemical additives in addition to naturally occurring substances released from the fractured formation. Once identified, EPA will assess the toxicity and human health effects of these potential drinking water contaminants.

Flowback and produced water: What are the possible impacts of releases of flowback and produced water on drinking water resources? EPA will compile a list of chemical constituents found in flowback and produced water through three sources: public data, data submitted by nine hydraulic fracturing

service companies, and data provided through prospective case studies. The list of chemical constituents will be used to identify and/or develop analytical methods needed for quantifying these chemicals and to assess the toxicity and human health effects associated with the components of flowback and produced water. EPA will assess possible impacts to drinking water resources for two cases: (1) contaminant migration up the well and (2) surface spills of flowback and produced water. Scenario evaluations will be used to explore contaminant migration up the well, while possible impacts from accidental surface releases of flowback and produced water will be identified by reviewing the existing scientific literature related to surface chemical releases or waste pit leakages with respect to the components found in hydraulic fracturing wastewaters. EPA may address both of these cases during retrospective case studies, which may use the analytical methods developed for flowback and produced water constituents as well as the results of the scientific literature review. Prospective case studies will look at current wastewater management practices to determine what approaches are used to contain or mitigate releases. The synthesis of these different research projects will allow EPA to assess the potential impacts of accidental releases of flowback and produced water on drinking water resources.

Wastewater treatment and waste management: What are the possible impacts of inadequate treatment of hydraulic fracturing wastewaters on drinking water resources? EPA will analyze existing data and data from prospective case studies to determine the overall effectiveness of current wastewater treatment methods on removing hydraulic fracturing-related contaminants from wastewaters as well as the composition and characteristics of solid residuals from wastewater treatment. More specifically, EPA will use the results from laboratory studies to identify hydraulic fracturing fluid chemical additives that may create disinfection byproducts during the treatment of hydraulic fracturing wastewaters and to study to the potential effects of high chloride concentrations on drinking water utilities. Together, these activities will allow EPA to assess the impacts of inadequate treatment of hydraulic fracturing wastewaters on drinking water resources.

The results of individual research projects will be made available after undergoing a quality assurance review. As illustrated in Figure 9, EPA anticipates that some of the research will be completed in time for a 2012 interim report while the remaining research is expected to be completed for a 2014 report. Both reports will synthesize the results of the research projects presented in Chapter 6 (and summarized above) to assess the impacts, if any, of hydraulic fracturing on drinking water resources. Overall, this study will provide data on the key factors that may be associated with the potential contamination of drinking water resources as well as information about the toxicity of contaminants of concern. The results may then be used to assess the potential risks to drinking water resources from hydraulic fracturing activities.

11 Areas of Concern Outside the Scope of This Study

Although EPA's current study focuses on impacts of hydraulic fracturing on drinking water resources, stakeholders identified additional research areas—discussed below—related to hydraulic fracturing operations. Future work in these areas would benefit from integrating the results from the current study to provide a holistic view of the impacts of hydraulic fracturing on human health and the environment.

11.1 Routine Disposal of Hydraulic Fracturing Wastewaters in Class II Underground Injection Wells

Particularly in the West, millions of gallons of produced water and flowback are transported to Class II underground injection control (UIC) wells for disposal. This study plan does not propose to evaluate the potential impacts of this regulated practice or the associated potential impacts due to the transport and storage leading up to ultimate disposal in a UIC well.

11.2 Air Quality

One of the largest potential sources of air emissions from hydraulic fracturing operations is the off-gassing of methane from flowback before the well is put into production. The NYS dSGEIS estimated that 10,200 mcf of methane is off gassed per well (ICF International, 2009a). One study in the Barnett Shale estimated that between 1,000 and 24,000 mcf of methane is released per well (Armendariz, 2009). This gas is typically vented or flared, although reduced emissions completion methods can capture up to 90 percent of the gas. High concentrations of methane could also pose an explosion threat. On-site fuel tanks and impoundment pits containing flowback may also be sources of VOC and hydrogen sulfide emissions (ICF International, 2009a). The VOCs found in flowback may include acetone, benzene, ammonia, ethylbenzene, phenol, toluene, and methyl chloride (NYSDEC, 2009).

Truck traffic is also a potential major source of air emissions. No study has examined the specific emissions associated with truck traffic, but the National Park Service estimated that total truck traffic of between 300 and 1,300 trucks per well would occur in the Marcellus Shale production areas. The NPS estimated that this could have a significant effect on regional nitrogen oxides levels (NPS, 2008). An ICF International report written in support of the NYS dSGEIS estimated truck traffic at 330 trucks per well (ICF International, 2009a). Emissions factors for heavy duty diesel trucks are 6.49 grams per mile (g/mile) for nitrogen oxides, 9.52 g/mile for carbon monoxide, and 2.1 g/mile for hydrocarbons for new trucks (USEPA, 1998). Additionally, the use of dirt roads can create dust that affects air quality.

There have been numerous reports of changes in air quality from natural gas drilling. For example, in Battlement Mesa, Colorado, residents complained of gases and vapors from a nearby natural gas well and state officials attributed the problem to flowback of hydraulic fracturing fluids (Webb, 2010). Reports from Texas have linked pollutant emissions from natural gas drilling in the Barnett Shale to substantial reductions in air quality (Michaels et al., 2010). Additionally, areas of highly concentrated natural gas development in southwest Wyoming and eastern Utah have experienced episodes of degraded air quality (e.g., high levels of winter time ozone concentrations). Diesel engines used to run compressors, generators, drill rigs, and pumps may also create significant emissions.

11.3 Terrestrial and Aquatic Ecosystem Impacts

Hydraulic fracturing could have effects on terrestrial ecosystems unrelated to its effects on drinking water resources. For example, chemicals used in hydraulic fracturing can contaminate soil if insufficient care is taken during their use, transport, storage, or disposal (Zoback et al., 2010). Additionally, wastewater impoundment pits can expose livestock and wildlife to flowback and produced water, which

could have adverse health effects for those animals. An increase in vehicle traffic associated with hydraulic fracturing activities may inadvertently spread invasive plants. Environmental impacts may also occur at the drilling site and in the nearby area. During site preparation, an area must be cleared to accommodate the wellhead(s), trucks, equipment, and other materials; access roads may need to be built; and both the site and the roads must be prepared to support heavy equipment. All of these steps can cause substantial disturbance to the local environment. Stakeholders have raised concerns that in areas where many wells will be drilled, environmental impacts could include loss of green space and habitat fragmentation.

Hydraulic fracturing could also affect aquatic ecosystems. For example, if untreated wastewater (e.g., from spills from well pads) is released into streams during transportation or planned releases from wastewater treatment plants, the streams may become unsuitable habitats for fish or other aquatic organisms that cannot tolerate high salt concentrations or the presence of other contaminants. This has occurred in Pennsylvania, where a fish kill was linked to a spill of hydraulic fracturing fluid that contaminated a stream (Lustgarten and ProPublica, 2009). Stormwater runoff from the drilling site may be another water issue of concern. Appropriate management practices need to be used to control runoff from both the site and the access roads (NYSDEC, 2009; USDOE, 2009).

11.4 Seismic Risks

It has been suggested that drilling and hydraulically fracturing shale gas wells might cause low-magnitude earthquakes. Public concern about this possibility emerged in 2008 and 2009, when the town of Cleburne, Texas—where there had been a recent increase in drilling into the Barnett Shale—experienced several clusters of weak earthquakes (3.3 or less on the Richter scale) for the first time in its history. A study by University of Texas and Southern Methodist University did not find a conclusive link between hydraulic fracturing and these earthquakes, but indicated that the injection of wastewater from gas operations into disposal wells (the preferred means of waste disposal for natural gas operations in the area) might have been responsible (GWPC and ALL Consulting, 2009).

11.5 Public Safety Concerns

Emergency situations such as blowouts, chemical spills from sites with hydraulic fracturing, or spills from the transportation of materials associated with hydraulic fracturing (either to or from the well pad) could jeopardize public safety, as well as the safety of workers. Stakeholders also have raised concerns about the possibility of public safety hazards as a result of sabotage and about the need for adequate security at drilling sites.

11.6 Occupational Risks

The oil and gas extraction industry has an annual occupational fatality rate eight times higher than the rate for all U.S. workers (NIOSH, 2009). The National Institute for Occupational Safety and Health (NIOSH) reports that fatality rates increase when the level of drilling activity increases, possibly because of an increase in the proportion of inexperienced workers, longer working hours, and the utilization of all available equipment, including older equipment with fewer safeguards (NIOSH, 2009). Exposure

potential and acute and chronic health effects associated with worker exposure to hydraulic fracturing fluid chemicals should be considered, including transport, mixing, delivery, and potential accidents (e.g., high pressure leak, valve, pipe, or tank failure). The nature of this work poses potential risks to workers that have not been well characterized. Therefore, the recent increase in gas drilling and hydraulic fracturing activities may be a cause for concern with regard to occupational safety.

Several types of problems can occur in conjunction with hydraulic fracturing: blowouts, chemical spills, vehicle accidents, and exposure to fumes. These problems are particularly likely to harm workers, although nearby people may also be affected. For example, there have been reported instances of illnesses that may be related to hydraulic fracturing operations, including one case in which a nurse who treated a worker exposed to hydraulic fracturing chemicals became seriously ill (Frankowski, 2008).

11.7 Economic Impacts

Some stakeholders value the funds they receive for allowing drilling and hydraulic fracturing operations on their properties, while others look forward to increased job availability and more prosperous businesses. It is unclear, however, what the local economic impacts of increased drilling activities are and how long these impacts may last. For example, are the high-paying jobs associated with oil and gas extraction available to local people or to those from traditional oil and gas states because specific skills are needed for the drilling and fracturing process? There may also be an impact on local response resources because of an increase in truck traffic or accidents at well sites. It is important to better understand the benefits and costs of hydraulic fracturing operations.

REFERENCES

API (American Petroleum Institute). (2009, October). *Hydraulic fracturing operations—well construction and integrity guidelines.* API Guidance Document HF1. Washington, DC: American Petroleum Institute.

API (American Petroleum Institute). (2010a, June). *Water management associated with hydraulic fracturing*. API Guidance Document HF2, first edition. Washington, DC: American Petroleum Institute. Retrieved January 20, 2011, from http://www.api.org/Standards/new/api-hf2.cfm.

API (American Petroleum Institute). (2010b, July 19). *Freeing up energy—hydraulic fracturing: Unlocking America's natural gas resources*. Washington, DC: American Petroleum Institute. Retrieved December 2, 2010, from http://www.api.org/policy/exploration/hydraulicfracturing/upload/HYDRAULIC_FRACTURING_PRIMER.pdf.

Armendariz, A. (2009, January 6). *Emissions from natural gas production in the Barnett Shale area and opportunities for cost-effective improvements.* Dallas, TX: Department of Environmental and Civil Engineering, Southern Methodist University. Retrieved January 19, 2011, from http://www.edf.org/documents/9235_Barnett_Shale_Report.pdf.

Armstrong, K., Card, R., Navarette, R., Nelson, E., Nimerick, K., Samuelson, M., Collins, J., Dumont, G., Priaro, M., Wasylycia, N., & Slusher, D. (1995, Autumn). Advanced fracturing fluids improve well economics. *Oil Field Review*, 34-51.

Arthur, J. D., Bohm, B., & Layne, M. (2008, September 21-24). *Hydraulic fracturing considerations for natural gas wells of the Marcellus Shale*. Presented at The Ground Water Protection Council 2008 Annual Forum, Cincinnati, OH.

Baker Hughes. (2010, June 11). *Baker Hughes rig count blog*. Retrieved August 10, 2010, from http://blogs.bakerhughes.com/rigcount.

Bellabarba, M., Bulte-Loyer, H., Froelich, B., Le Roy-Delage, S., Kujik, R., Zerouy, S., Guillot, D., Meroni, N., Pastor, S., & Zanchi, A. (2008, Spring). Ensuring zonal isolation beyond the life of the well. *Oil Field Review,* 18-31.

Berman, A. (2009, August 1). Lessons from the Barnett Shale suggest caution in other shale plays. *World Oil, 230*(8).

Bielo, D. (2010, March 30). What the frack? Natural gas from subterranean shale promises U.S. energy independence-with environmental costs. *Scientific American*. Retrieved July 24, 2010, from http://www.scientificamerican.com/article.cfm?id=shale-gas-and-hydraulic-fracturing.

Bryant, J., Welton, T., & Haggstrom, J. (2010, September 1). Will flowback or produced water do? *E&P.* Retrieved January 19, 2011, from http://www.epmag.com/Magazine/2010/9/item65818.php.

Carter, R. H., Holditch, S. A., & Wolhart, S. L. (1996, October 6-9). *Results of a 1995 hydraulic fracturing survey and a comparison of 1995 and 1990 industry practices*. Presented at the Society of Petroleum Engineers Annual Technical Conference, Denver, CO.

Castle, J. W., Falta, R. W., Bruce, D., Murdoch, L., Foley, J., Brame, S. E., & Brooks, D. (2005). *Fracture dissolution of carbonate rock: an innovative process for gas storage.* Topical Report, DOE, NETL, DE-FC26-02NT41299. Washington, DC: Department of Energy.

Chesapeake Energy. (2009). *Barnett Shale—natural gas production*. Retrieved August 9, 2010, from http://www.askchesapeake.com/Barnett-Shale/Production/Pages/information.aspx.

Chesapeake Energy. (2010, July). *Hydraulic fracturing fact sheet*. Retrieved August 9, 2010, from http://www.chk.com/Media/CorpMediaKits/Hydraulic_Fracturing_Fact_Sheet.pdf.

Cipolla, C. L., & Wright, C. A. (2000, April 3-5). *Diagnostic techniques to understand hydraulic fracturing: What? Why? And how?* Presented at the Society of Petroleum Engineers/Canadian Energy Research Institute Gas Technology Symposium, Calgary, Alberta, Canada.

Clark, C. E, & Veil, J. A. (2009). *Produced water volumes and management practices in the U.S.* Washington, DC: United States Department of Energy, National Energy Technology Laboratory, Project No. DE-AC02-06CH11357. Retrieved July 27, 2010, from http://www.netl.doe.gov/technologies/coalpower/ewr/water/pdfs/anl%20produced%20water%20volumes%20sep09.pdf.

Daneshy, A. A. (2003, April). Off-balance growth: A new concept in hydraulic fracturing. No. SPE 80992. *Journal of Petroleum Technology (Distinguished Author Series)*, *55*(4), 78-85.

Eby, G. N. (2004). *Principles of environmental geochemistry*. Pacific Grove, CA: Thompson-Brooks/Cole.

Economides, M. J., Mikhailov, D. N., & Nikolaevskiy, V. N. (2007). On the problem of fluid leakoff during hydraulic fracturing. *Transport in Porous Media*, *67*(3), 487-499.

Ewing, J. (2008, February 29). *Taking a proactive approach to water recycling in the Barnett Shale*. Presented at the Fort Worth Business Press Barnett Shale Symposium. Retrieved January 24, 2011, from http://www.barnettshalenews.com/documents/EwingPres.pdf.

Falk, H., Lavergren, U., & Bergback, B. (2006). Metal mobility in alum shale from Öland, Sweden. *Journal of Geochemical Exploration*, *90*(3), 157-165.

Frankowski, E. (2008, July 28). Gas industry secrets and a nurse's story. *High Country News*. Retrieved October 9, 2010, from http://www.hcn.org/wotr/gas-industry-secrets-and-a-nurses-story.

Gadd, G. M. (2004). Microbial influences on metal mobility and application for bioremediation. *Geoderma*, *122*, 109-119.

Galusky, L. P., Jr. (2007, April 3). *Fort Worth Basin/Barnett Shale natural gas play: An assessment of present and projected fresh water use*. Fort Worth, TX: Barnett Shale Water Conservation and Management Committee. Retrieved July 21, 2010, from www.barnettshalewater.org/uploads/Barnett_Water_Availability_Assessment__Apr_3__2007.pdf.

Gaudlip, A. W., & Paugh, L. O. (2008, November 18). *Marcellus Shale water management challenges in Pennsylvania* (No. SPE 119898). Presented at the Society of Petroleum Engineers Shale Gas Production Conference, Irving, TX.

Glenn, P. S., Conway, M. W., & Wellington, L. (1985). Control and modeling of fluid leakoff during hydraulic fracturing. *Journal of Petroleum Technology*, *37*(6), 1071-1081.

GWPC (Ground Water Protection Council). (2009). *State oil and natural gas regulations designed to protect water resources*. Washington, DC: United States Department of Energy, National Energy Technology Laboratory. Retrieved July 23, 2010, from http://data.memberclicks.com/site/coga/GWPC.pdf.

GWPC (Ground Water Protection Council) & ALL Consulting. (2009). *Modern shale gas development in the United States: A primer.* Contract DE-FG26-04NT15455. Washington, DC: United States Department of Energy, Office of Fossil Energy and National Energy Technology Laboratory. Retrieved August 2, 2010, from http://www.netl.doe.gov/technologies/oil-gas/publications/EPreports/Shale_Gas_Primer_2009.pdf.

Hall, B. E., & Larkin, S. D. (1989). On-site quality control of fracture treatments. *Journal of Petroleum Technology, 41*(5), 526-532.

Harper, J. A. (2008). The Marcellus Shale—An old "new" gas reservoir in Pennsylvania. *Pennsylvania Geology, 38*(1), 2-13.

Hayes, T. (2009a, June 4). *Gas shale produced water*. Presented at the Research Partnership to Secure Energy for America/Gas Technology Institute Gas Shales Forum, Des Plaines, IL. Retrieved August 11, 2010, from http://www.rpsea.org/attachments/contentmanagers/429/Gas_Shale_Produced_Water_-_Dr._Tom_Hayes_GTI.pdf.

Hayes, T. (2009b, December 31). *Sampling and analysis of water streams associated with the development of Marcellus Shale gas, final report*. Canonsburg, PA: Marcellus Shale Coalition, Gas Technology Institute.

Hess, G. (2010). Drilling process draws scrutiny. *Chemical & Engineering News*, *88*(22), 42-45.

Holditch, S. A. (1990). Completion methods in coal seam reservoirs (No. SPE 20670). *Proceedings of the 1990 Society of Petroleum Engineers Annual Technical Conference and Exhibition (Production Operations and Engineering)*, 533-542.

Holditch, S. A. (1993, March). Completion methods in coal-seam reservoirs. *Journal of Petroleum Technology, 45*(3), 270-276.

Horn, A. D. (2009, March 24). *Breakthrough mobile water treatment converts 75% of fracturing flowback fluid to fresh water and lowers CO_2 emissions* (No. SPE 121104). Presented at the Society of Petroleum Engineers E&P Environmental and Safety Conference, San Antonio, TX.

Hossain, Md. M., & Rahman, M. K. (2008). Numerical simulation of complex fracture growth during tight reservoir stimulation by hydraulic fracturing. *Journal of Petroleum Science and Engineering, 60*, 86-104.

ICF International. (2009a, August 5). *Technical assistance for the draft supplemental generic EIS: oil, gas and solution mining regulatory program. Well permit issuance for horizontal drilling and high-volume hydraulic fracturing to develop the Marcellus Shale and other low permeability gas reservoirs—Task 2*. Albany, NY: ICF Incorporated, LLC, New York State Energy Research and Development Authority Contract PO Number 9679. Retrieved July 25, 2010, from http://www.nyserda.org/publications/ICF%20Task%202%20Report_Final.pdf.

ICF International. (2009b, August 7). *Technical assistance for the draft supplemental generic EIS: oil, gas and solution mining regulatory program. Well permit issuance for horizontal drilling and high-volume hydraulic fracturing to develop the Marcellus Shale and other low permeability gas reservoirs—Task 1*. Albany, NY: ICF Incorporated, LLC , New York State Energy Research and Development Authority Contract PO Number 9679. Retrieved July 25, 2010, from http://www.nyserda.com/publications/ICF%20Task%201%20Report_Final.pdf.

Jeu, S. J., Logan, T. L., & McBane, R. A. (1988, October 2-5). *Exploitation of deeply buried coalbed methane using different hydraulic fracturing techniques in the Piceance Basin, Colorado, and San Juan Basin, New Mexico*. Presented at the Society of Petroleum Engineers Annual Technical Conference and Exhibition, Houston, TX.

Judson, R. S., Martin, M. T., Reif, D. M., Houck, K. A., Knudsen, T. B., Rotroff, D. M., Xia, M., Sakamuru, S., Huang, R., Shinn, P., Austin, C. P., Kavlock, R. J., & Dix, D. J. (2010a). Analysis of eight oil spill dispersants using rapid, *in vitro* tests for endocrine and other biological activity. *Environmental Science & Technology*, *44*, 5979-5985.

Judson, R. S., Houck, K. A., Kavlock, R. J., Knudsen, T. B., Martin, M. T., Mortensen, H. M., Reif, D. M., Rotroff, D. M., Shah, I., Richard, A. M., & Dix, D. J. (2010b). *In vitro* screening of environmental chemicals for targeted testing prioritization: The ToxCast project. *Environmental Health Perspectives*, *118*, 485-492.

Kargbo, D. M., Wilhelm, R. G., & Campbell, D. J. (2010). Natural gas plays in the Marcellus Shale: challenges and potential opportunities. *Environmental Science & Technology, 44*(15), 5679-5684.

Keister, T. (2009, January 12). *Marcellus gas well water supply and wastewater disposal, treatment, and recycle technology*. Brockway, PA: ProChemTech International, Inc. Retrieved July 29, 2010, from http://www.prochemtech.com/Literature/TAB/PDF_TAB_Marcellus_Gas_Well_Water_Recycle.pdf.

Kellman, S., & Schneider, K. (2010, September 15). Water demand is flash point in Dakota oil boom. *Circle of Blue Waternews*. Retrieved September 18, 2010, from http://www.circleofblue.org/waternews/2010/world/scarce-water-is-no-limit-yet-to-north-dakota-oil-shale-boom/.

Leventhal, J. S., & Hosterman, J. W. (1982). Chemical and mineralogical analysis of Devonian black shale samples from Martin County, Kentucky; Caroll and Washington Counties, Ohio; Wise County, Virginia; and Overton County, Tennessee. *Chemical Geology, 37,* 239-264.

Long, D. T., & Angino, E. E. (1982). The mobilization of selected trace metals from shales by aqueous solutions: Effects of temperature and ionic strength. *Economic Geology*, *77*(3), 646-652.

Lustgarten, A., & ProPublica. (2009, August 26). EPA: Chemicals found in Wyoming drinking water might be from natural gas drilling. *Scientific American*. Retrieved July 25, 2010, from http://www.scientificamerican.com/article.cfm?id=chemicals-found-in-drinking-water-from-natural-gas-drilling.

Maclin, E., Urban, R., & Haak, A. (2009, December 31). *Re: New York State Department of Environmental Conservation's draft supplemental generic environmental impact statement on the oil, gas, and solution mining regulatory program*. Arlington, VA: Trout Unlimited. Retrieved July 26, 2010, from http://www.tcgasmap.org/media/Trout%20Unlimited%20NY%20Comments%20on%20Draft%20SGEIS.pdf.

McLean, J. S., & Beveridge, T. J. (2002). Interactions of bacteria and environmental metals, fine-grained mineral development, and bioremediation strategies. In P. M. Haung, et al. (Eds.), *Interactions between soil particles and microrganisms* (pp. 67-86). New York, NY: Wiley.

McMahon, P. B., Thomas, J. C., & Hunt, A. G. (2011). *Use of diverse geochemical data sets to determine sources and sinks of nitrate and methane in groundwater, Garfield County, Colorado, 2009.* U.S. Geological Survey Scientific Investigations Report 2010–5215. Reston, VA: United States Department of the Interior, United States Geological Survey.

Michaels, C., Simpson, J. L., & Wegner, W. (2010, September). *Fractured communities: Case studies of the environmental impacts of industrial gas drilling*. Ossining, NY: New York Riverkeeper. Retrieved September 16, 2010, from http://www.riverkeeper.org/wp-content/uploads/2010/09/Fractured-Communities-FINAL-September-2010.pdf.

Myers, T. (2009). *Technical memorandum: Review and analysis of draft supplemental generic environmental impact statement on the oil, gas and solution mining regulatory program. Well permit issuance for horizontal drilling and high-volume hydraulic fracturing to develop the Marcellus Shale and other low-permeability gas reservoirs*. New York, NY: Natural Resources Defense Council. Retrieved

July 26, 2010, from http://www.tcgasmap.org/media/NRDCMyers%20Comments%20on%20Draft%20SGEIS.pdf.

National Research Council. (2010). *Management and effects of coalbed methane produced water in the western United States*. Washington, DC: National Academies Press.

Nemat-Nassar, S., Abe, H., & Hirakawa, S. (1983). *Hydraulic fracturing and geothermal energy*. The Hague, The Netherlands: Kluwer Academic Publishers.

New Hampshire Department of Environmental Services. (2010). *Environmental fact sheet. Well development by hydro-fracturing*. Concord, NH: New Hampshire Department of Environmental Services. Retrieved January 11, 2011, from http://des.nh.gov/organization/commissioner/pip/factsheets/dwgb/documents/dwgb-1-3.pdf.NIOSH (National Institute for Occupational Safety and Health). (2009, February). *Oil and gas extraction. Inputs: Occupational safety and health risks*. Atlanta, GA: Centers for Disease Control and Prevention. Retrieved September 17, 2010, from http://www.cdc.gov/niosh/programs/oilgas/risks.html.

NPS (National Park Service). (2008). *Potential development of the natural gas resources in the Marcellus Shale, New York, Pennsylvania, West Virginia, and Ohio*. Washington, DC: U.S. Department of the Interior. Retrieved December 1, 2010, from http://www.eesi.psu.edu/news_events/EarthTalks/2009Spring/materials2009spr/NatParkService-GRD-M-Shale_12-11-2008_view.pdf.

NYSDEC (New York State Department of Environmental Conservation). (2009, September). *Supplemental generic environmental impact statement on the oil, gas and solution mining regulatory program (draft). Well permit issuance for horizontal drilling and high-volume hydraulic fracturing to develop the Marcellus Shale and other low-permeability gas reservoirs*. Albany, NY: New York State Department of Environmental Conservation. Retrieved January 20, 2010, from ftp://ftp.dec.state.ny.us/dmn/download/OGdSGEISFull.pdf.

Oil and Gas Investor. (2005, March). *Tight Gas* (special supplement). Houston, TX: Oil and Gas Investor/Hart Energy Publishing LP. Retrieved August 9, 2010, from http://www.oilandgasinvestor.com/pdf/Tight%20Gas.pdf.

OilGasGlossary.com. (2010). *Drilling fluid definition.* Retrieved February 3, 2011, from http://oilgasglossary.com/drilling-fluid.html.

OilShaleGas.com. (2010). OilShaleGas.com—oil & shale gas discovery news. Retrieved January 17, 2011, from http://oilshalegas.com.

PADEP (Pennsylvania Department of Environmental Protection). (2010a). *Marcellus Shale*. Harrisburg, PA: Pennsylvania Department of Environmental Protection. Retrieved August 9, 2010, from http://www.elibrary.dep.state.pa.us/dsweb/Get/Document-77964/0100-FS-DEP4217.pdf.

PADEP (Pennsylvania Department of Environmental Protection). (2010b, December 15). *Consent order and settlement agreement (Commonwealth of Pennsylvania Department of Environmental Protection and Cabot Oil & Gas Corporation)*. PA: Pennsylvania Department of Environmental Protection.

Palisch, T. T., Vincent, M. C., & Handren, P. J. (2008, September 21-24). *Slickwater fracturing—food for thought.* No. 115766-MS. Paper presented at the Society of Petroleum Engineers Annual Technical Conference, Denver, CO.

Palmer, I. D., Fryan, R. T., Tumino, K. A., & Puri, R. (1991, August 12). Water fracs outperform gel fracs in coalbed pilot. *Oil and Gas Journal*, 71-76.

Palmer, I. D., Lambert, S. W., & Spitler, J. L. (1993). Coalbed methane well completions and stimulations. *AAPG Studies in Geology, 38*, 303-341.

Pashin, J. C. (2007). Hydrodynamics of coalbed methane reservoirs in the Black Warrior Basin: Key to understanding reservoir performance and environmental Issues. *Applied Geochemistry*, *22*, 2257-2272.

Pearson, C. M. (1989). *U.S. Patent No. 4,845,981,1989. System for monitoring fluids during well stimulation processes*. Washington, DC: U.S. Patent and Trademark Office.

Pennsylvania Environmental Quality Board. (2009, November 7). Proposed Rulemaking [25 PA. CODE CH. 95] wastewater treatment requirements [39 Pa.B. 6467] [Saturday, November 7, 2009]. *The Pennsylvania Bulletin, 39*(45), Doc. No. 09-2065. Retrieved January 21, 2011, from http:// www.pabulletin.com/secure/data/vol39/39-45/2065.html.

Pennsylvania State University. (2010). *Marcellus education fact sheet. Water withdrawals for development of Marcellus Shale gas in Pennsylvania: Introduction to Pennsylvania's water resources*. University Park, PA: College of Agricultural Sciences, Pennsylvania State University. Retrieved November 26, 2010, from http://pubs.cas.psu.edu/freepubs/pdfs/ua460.pdf.

Pickett, A. (2009, March). New solutions emerging to treat and recycle water used in hydraulic fracs. *American Oil & Gas Reporter*. Retrieved July 29, 2010, from http://www.aogr.com/index.php/ magazine/cover_story_archives/march_2009_cover_story/.

Piggot, A. R., & Elsworth, D. (1996). Displacement of formation fluids by hydraulic fracturing. *Geotechnique, 46*(4), 671-681.

Prouty, J. L. (2001). Tight gas in the spotlight. *Gas Technology Institute GasTIPS, 7*(2), 4-10.

Reif, D. M., Martin, M. T., Tan, S. W., Houck, K. A., Judson, R. S., Richard, A. M., Knudsen, T. B., Dix, D. J., & Kavlock, R. J. (2010). Endocrine profiling and prioritization of environmental chemicals using ToxCast data. *Environmental Health Perspectives*, *118*, 1714-1720.

Rogers, R. E., Ramurthy, M., Rodvelt, G., & Mullen, M. (2007). *Coalbed methane: Principles and practices.* Third edition. Starkville, MS: Oktibbeha Publishing Co. Retrieved August 2, 2010, from http://www.halliburton.com/public/pe/contents/Books_and_Catalogs/web/CBM/CBM_Book_Intro.pdf.

Rowan, T. M. (2009, September 23-25). *Spurring the Devonian: Methods of fracturing the lower Huron in southern West Virginia and eastern Kentucky*. Presented at the Society for Petroleum Engineers Eastern Regional Meeting, Charleston, WV.

Ruszka, J. (2007, August 1). Global challenges drive multilateral drilling. *E&P*. Retrieved August 13, 2010, from http://www.epmag.com/archives/features/583.htm.

Satterfield, J., Kathol, D., Mantell, M., Hiebert, F., Lee, R., & Patterson, K. (2008, September 20-24). *Managing water resource challenges in select natural gas shale plays. GWPC Annual Forum*. Oklahoma City, OK: Chesapeake Energy Corporation. Retrieved July 21, 2010, from http://www.gwpc.org/meetings/forum/2008/proceedings/Ground%20Water%20&%20Energy/SatterfieldWaterEnergy.pdf.

Southam, G. (2000). Bacterial surface-mediated mineral formation. In D. R. Lovely (Ed.), *Environmental Microbe-Metal Interactions* (pp. 257-276). Washington, DC: American Society of Microbiology.

Sparks, D. L. (1995). *Environmental soil chemistry*. San Diego, CA: Academic Press.

Sposito, G. (1989). *The chemistry of soils*. New York, NY: Oxford University Press.

State of Colorado Oil and Gas Conservation Commission. (2009a, October 5). *Bradenhead test report*. OGCC Operator Number 26420, API Number 123-11848. Denver, CO: State of Colorado Oil and Gas Conservation Commission.

State of Colorado Oil and Gas Conservation Commission. (2009b, December 7). *Sundry notice*. OGCC Operator Number 26420, API Number 05-123-11848. Denver, CO: State of Colorado Oil and Gas Conservation Commission.

State of Colorado Oil and Gas Conservation Commission. (2009c, December 17). *Colorado Oil and Gas Conservation Commission approved Wattenberg Bradenhead testing and staff policy.* Letter sent to all oil and gas operators active in the Denver Basin. Denver, CO: State of Colorado Oil and Gas Conservation Commission.

Stepan, D. J., Shockey, R. E., Kurz, B. A., Kalenze, N. S., Cowan, R. M., Ziman, J. J., & Harju, J. A. (2010). *Bakken water opportunities assessment—Phase I.* Publication No. 2010-EERC-04-03. Grand Forks, ND: Energy and Environmental Research Center.

STRONGER, Inc. (State Review of Oil and Natural Gas Regulations, Inc.). (2010, January 10). *Section X: Hydraulic fracturing.* Draft guidelines. Oklahoma City, OK: STRONGER, Inc. Retrieved July 27, 2010, from http://www.strongerinc.org/documents/HF%20Guideline%20Web%20posting.pdf.

Stumm, W., & Morgan, J. J. (1996). *Chemical equilibria and rates in natural waters.* Third edition. New York, NY: John Wiley & Sons, Inc.

Subra, W. (2010). *Contamination of water resources by hydraulic fracturing operations in Marcellus Shale*. Baton Rouge, LA: Louisiana Environmental Action Network. Retrieved July 26, 2010, from

http://leanweb.org/campaigns/produced-waters/contamination-of-water-resources-by-hydraulic-fracturing-operations-in-marcellus-shale.html.

TOXNET (Toxicology Data Network). (2011). *Hazardous Substances Data Bank (HSDB)*. Retrieved January 17, 2011, from http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB.htm.

Tuttle, M. L. W., Briet, G. N., & Goldhaber, M. B. (2009). Weathering of the New Albany Shale, Kentucky: II. Redistribution of minor and trace elements. *Applied Geochemistry, 24*, 1565-1578.

URS Corporation. (2009, September 16). *Water-related issues associated with gas production in the Marcellus Shale: Additives use, flowback quality and quantities, regulations, on-site treatment, green technologies, alternate water sources, water well-testing.* Prepared for New York State Energy Research and Development Authority, Contract PO No. 10666. Fort Washington, PA: URS Corporation. Retrieved August 2, 2010, from http://www.nyserda.org/publications/02%20Chapter%202%20-%20URS%202009-9-16.pdf.

USDOE (United States Department of Energy). (2009, May). *State oil and natural gas regulations designed to protect water resources*. Washington, DC: U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory.

USEIA (United States Energy Information Administration). (2010, December). *Annual energy outlook 2011: Early release overview*. Washington, DC: U.S. Department of Energy. Retrieved January 17, 2011, from http://www.eia.gov/forecasts/aeo/.

USEPA (United States Environmental Protection Agency). (1998). *AP-42 air pollutant emission factors, volume II, appendix H*. Washington, DC: U.S. Environmental Protection Agency, Office of Mobile Sources. Retrieved December 1, 2010, from http://www.epa.gov/otaq/models/ap42/ap42-h7.pdf.

USEPA (United States Environmental Protection Agency). (2002a, October). *Exemption of oil and gas exploration and production wastes from federal hazardous waste regulations*. Washington, DC: U.S. Environmental Protection Agency, Office of Solid Waste. Retrieved January 20, 2011, from http://www.epa.gov/osw/nonhaz/industrial/special/oil/oil-gas.pdf.

USEPA (United States Environmental Protection Agency). (2002b, November). *Overview of the EPA quality system for environmental data and technology.* No. EPA/240/R-02/003. Washington, DC: U.S. Environmental Protection Agency, Office of Environmental Information. Retrieved January 20, 2011, from http://www.epa.gov/QUALITY/qs-docs/overview-final.pdf.

USEPA (United States Environmental Protection Agency). (2004, June). *Evaluation of impacts to underground sources of drinking water by hydraulic fracturing of coalbed methane reservoirs.* No. EPA/816/R-04/003. Washington, DC: U.S. Environmental Protection Agency, Office of Water. Retrieved January 21, 2011, from http://water.epa.gov/type/groundwater/uic/class2/hydraulicfracturing/wells_coalbedmethanestudy.cfm.

USEPA (United States Environmental Protection Agency). (2010a, March). *Scoping materials for initial design of EPA research study on potential relationships between hydraulic fracturing and drinking water resources*. Washington, DC: U.S. Environmental Protection Agency, Office of Research and Development. Retrieved September 16, 2010, from http://yosemite.epa.gov/sab/sabproduct.nsf/0/3B745430D624ED3B852576D400514B76/$File/Hydraulic+Frac+Scoping+Doc+for+SAB-3-22-10+Final.pdf.

USEPA (United States Environmental Protection Agency). (2010b, April 23). *Trip report* (EXCO Resources' gas well drilling site, Norris Ferry Road, southern Caddo Parish (Shreveport), LA). Dallas, TX: U.S. Environmental Protection Agency Region 6.

USEPA (United States Environmental Protection Agency). (2010c, June). *Advisory on EPA's research scoping document related to hydraulic fracturing*. Washington, DC: U.S. Environmental Protection Agency, Office of the Administrator, Science Advisory Board. Retrieved September 16, 2010, from http://yosemite.epa.gov/sab/sabproduct.nsf/0/CC09DE2B8B4755718525774D0044F929/$File/EPA-SAB-10-009-unsigned.pdf.

USEPA (United States Environmental Protection Agency). (2010d, July). *EPA's action development process: Interim guidance on considering environmental justice during the development of an action.* OPEI Regulatory Development Series. Washington, DC: U.S. Environmental Protection Agency. Retrieved January 17, 2011, from http://www.epa.gov/environmentaljustice/resources/policy/considering-ej-in-rulemaking-guide-07-2010.pdf.

USGS (United States Geological Survey). (2002, May 29). *Produced waters database*. Reston, VA: U.S. Geological Survey National Center. Retrieved January 17, 2011, from http://energy.cr.usgs.gov/prov/prodwat/data2.htm.

Veil, J. A., Puder, M. G., Elcock, D., Redweik, R. J. (2004). *A white paper describing produced water from production of crude oil, natural gas, and coal bed methane.* Prepared for the U.S. Department of Energy, National Energy Technology Laboratory, contract W-31-109-ENG-38. Argonne, IL: Argonne National Laboratory. Retrieved January 20, 2011, from http://www.evs.anl.gov/pub/doc/ProducedWatersWP0401.pdf.

Veil, J. A. (2007, August). *Trip report for field visit to Fayetteville Shale gas wells.* No. ANL/EVS/R-07/4. Prepared for the U.S. Department of Energy, National Energy Technology Laboratory, project no. DE-FC26-06NT42930. Argonne, IL: Argonne National Laboratory. Retrieved July 27, 2010, from http://www.evs.anl.gov/pub/doc/ANL-EVS_R07-4TripReport.pdf.

Veil, J. A. (2008, May 13). *Thermal distillation technology for management of produced water and frac flowback water.* Water Technology Brief #2008-1. Prepared for the U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, contract no. DE-AC02-06CH11357. Argonne, IL: Argonne National Laboratory. Retrieved July 29, 2010, from http://www.evs.anl.gov/pub/doc/ANL-EVS-evaporation_technologies2.pdf.

Veil, J. A. (2010, July). *Final report: Water management technologies used by Marcellus Shale gas producers.* Prepared for the U.S. Department of Energy, National Energy Technology Laboratory, Department of Energy award no. FWP 49462. Argonne, IL: Argonne National Laboratory. Retrieved on January 20, 2011, from http://www.evs.anl.gov/pub/doc/Water%20Mgmt%20in%20Marcellus-final-jul10.pdf.

Vejahati, F., Xu, Z., & Gupta, R. (2010). Trace elements in coal: Associations with coal and minerals and their behavior during coal utilization—a review. *Fuel*, *89*, 904-911.

Vidas, H., & Hugman, B. (2008, November). *Availability, economics and production potential of North American unconventional natural gas supplies* (prepared for the Interstate National Gas Association of America Foundation, Inc.). Fairfax, VA: ICF International. Retrieved December 22, 2010, from http://www.ingaa.org/File.aspx?id=7878.

Vidic, R. D. (2010, March 18). *Sustainable water management for Marcellus Shale development*. Presented at Marcellus Shale natural gas stewardship: Understanding the environmental impact, Marcellus Shale Summit, Temple University, Philadelphia, PA. Retrieved July 29, 2010, from http://www.temple.edu/environment/NRDP_pics/shale/presentations_TUsummit/Vidic-Temple-2010.pdf.

Walther, J. V. (2009). *Essentials of geochemistry.* Second edition. Boston, MA: Jones and Bartlett Publishers.

Warpinski, N. R., Branagan, P. T., Peterson, R. E., & Wolhart, S. L. (1998, March 15-18). *Mapping hydraulic fracture growth and geometry using microseismic events detected by a wireline retrievable accelerometer array*. Presented at the Society of Petroleum Engineers Gas Technology Symposium, Calgary, Alberta, Canada.

Warpinski, N. R., Walhart, S. L., & Wright, C. A. (2001, September 30-October 3). *Analysis and prediction of microseismicity induced by hydraulic fracturing*. Presented at the Society of Petroleum Engineers Annual Technical Conference, New Orleans, LA.

Waxman, H. A., Markey, E. J., & DeGette, D. (2011, January 31). *Letter to EPA Administrator Lisa Jackson regarding the use of diesel fuel in hydraulic fracturing fluids.* Retrieved February 7, 2011, from http://democrats.energycommerce.house.gov/index.php?q=news/waxman-markey-and-degette-investigation-finds-continued-use-of-diesel-in-hydraulic-fracturing-f.

Webb, D. (2010, July 22). State cites gas firm after complaints. *The Daily Sentinel*. Retrieved August 13, 2010, from http://www.gjsentinel.com/news/articles/state_cites_gas_firm_after_com.

West Virginia Water Research Institute. (2010). *Zero discharge water management for horizontal shale gas well development: Technology status assessment.* Prepared for the U.S. Department of Energy, National Energy Technology Laboratory, Department of Energy award no. DE-FE0001466. Morgantown, WV: West Virginia Water Research Institute, West Virginia University. Retrieved July 29, 2010, from http://prod75-inter1.netl.doe.gov/technologies/oil-gas/publications/ENVreports/FE0001466_TSA.pdf.

Winter, T. C., Harvey J. W., Franke O. L., & Alley W. M. (1998). Ground water and surface water: A single resource. *U.S. Geological Survey Circular*, *1139*, 1-78.

Yang, T. H., Tham, L. G., Tang, C. A., Liang, Z. Z., & Tsui, Y. (2004). Influence of heterogeneity of mechanical properties on hydraulic fracturing in permeable rocks. *Rock Mechanics and Rock Engineering*, *37*(4), 251-275.

Zoback, M., Kitasei, S., & Copithorne, B. (2010, July). *Addressing the environmental risks from shale gas development.* Briefing paper 1. Washington, DC: Worldwatch Institute. Retrieved January 20, 2011, from http://www.worldwatch.org/files/pdf/Hydraulic%20Fracturing%20Paper.pdf.

Zorn, T. G., Seelbach, P. W., Rutherford, E. S., Wills, T. C., Cheng, S., & Wiley, M. J. (2008, November). *A regional-scale habitat suitability model to assess the effects of flow reduction on fish assemblages in Michigan streams.* Fisheries Division Research Report 2089. Lansing, MI: State of Michigan Department of Natural Resources. Retrieved January 20, 2011, from http://www.michigandnr.com/PUBLICATIONS/PDFS/ifr/ifrlibra/Research/reports/2089/RR2089.pdf.

APPENDIX A: PROPOSED RESEARCH SUMMARY

TABLE A1. PROPOSED RESEARCH FOR WATER ACQUISITION

Water Acquisition: How might large volume water withdrawals from ground and surface water impact drinking water resources?				
Secondary Question	**Research**	**Potential Product(s)**	**Year Due**	**EPA's Role**
What are the impacts on water availability?	*Analyze Existing Data* • Survey and map HF sites and water resources • Analyze trends in water flow and usage patterns • Compare areas with HF activity to areas without	• Maps of HF activity and drinking water resources • Identification of impacts of HF on water availability at various spatial and temporal scales	2012	Research by ORD (NRMRL)
	Prospective Case Studies • Collect data on water use and the availability of drinking water resources near HF sites before and after water withdrawals • Monitor current management practices relating to water acquisition	• Identification of impacts of HF on water availability • Assessment of current water withdrawal management practices	2014	Research by ORD (NRMRL, NERL)
	Scenario Evaluation • Assess impacts of cumulative water withdrawals on water availability at watershed and aquifer levels	• Identification of impacts on drinking water resources due to cumulative water withdrawals • Estimate of the sustainable number of HF operations per year for a given region or formation	2014	Research by ORD (NERL)
What are the impacts on water quality?	*Analyze Existing Data* • Survey and map HF sites and water quality • Analyze trends in water quality • Compare areas with HF activity to areas without	• Maps of HF activity and drinking water resources • Identification of impacts of HF on water quality	2012	Research by ORD (NRMRL)
	Prospective Case Studies • Collect data on the quality of drinking water resources near HF sites before and after water withdrawals	• Identification of impacts of HF on water quality	2014	Research by ORD (NRMRL, NERL)

TABLE A2. PROPOSED RESEARCH FOR CHEMICAL MIXING

Chemical Mixing: What are the possible impacts of releases of hydraulic fracturing fluids on drinking water resources?				
Secondary Question	**Research**	**Potential Product(s)**	**Year Due**	**EPA's Role**
What is the composition of HF fluids and what are the toxic effects of these constituents?	*Analyze Existing Data* • Compile list of chemicals used in HF fluids based on publically available data and data provided by nine HF service companies • Compare chemical list with databases of known toxic chemicals • Predict hazards in cases where toxicity is unknown • Identify or develop analytical methods for detecting HF chemical additives	• List of chemicals used in HF (subject to TSCA CBI rules), including concentrations used and known toxicity levels • Prioritized list of chemicals requiring further toxicity studies, including additional screening activities • Analytical methods for detecting HF chemical additives, including up to 10–20 possible indicators to track fate and transport of HF fluids	2012*	Research by EPA (OSP, NERL, NCEA, NHEERL, NCCT, OPPT)
What factors may influence the likelihood of contamination of drinking water resources?	*Analyze Existing Data* • Review existing scientific literature on surface chemical spills with respect to HF chemical additives	• Summary of existing research that describes the fate and transport of HF chemical additives • Identify knowledge gaps for future research, if necessary	2012	Research by ORD (NERL)
	Retrospective Case Studies • Possible investigation of an HF site where a spill of HF fluid has been reported	• Identification of impacts to drinking water resources resulting from the accidental release of HF fluid	2012/2014	Research by ORD (NRMRL, NERL)
How effective are mitigation approaches in reducing impacts to drinking water resources?	*Prospective Case Studies* • Monitor and assess current chemical management practices	• Assessment of current management practices related to on-site chemical storage and mixing	2014	Research by ORD (NRMRL, NERL)

* Additional analytical methods will be developed as needed and may be available in 2014. Also available in 2014 would be predictions of the toxicity of selected chemicals as well as the development of PPRTVs for high-priority chemicals of concern (if needed).

TABLE A3. PROPOSED RESEARCH FOR WELL INJECTION

Well Injection: What are the possible impacts of the injection and fracturing process on drinking water resources?				
Secondary Question	**Research**	**Potential Product(s)**	**Year Due**	**EPA's Role**
How effective are well construction and operation practices at containing fluids during and after fracturing?	*Analysis of Existing Data* • Analyze a representative selection of well files	• Data on the frequency, severity, and contributing factors leading to well failures	2014	Research by ORD (OSP)
	Retrospective Case Studies • Investigate the cause(s) of reported drinking water contamination, including testing well mechanical integrity	• Data on the role of mechanical integrity in suspected cases of drinking water contamination due to HF	2012/2014	Research by ORD (NRMRL, NERL)
	Prospective Case Studies • Conduct tests to assess well mechanical integrity before and after fracturing	• Data on changes (if any) in mechanical integrity due to HF • Identification of methods being used (if any) to monitor mechanical integrity after HF	2014	Research by ORD (NRMRL, NERL)
	Scenario Evaluation • Test various scenarios involving well failure that may result in drinking water contamination	• Identification and assessment of well failure scenarios during well injection that lead to drinking water contamination	2012	Research by ORD (NERL)

Table continued on next page

Table continued from previous page

Secondary Question	Research	Potential Product(s)	Year Due	EPA's Role
What are the potential impacts of pre-existing man-made or natural pathways/features on contaminant transport?	*Retrospective Case Studies* • Investigate the cause(s) of reported drinking water contamination	• Assessment of the role of pre-existing pathways in the transport of HF fluids, natural gas, or naturally occurring substances to drinking water resources • Data on the location of hydraulic fractures and their potential connection to other pathways	2012/2014	Research by ORD (NRMRL, NERL); collaboration with USGS
	Prospective Case Studies • Identify the impacts of natural and artificial pathways on contaminant transport	• Identification of processes and tools used to determine fracture location and properties • Data on water quality before, during, and after injection (possibly using chemical tracers)	2014	Research by ORD (NRMRL, NERL); collaboration with DOE NETL
	Scenario Evaluation • Test scenarios where faults or fractures intersect natural and artificial pathways	• Assessment of key conditions that affect the interaction of pre-existing pathways with HF fractures • Identification of the area of potential impact	2012	Research by ORD (NERL)
What chemical/physical/ biological processes could impact the fate and transport of substances in the subsurface?	*Laboratory Studies* • Identify relevant reactions between HF fluid additives and naturally occurring substances • Determine degradation products of HF fluid additives • Determine important properties of gas-bearing formations, solid residues, and fracturing conditions that may lead to drinking water contamination	• Assessment of fate of HF fluid components and naturally occurring substances • Assessment of the identity, physical and chemical characteristics, mobility, and concentration of potential drinking water contaminants	2014	Research by ORD (NRMRL)
What are the toxic effects naturally occurring substances?	*Analysis of Data* • Compare list of naturally occurring substances with databases of known toxic chemicals • Predict hazards in cases where toxicity is unknown	• Compilation of information on the toxicity of naturally occurring substances • Prioritized list of chemicals requiring further toxicity study • PPRTVs for chemicals of concern	2012/2014	Research by EPA (NCEA, NCCT, NHEERL, OPPT)

TABLE A4. PROPOSED RESEARCH FOR FLOWBACK AND PRODUCED WATER

Flowback and Produced Water: What are the possible impacts of releases of flowback and produced water on drinking water resources?				
Secondary Question	**Research**	**Potential Product(s)**	**Year Due**	**EPA's Role**
What is the composition, quantity, and variability of flowback and produced water and what are the toxic effects of these constituents?	*Analysis of Existing Data* • Compile list of chemicals found in flowback and produced water • Compare chemical list with databases of known toxic chemicals • Predict hazards in cases where toxicity is unknown • Identify or develop analytical methods for detecting chemicals in flowback and produced water	• List of identity, quantity, and known toxicity of flowback and produced water components • Prioritized list of chemicals for which further toxicity studies are warranted • PPRTVs for chemicals of concern • Analytical methods for quantifying components of flowback and produced water	2014	Research by EPA (NRMRL, NERL, NCCT, NCEA, NHEERL, OPPT)
	Prospective Case Studies • Sample flowback and produced water periodically after injection is completed	• Data on the composition, quantity, and variability of flowback and produced water and how that composition changes with time	2014	Research by ORD (NRMRL, NERL)
What factors may influence the likelihood of contamination of drinking water resources?	*Analysis of Existing Data* • Review existing scientific literature on surface chemical spills and pit leakage with respect to the constituents of flowback and produced water	• Summary of existing research that describes the fate and transport of flowback and produced water constituents • Identify knowledge gaps for future research, if necessary	2012	Research by ORD (NERL)
	Retrospective Case Studies • May investigate a case study where a spill of flowback and produced water has been reported	• Evaluate risks posed to drinking water resources by the production and management of HF wastewaters	2012/2014	Research by ORD (NRMRL, NERL)
	Analysis of Existing Data • Test scenarios involving contaminant migration up the wellbore	• Assessment of key conditions that affect the migration of flowback and produced water to aquifers	2012	Research by ORD (NERL)
How effective are mitigation approaches in reducing impacts to drinking water resources?	*Prospective Case Studies* • Monitor on-site management of flowback and produced water	• Information on the effectiveness of existing practices for containing or mitigating accidental releases of HF wastewaters	2014	Research by ORD (NRMRL, NERL)

TABLE A5. PROPOSED RESEARCH FOR WASTEWATER TREATMENT AND WASTE DISPOSAL

Wastewater Treatment and Waste Disposal: What are the possible impacts of inadequate treatment of hydraulic fracturing wastewaters on drinking water resources?				
Secondary Question	**Research**	**Potential Product(s)**	**Year Due**	**EPA's Role**
How effective are treatment and disposal methods?	*Analysis of Existing Data* • Assess data on direct treatment, pre-treatment, and treatment for reuse of HF wastewaters	• Identify research gaps, focusing treatment relating of inorganic and organic contaminants • Information on the relative effectiveness of various approaches to treatment and disposal of flowback and produced water	2012	Research by ORD (NRMRL)
	Laboratory Studies • Investigate the role of HF chemical additives in creating disinfection byproducts during wastewater treatment • Identify the effects of HF wastewaters on drinking water utilities	• Identification of HF-related chemicals that create disinfection byproducts • Assessment of the potential impacts of high chloride levels on drinking water utilities	2012	Research by ORD (NRMRL)
	Prospective Case Studies • Monitor treatment and disposal/reuse of hydraulic fracturing wastewaters, including solid residuals from treatment facilities	• Data on the effectiveness of current treatment and disposal approaches for HF wastewaters • Identify areas for additional study	2014	Research by ORD (NRMRL, NERL)

TABLE A6. PROPOSED RESEARCH FOR ENVIRONMENTAL JUSTICE

Research	Potential Product(s)	Year Due	EPA's Role
Analysis of Existing Data • Combine information on HF locations in the United States with demographic information (e.g., income and race)	• Map of HF activity, income, and race information	2012	Research by ORD (OSP)

List of Acronyms

CBI	confidential business information
HF	hydraulic fracturing
NCCT	National Center for Computational Toxicology
NCEA	National Center for Environmental Assessment
NERL	National Exposure Research Laboratory
NETL	National Energy Technology Laboratory
NHEERL	National Health and Environmental Effects Research Laboratory
NRMRL	National Risk Management Research Laboratory
OPPT	Office of Pollution Prevention and Toxics
ORD	Office of Research and Development
OSP	Office of Science Policy
PPRTV	Provisional Peer Reviewed Toxicity Value
TSCA	Toxic Substances Control Act

APPENDIX B: STAKEHOLDER COMMENTS

In total, EPA received 5,521 comments that were submitted electronically to hydraulic.fracturing@epa.gov or mailed to EPA. This appendix provides a summary of those comments.

More than half of the electronic comments received consisted of a form letter written by Energycitizens.org[5] and sent by citizens. This letter states that "Hydraulic fracturing has been used safely and successfully for more than six decades to extract natural gas from shale and coal deposits. In this time, there have been no confirmed incidents of groundwater contamination caused by the hydraulic fracturing process." Additionally, the letter states that protecting the environment "should not lead to the creation of regulatory burdens or restrictions that have no valid scientific basis." We have interpreted this letter to mean that the sender supports hydraulic fracturing and does support the need for additional study.

Table B1 provides an overall summary of the 5,521 comments received.

TABLE B1. SUMMARY OF STAKEHOLDER COMMENTS

Stakeholder Comments	Percentage of Comments (w/ Form Letter)	Percentage of Comments (w/o Form Letter)
Position on Study Plan		
For	18.2	63.2
Opposed	72.1	3.0
No Position	9.7	33.8
Expand Study	8.8	30.5
Limit Study	0.7	2.5
Position on Hydraulic Fracturing		
For	75.7	15.7
Opposed	11.6	40.3
No Position	12.7	44.1

Table B2 further provides the affiliations (e.g., citizens, government, industry) associated with the stakeholders, and indicates that the majority of comments EPA received came from citizens.

[5] Energy Citizens is financially sponsored by API, as noted at http://energycitizens.org/ec/advocacy/content-rail.aspx?ContentPage=About.

TABLE B2. SUMMARY OF COMMENTS ON HYDRAULIC FRACTURING AND RELATED STUDY PLAN

Category	Percentage of Comments (w/ Form Letter)	Percentage of Comments (w/o Form Letter)
Association	0.24	0.82
Business association	0.69	2.39
Citizen	23.47	81.56
Citizen (form letter Energycitizens.org)	71.22	NA
Environmental	1.10	3.84
Federal government	0.07	0.25
Lobbying organization	0.04	0.13
Local government	0.62	2.14
Oil and gas association	0.09	0.31
Oil and gas company	0.38	1.32
Political group	0.16	0.57
Politician	0.18	0.63
Private company	0.78	2.71
Scientific organization	0.02	0.06
State government	0.13	0.44
University	0.24	0.82
Water utility	0.02	0.06
Unknown	0.56	1.95

Table B3 provides a summary of the frequent research areas requested in the stakeholder comments.

TABLE B3. FREQUENT RESEARCH AREAS REQUESTED IN STAKEHOLDER COMMENTS

Research Area	Number of Requests*
Ground water	292
Surface water	281
Air pollution	220
Water use (source of frac water)	182
Flowback treatment/disposal	170
Public health	165
Ecosystem effects	160
Toxicity and chemical identification	157
Chemical fate and transport	107
Radioactive issues	74
Seismic issues	36
Noise pollution	26

* Out of 485 total requests to expand the hydraulic fracturing study.

In addition to the frequently requested research areas, there were a variety of other comments and recommendations related to potential research areas. These comments and recommendations are listed below:

- Abandoned and undocumented wells
- Auto-immune diseases related to hydraulic fracturing chemicals
- Bioaccumulation of hydraulic fracturing chemicals in the food chain
- Biodegradable/nontoxic fracturing liquids
- Carbon footprint of entire hydraulic fracturing process
- Comparison of accident rates to coal/oil mining accident rates
- Disposal of drill cuttings
- Effects of aging on well integrity
- Effects of hydraulic fracturing on existing public and private wells
- Effects of truck/tanker traffic
- Effects on local infrastructure (e.g., roads, water treatment plants)
- Effects on tourism
- Hydraulic fracturing model
- Economic impacts on landowners
- Land farming on fracturing sludge
- Light pollution
- Long-term corrosive effects of brine and microbes on well pipes
- Natural flooding near hydraulic fracturing operations
- Radioactive proppants
- Recovery time and persistence of hydraulic fracturing chemicals in contaminated aquifers
- Recycling of flowback and produced water
- Removal of radium and other radionuclides from flowback and produced water
- Restoration of drill sites
- Review current studies of hydraulic fracturing with microseismic testing
- Sociological effects (e.g., community changes with influx of workers)
- Soil contamination at drill sites
- Volatile organic compounds emissions from hydraulic fracturing operations and impoundments
- Wildlife habitat fragmentation
- Worker occupational health

APPENDIX C: INFORMATION REQUEST

In September 2010, EPA issued information requests to collect data that will inform this study. The requests were sent to the following companies: BJ Services, Complete Well Services, Halliburton, Key Energy Services, Patterson-UTI, RPC, Schlumberger, Superior Well Services, and Weatherford. These companies are a subset of those from whom the House Committee on Energy and Commerce requested comment. Halliburton, Schlumberger, and BJ Services are the three largest companies operating in the United States; the others are companies of varying size that operate in the major United States shale plays. EPA sent a mandatory request to Halliburton on November 9, 2010, to compel Halliburton to provide the requested information. As of December 6, 2010, all companies have committed to provide the requested information on a rolling schedule that ended on January 31, 2011.

The questions asked in the voluntary information request are stated below.

QUESTIONS

Your response to the following questions is requested within thirty (30) days of receipt of this information request:

1. Provide the name of each hydraulic fracturing fluid formulation/mixture distributed or utilized by the Company within the past five years from the date of this letter. For each formulation/mixture, provide the following information for each constituent of such product. "Constituent" includes each and every component of the product, including chemical substances, pesticides, radioactive materials and any other components.

    a. Chemical name (e.g., benzene—use IUPAC nomenclature);

    b. Chemical formula (e.g., C_6H_6);

    c. Chemical Abstract System number (e.g., 71-43-2);

    d. Material Safety Data Sheet;

    e. Concentration (e.g., ng/g or ng/L) of each constituent in each hydraulic fracturing fluid product. Indicate whether the concentration was calculated or determined analytically. This refers to the actual concentration injected during the fracturing process following mixing with source water, and the delivered concentration of the constituents to the site. Also indicate the analytical method which may be used to determine the concentration (e.g., SW-846 Method 8260, in-house SOP), and include the analytical preparation method (e.g., SW-846 Method 5035), where applicable;

    f. Identify the persons who manufactured each product and constituent and the persons who sold them to the Company, including address and telephone numbers for any such persons;

g. Identify the purpose and use of each constituent in each hydraulic fracturing fluid product (e.g., solvent, gelling agent, carrier);

h. For proppants, identify the proppant, whether or not it was resin coated, and the materials used in the resin coating;

i. For the water used, identify the quantity, quality and the specifications of water needed to meet site requirements, and the rationale for the requirements;

j. Total quantities of each constituent used in hydraulic fracturing and the related quantity of water in which the chemicals were mixed to create the fracturing fluids to support calculated and/or measured composition and properties of the hydraulic fracturing fluids; and

k. Chemical and physical properties of all chemicals used, such as Henry's law coefficients, partitioning coefficients (e.g., K_{ow} $K_{OC,}$ K_d), aqueous solubility, degradation products and constants and others.

2. Provide all data and studies in the Company's possession relating to the human health and environmental impacts and effects of all products and constituents identified in Question 1.

3. For all hydraulic fracturing operations for natural gas extraction involving any of the products and constituents identified in the response to Question 1, describe the process including the following:

a. Please provide any policies, practices and procedures you employ, including any Standard Operating Procedures (SOPs) concerning hydraulic fracturing sites, for all operations including but not limited to: drilling in preparation for hydraulic fracturing including calculations or other indications for choice and composition of drilling fluids/muds; water quality characteristics needed to prepare fracturing fluid; relationships among depth, pressure, temperature, formation geology, geophysics and chemistry and fracturing fluid composition and projected volume; determination of estimated volumes of flowback and produced waters; procedures for managing flowback and produced waters; procedures to address unexpected circumstances such as loss of drilling fluid/mud, spills, leaks or any emergency conditions (e.g., blow outs), less than fully effective well completion; modeling and actual choice of fracturing conditions such as pressures, temperatures, and fracturing material choices; determination of exact concentration of constituents in hydraulic fracturing fluid formulations/mixtures; determination of dilution ratios for hydraulic fracturing fluids, and

b. Describe how fracturing fluid products and constituents are modified at a site during the fluid injection process.

4.

a. Identify all sites where, and all persons to whom, the Company:

   i. provided hydraulic fracturing fluid services that involve the use of hydraulic fracturing fluids for the year prior to the date of this letter, and

   ii. plans to provide hydraulic fracturing fluid services that involve the use of hydraulic fracturing fluids during one year after the date of this letter.

b. Describe the specific hydraulic fracturing fluid services provided or to be provided for each of the sites in Question 4.a.i. and ii., including the identity of any contractor that the Company has hired or will hire to provide any portion of such services.

For each site identified in response to Question 4, please provide all information specified in the enclosed electronic spreadsheet.

APPENDIX D: CHEMICALS IDENTIFIED IN HYDRAULIC FRACTURING FLUID AND FLOWBACK/PRODUCED WATER

TABLE D1. CHEMICALS FOUND IN HYDRAULIC FRACTURING FLUIDS

Chemical	Use	Ref.
[[(phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis phosphonic acid ammonium salt		1
1-(phenylmethyl) quinolinium chloride		1
1-(phenylmethyl)-ethyl pyridinium, methyl derivatives	acid corrosion inhibitor	2,3
1,2,4-trimethylbenzene/1,3,5-trimethylbenzene	non-ionic surfactant	4,5
1,2-diethoxyethane	foaming agent	2
1,2-dimethoxyethane	foaming agent	2
1,4-dioxane		1
1,2-benzisothiazolin-2-one		1
1-eicosene		1
1-hexadecene		1
1-methylnaphthalene		2
1-octadecene		1
1-tetradecene		1
1-undecanol	surfactant	
1,6 hexanediamine	clay control, fracturing	
2-(2-butoxyethoxy)ethanol	foaming agent	2
2-(2-ethoxyethoxy)ethanol	foaming agent	2
2-(2-methoxyethoxy)ethanol	foaming agent	2
2,2'-azobis-{2-(imidazlin-2-yl)propane dihydrochloride		1
2,2-dibromo-3-nitrilopropionamide	biocide	1,2,3,5
2,2-dibromomalonamide		1
2,2',2"-nitriloethanol		4
2-acrylamido-2-methylpropansulphonic acid sodium salt		1
2-acrylethyl(benzyl)dimethylammonium chloride		1
2-bromo-2-nitro-1,3-propandiol	microbiocide	3,4
2-bromo-2-nitro-3-propanol	microbiocide	2
2-bromo-3-nitrilopropionamide	biocide	2,3
2-butoxyethanol	foaming agent	2,3,6
2-ethoxyethanol	foaming agent	2,3
2-ethoxyethyl acetate	foaming agent	2
2-ethoxynaphthalene		1
2-ethyl hexanol		4,6
2-methoxyethanol	foaming agent	2
2-methoxyethyl acetate	foaming agent	2
2-methylnaphthalene		2
2-methyl-quinoline hydrochloride		1

Table continued on next page

Table continued from previous page

Chemical	Use	Ref.
2-monobromo-3-nitrilopropionamide	biocide	5
2-propen-1-aminium,N,N-dimethyl-N-2-propenyl-chloride, homopolymer		1
2-propenoic acid, homopolymer, ammonium salt		1
2-propenoic acid, polymer with sodium phosphinate		1
2-propenoic acid, telomer with sodium hydrogen sulfite		1
2-propoxyethanol	foaming agent	2
2-(thiocyanomethylthio) benzothiazole	biocide	
2-ethyl-3-propylacrolein	defoamer	
3,5,7-triaza-1-azoniatricyclo(3.3.1.13,7)decane, 1-(3-propenyl)-chloride		1
3-methyl-1-butyn-3-ol		1
4-(1,1-dimethylethyl)phenol, methyloxirane formaldehyde polymer		1
4-nonylphenol polyethylene glycol ether		1
5-chloro-2-methyl-4-isothiazolin-3-one	biocide	
acetic acid	acid treatment, buffer	3,4,5
acetic anhydride		4
acetone	corrosion inhibitor	3,4
acrolein	biocide	
acrylamide		1
acrylamide-sodium acrylate copolymer		1
acrylamide-sodium-2-acrylamido-2-methylpropane sulfonate copolymer	gelling agent	1
adipic acid	linear gel polymer	3
aldehyde	corrosion inhibitor	5
aliphatic acids		1
aliphatic alcohol polyglycol ether		1
aliphatic hydrocarbon (naphthalenesulfonic acid, sodium salt, isopropylated)	surfactant	
alkenes		1
alkyl (C_{14}-C_{16}) olefin sulfonate, sodium salt		1
alkyl amines	foaming agent	4
alkyl aryl polyethoxy ethanol		1
alkylamine salts	foaming agent	3,4
alkylaryl sulfonate		1
alkylphenol ethoxylate surfactants		1
aluminum	crosslinker	3
aluminum chloride		1
aluminum oxide	proppant	
aluminum silicate	proppant	

Table continued on next page

Table continued from previous page

Chemical	Use	Ref.
amine treated hectorite	viscosifier	
ammonia		1
ammonium acetate	buffer	4,5
ammonium alcohol ether sulfate		1
ammonium bifluoride		
ammonium bisulfite	oxygen scavenger	7
ammonium chloride	crosslinker	2,3,5
ammonium citrate		1
ammonium cumene sulfonate		1
ammonium hydrogen difluoride		1
ammonium nitrate		1
ammonium persulfate	breaker fluid	2,3
ammonium sulfate	breaker fluid	3,4
ammonium thiocyanate		1
anionic polyacrylamide copolymer	friction reducer	3,4
anionic surfactants	friction reducer	3,4
aromatic hydrocarbons		
aromatic naphtha	surfactant	
aromatic solvent		4
aromatics		2
asphalite	viscosifier	
attapulgite	gelling agent	
barium sulfate		4
bauxite	proppant	
bentonite	fluid additive	3,4
benzene	gelling agent	2
benzyl chloride-quaternized tar bases, quinoline derivatives		1
bis(1-methylethyl) naphthalene		1
bis(2-methoxyethyl)ether	foaming agent	2
bis(chloroethyl) ether dimethylcocoamine, diquaternary ammonium salt		1
blast furnace slag	viscosifier	
borate salts	crosslinker	7
boric acid	crosslinker	2,3
boric oxide		1
butan-1-ol		1
butane		4
C_{12}-C_{14}-tert-alkyl ethoxylated amines		1
calcium carbonate	pH control	
calcium chloride		1

Table continued on next page

Table continued from previous page

Chemical	Use	Ref.
calcium hydroxide	pH control	
calcium magnesium phosphate		1
calcium oxide	proppant	
carbohydrates		4
carbon black	resin	
carbon dioxide	foaming agent	3,4
carboxymethyl guar	linear gel polymer	3
carboxymethylhydroxypropyl guar	linear gel polymer	3
cationic polymer	friction reducer	3,4
cellulose		1
chlorine	lubricant	
chlorine dioxide		1
chloromethylnaphthalene quinoline quaternary amine	corrosion inhibitor	5
chromium	crosslinker	3
chrome acetate		
citric acid	iron control	6,7
citrus terpenes		1
cocamidopropyl betaine		1
cocamidopropylamine oxide		1
coco-betaine		1
copper compounds	breaker fluid	2,3
copper iodide	breaker fluid	3,4
copper(II) sulfate		1
cottonseed flour		
crissanol A-55		1
crystalline silica	proppant	3,4
cupric chloride dihydrate		1
dazomet	biocide	
decyldimethyl amine		1
diammonium peroxidisulfate	breaker fluid	2,3
diammonium phosphate	corrosion inhibitor	
diatomaceous earth	proppant	
dibromoacetonitrile		1
didecyl dimethyl ammonium chloride	biocide	
diesel	linear gel delivery	2,3
diethanolamine	foaming agent	2,3
diethylbenzene		1
diethylene glycol		4,6
diethylenetriamine	activator	5
diethylenetriamine penta (methylenephonic acid) sodium salt		1

Table continued on next page

Table continued from previous page

Chemical	Use	Ref.
diisopropyl naphthalenesulfonic acid		1
dimethyl formamide		4
dimethyldiallylammonium chloride		1
dipotassium phosphate		4
dipropylene glycol		1
disodium EDTA		1
ditallow alkyl ethoxylated amines		1
D-limonene		1,4
dodecylbenzene		1
dodecylbenzene sulfonic acid		1
dodecylbenzenesulfonate isopropanolamine		1
D-sorbitol		1
EDTA copper chelate	breaker fluid, activator	3,4,5
eo-C7-C9-iso-,C8 rich-alcohols		6
eo-C9-11-iso, C10-rich alcohols		6
erucic amidopropyl dimethyl detaine		1
erythorbic acid, anhydrous		1
ester salt	foaming agent	2
ethane		4
ethanol	foaming agent, non-ionic surfactant	2,3,5
ethoxylated 4-tert-octylphenol		1
ethoxylated alcohols		4,6
ethoxylated alcohols, C6-C10		4
ethoxylated castor oil		1
ethoxylated hexanol		1
ethoxylated 4-nonylphenol	acid inhibitor	
ethoxylated octylphenol		1
ethoxylated sorbitan trioleate		1
ethoxylated, propoxylated trimethylolpropane		1
ethyl lactate		1
ethyl octynol	acid inhibitor	4
ethylbenzene	gelling agent	2
ethylcellulose	fluid additive	
ethylene glycol	crosslinker/breaker fluid/ scale inhibitor	2,3,6
ethylene glycol monobutyl ether		4
ethylene oxide		1
ethyloctynol		1
exxal 13		1
fatty acids		1

Table continued on next page

Table continued from previous page

Chemical	Use	Ref.
fatty alcohol polyglycol ether surfactant		1
ferric chloride		1
ferrous sulfate, heptahydrate		1
fluorene		2
formaldehyde		1
formamide		1
formic acid	acid treatment	2,3
fuller's earth	gelling agent	
fumaric acid	water gelling agent	2,3
galactomannan	gelling agent	
glutaraldehyde	biocide	6,7
glycerine	crosslinker	1,5
glycol ether	foaming agent, breaker fluid	2,3
graphite	fluid additive	
guar gum	linear gel delivery, water gelling agent	2,3,5
gypsum	gellant	
heavy aromatic petroleum naphtha	non-ionic surfactant	4,5
hemicellulase enzyme		4
heptane		4
hydrochloric acid	acid treatment, solvent	2,3,5,6
hydrodesulfurized kerosene		1
hydrofluoric acid	acid treatment	
hydrogen peroxide		1
hydrotreated heavy naphthalene		4
hydrotreated light petroleum	friction reducer	4,5,6
hydrotreated naphtha		1
hydroxy acetic acid		1
hydroxy acetic acid ammonium salt		1
hydroxycellulose	linear gel polymer	3
hydroxyethyl cellulose	gel	7
hydroxylamine hydrochloride		1
hydroxypropyl guar	linear gel polymer	3
iron	emulsifier/surfactant	
iron oxide	proppant	
isobutyl alcohol	fracturing fluid	
isomeric aromatic ammonium salt		1
isooctanol		4
isoparaffinic petroleum hydrocarbons		1
isopropanol	foaming agent/surfactant	2,3,6

Table continued on next page

Table continued from previous page

Chemical	Use	Ref.
isopropylbenzene		1
kerosene		1
kyanite	proppant	
lactose		1
light aromatic solvent naphtha		1
light paraffin oil		1
lignite	fluid additive	
lime		4
magnesium aluminum silicate	gellant	
magnesium chloride	biocide	
magnesium nitrate	biocide	
mercaptoacetic acid	iron control	
metallic copper		4
methane		4
methanol	acid corrosion inhibitor	2,3,5,6
methyl isobutyl ketone		4
methyl tert-butyl ether	gelling agent	2
methyl-4-isothiazolin	biocide	
methylene bis(thiocyanate)	biocide	
methylene phosphonic acid	scale inhibiter	
mica	fluid additive	3,4
mineral oil	friction reducer	7
mineral spirits		1
monoethanolamine	crosslinker	2,3
mullite	proppant	
muriatic acid	acid treatment	7
N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]-ethanaminium chloride homopolymer		1
N,N-dimethylformamide	breaker	7
N,N-dimethyl-methanamine-n-oxide		1
N,N-dimethyl-N-[2-[(1-oxo-2-propenyl)oxy]ethyl]-benzenemethanaminium chloride		1
naphthalene	gelling agent, non-ionic surfactant	2,5,6
N-benzyl-alkyl-pyridinium chloride		1
N-cocamidopropyl-N,N-dimethyl-N-2-hydrooxypropylsulfobetaine		1
n-hexane		4
nickel sulfate	corrosion inhibitor	
nitrogen	foaming agent	3,4
nitrilotriacetamide	scale inhibiter	

Table continued on next page

Table continued from previous page

Chemical	Use	Ref.
nonylphenol polyethoxylate		1
organophilic clays		1
oxyalkylated alkylphenol		1
oxylated alcohol		4
polyaromatic hydrocarbons	gelling agent/bactericide	2,3
pentane		4
petroleum distillates		4
petroleum grease mix		4
petroleum naphtha		1
phenolic resin	proppant	
phenanthrene	biocide	2,3
pine oil		1
poly anionic cellulose		4
poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy	acid corrosion inhibitor, non-ionic surfactant	2,3,5
polyacrylamide	friction reducer	3,7
polycyclic organic matter	gelling agent/bactericide	2,3
polyethene glycol oleate ester		1
polyethoxylated alkanol		1
polyethylene glycol		4,6
polyglycol ether	foaming agent	2,3
polyhexamethylene adipamide	resin	
polyoxyethylene sorbitan monooleate		1
polyoxylated fatty amine salt		1
polypropylene glycol	lubricant	
polysaccharide		
polyvinyl alcohol	fluid additive	
potassium acetate		1
potassium aluminum silicate		4
potassium borate		1
potassium carbonate	pH control	5,7
potassium chloride	brine carrier fluid	2,3
potassium formate		1
potassium hydroxide	crosslinker	2,3
potassium metaborate		4
potassium persulfate	fluid additive	
potassium sorbate		1
propan-2-ol	acid corrosion inhibitor	2,3,5
propane		4
propanol	crosslinker	5
propargyl alcohol	acid corrosion inhibitor	2,3,6

Table continued on next page

Table continued from previous page

Chemical	Use	Ref.
propylene		
propylene glycol monomethyl ether		1
pyridinium,1-(phenylmethyl)-, Et Me derivs., chlorides	corrosion inhibitor	
quartz sand	proppant	7
quaternary ammonium compounds	corrosion inhibitor	1
raffinates (petroleum)		4
salts of alkyl amines	foaming agent	2,3
silica	proppant	7
sodium 1-octanesulfonate		1
sodium acetate		1
sodium acid polyphosphate		4
sodium aluminum phosphate	fluid additive	
sodium benzoate		1
sodium bicarbonate		4
sodium bisulfate		1
sodium bromate	breaker	
sodium bromide		1
sodium carbonate	pH control	7
sodium carboxymethylcellulose	fluid additive	
sodium chloride	brine carrier fluid, breaker	4,5
sodium chlorite	breaker	1,5
sodium chloroacetate		1
sodium citrate		1
sodium dichloro-s-triazinetrione	biocide	
sodium erythorbate		1
sodium glycolate		1
sodium hydroxide	gelling agent	2
sodium hypochlorite		1
sodium ligninsulfonate	surfactant	
sodium mercaptobenzothiazole	corrosion inhibitor	
sodium nitrate	fluid additive	
sodium nitrite	corrosion inhibitor	
sodium metaborate octahydrate		1
sodium perborate tetrahydrate	concentrate	1,5
sodium persulfate		4
sodium polyacrylate		1
sodium sulfate		1
sodium tetraborate decahydrate	crosslinker	2,3
sodium thiosulfate		1
sodium α-olefin sulfonate		1
sorbitan monooleate		1

Table continued on next page

Table continued from previous page

Chemical	Use	Ref.
starch blends	fluid additive	3
styrene	proppant	
sucrose		1
sulfamic acid		1
sulfomethylated tannin		4
talc	fluid additive	3,4
tallow fatty acids sodium salt		1
terpene and terpenoids		1
terpene hydrocarbons		1
tetrachloroethylene		1
tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione		1
tetrakis(hydroxymethyl)phosphonium sulfate		1
tetramethyl ammonium chloride		1
tetrasodium EDTA		1
thioglycolic acid		1
thiourea	acid corrosion inhibitor	2,3
titanium	crosslinker	3
titanium dioxide	proppant	
toluene	gelling agent	2
tributyl phosphate	defoamer	
tributyl tetradecyl phosphonium chloride		1
triethanolamine hydroxyacetate		1
triethanolamine zirconate	crosslinker	5
triethylene glycol		4
trimethylbenzene	fracturing fluid	
trimethyl polyepichlorohydrin		4
tripropylene glycol methyl ether	viscosifier	
trimethylamine hydrochloride		4
trimethylamine quaternized polyepichlorohydrin		1
trisodium nitrilotriacetate		1
trisodium ortho phosphate		1
urea		1
vermiculite	lubricant	
vinylidene chloride		1
water	water gelling agent/ foaming agent	2
xanthum gum	corrosion inhibitor	
xylenes	gelling agent	2
zinc	lubricant	
zinc carbonate	corrosion inhibitor	

Table continued on next page

Table continued from previous page

Chemical	Use	Ref.
zirconium complex	crosslinker	4,5
zirconium nitrate	crosslinker	2,3
zirconium oxychloride	crosslinker	
zirconium sulfate	crosslinker	2,3
zirconium,tetrakis[2-[bis(2-hydroxyethyl)amino-kN]ethanolato-kO]-	crosslinker	
α-[3,5-dimethyl-1-(2-methylpropyl)hexyl]-w-hydroxy-poly(oxy-1,2-ethandiyl)		1

References

1. New York State Department of Environmental Conservation. (2009, September). *Supplemental generic environmental impact statement on the oil, gas and solution mining regulatory program (draft).* Well permit issuance for horizontal drilling and high-volume hydraulic fracturing to develop the Marcellus Shale and other low-permeability gas reservoirs. Albany, NY: New York State Department of Environmental Conservation. Retrieved January 20, 2010, from ftp://ftp.dec.state.ny.us/dmn/download/OGdSGEISFull.pdf.
2. Sumi, L. (2005). *Our drinking water at risk. What EPA and the oil and gas industry don't want us to know about hydraulic fracturing.* Durango, CO: Oil and Gas Accountability Project/Earthworks. Retrieved January 21, 2011, from http://www.earthworksaction.org/pubs/DrinkingWaterAtRisk.pdf.
3. U.S. Environmental Protection Agency. (2004). *Evaluation of impacts to underground sources of drinking water by hydraulic fracturing of coalbed methane reservoirs.* No. EPA/816/R-04/003. Washington, DC: U.S. Environmental Protection Agency, Office of Water.
4. Material Safety Data Sheets; EnCana Oil & Gas (USA), Inc.: Denver, CO. Provided by EnCana upon U.S. EPA Region 8 request as part of the Pavillion, WY, ground water investigation.
5. Material Safety Data Sheets; Halliburton Energy Services, Inc.: Duncan, OK. Provided by Halliburton Energy Services during an on-site visit by EPA on May 10, 2010.
6. Personal communication by Angela McFadden, US EPA Region 3, Philadelphia, PA.
7. Ground Water Protection Council & ALL Consulting. (2009). *Modern shale gas development in the United States: A primer.* Contract DE-FG26-04NT15455. Washington, DC: United States Department of Energy, Office of Fossil Energy and National Energy Technology Laboratory. Retrieved January 19, 2011, from http://www.netl.doe.gov/technologies/oil-gas/publications/EPreports/Shale_Gas_Primer_2009.pdf.

TABLE D2. CHEMICALS IDENTIFIED IN FLOWBACK/PRODUCED WATER

Chemical	Ref.
1,1,1-trifluorotoluene	1
1,4-dichlorobutane	1
2,4,6-tribromophenol	1
2,4-dimethylphenol	2
2,5-dibromotoluene	1
2-butanone	2
2-fluorobiphenyl	1
2-fluorophenol	1
4-nitroquinoline-1-oxide	1
4-terphenyl-d14	1
aluminum	2
anthracene	2
antimony	1
arsenic	2
barium	2
benzene	2
benzo(a)pyrene	2
bicarbonate	1
bis(2-ethylhexyl)phthalate	1
biochemical oxygen demand	1
boron	1,2
bromide	1
bromoform	1
cadmium	2
calcium	2
carbonate alkalinity	1
alkalinity	
chloride	2
chlorobenzene	2
chlorodibromomethane	1
cobalt	1
chemical oxygen demand	1
copper	2
cyanide	1
dichlorobromomethane	1
di-n-butylphthalate	2
ethylbenzene	2
fluoride	1
iron	2
lead	2
lithium	1
magnesium	2
manganese	2
methyl bromide	1
methyl chloride	1
molybdenum	1
n-alkanes, C10-C18	2
n-alkanes, C18-C70	2
n-alkanes, C1-C2	2
n-alkanes, C2-C3	2
n-alkanes, C3-C4	2
n-alkanes, C4-C5	2
n-alkanes, C5-C8	2
naphthalene	2
nickel	2
nitrobenzene-d5	1
oil and grease	2
o-terphenyl	1
p-chloro-m-cresol	2
petroleum hydrocarbons	1
phenol	2
phosphorus	1
potassium	1
radium (226)	2
radium (228)	2
selenium	1
silver	1
sodium	2
steranes	2
strontium	1
strontium (89&90)	
sulfate	1,2
sulfide	1
sulfite	1
TDS	1,2
thallium	1
titanium	2
total organic carbon	1
toluene	2
triterpanes	2
xylene (total)	2
zinc	2
zirconium	1

Table continued on next page

Table continued from previous page

Chemical	Ref.
1,2-bromo-2-nitropropane-1,3-diol (2-bromo-2-nitro-1,3-propanediol or bronopol)	3
1,6-hexanediamine	3
1-3-dimethyladamantane	3
1-methoxy-2-propanol	3
2-(2-methoxyethoxy)ethanol	3
2-(thiocyanomethylthio) benzothiazole	3
2,2,2-nitrilotriethanol	3
2,2-dibromo-3-nitrilopropionamide	3
2,2-dibromoacetonitrile	3
2,2-dibromopropanediamide	3
2-butoxyacetic acid	3
2-butoxyethanol	3
2-butoxyethanol phosphate	3
2-ethyl-3-propylacrolein	3
2-ethylhexanol	3
3,5-dimethyl-1,3,5-thiadiazinane-2-thione	3
5-chloro-2-methyl-4-isothiazolin-3-one	3
6-methylquinoline	3
acetic acid	3
acetic anhydride	3
acrolein	3
acrylamide (2-propenamide)	3
adamantane	3
adipic acid	3
ammonia	4
ammonium nitrate	3
ammonium persulfate	3
atrazine	3
bentazon	3
benzyl-dimethyl-(2-prop-2-enoyloxyethyl)ammonium chloride	3
benzylsuccinic acid	3
beryllium	4
bis(2-ethylhexyl)phthalate	4
bisphenol a	3
boric acid	3
boric oxide	3
butanol	3
cellulose	3
chloromethane	4
chrome acetate	3
chromium	4
chromium hexavalent	
citric acid	3
cyanide	4
decyldimethyl amine	3
decyldimethyl amine oxide	3
diammonium phosphate	3
didecyl dimethyl ammonium chloride	3
diethylene glycol	3
diethylene glycol monobutyl ether	3
dimethyl formamide	3
dimethyldiallylammonium chloride	3
dipropylene glycol monomethyl ether	3
dodecylbenzene sulfonic acid	3
eo-C7-9-iso-,C8 rich-alcohols	3
eo-C9-11-iso, C10-rich alcohols	3
ethoxylated 4-nonylphenol	3
ethoxylated nonylphenol	3
ethoxylated nonylphenol (branched)	3
ethoxylated octylphenol	3
ethyl octynol	3
ethylbenzene	3
ethylcellulose	3
ethylene glycol	3
ethylene glycol monobutyl ether	3
ethylene oxide	3
ferrous sulfate heptahydrate	3
formamide	3
formic acid	3
fumaric acid	3
glutaraldehyde	3
glycerol	3

Table continued on next page

Table continued from previous page

Chemical	Ref.
hydroxyethylcellulose	3
hydroxypropylcellulose	3
isobutyl alcohol (2-methyl-1-propanol)	3
isopropanol (propan-2-ol)	3
limonene	3
mercaptoacidic acid	3
mercury	4
methanamine,N,N-dimethyl-,N-oxide	3
methanol	3
methyl-4-isothiazolin	3
methylene bis(thiocyanate)	3
methylene phosphonic acid (diethylenetriaminepenta[methyl enephosphonic] acid)	3
modified polysaccharide or pregelatinized cornstarch or starch	3
monoethanolamine	3
monopentaerythritol	3
muconic acid	3
N,N,N-trimethyl-2[1-oxo-2-propenyl]oxy ethanaminium chloride	3
nitrazepam	3
nitrobenzene	3
n-methyldiethanolamine	3
oxiranemethanaminium, N,N,N-trimethyl-, chloride, homopolymer	3
phosphonium, tetrakis(hydroxymethly)-sulfate	3
polyacrylamide	3
polyacrylate	3
polyethylene glycol	3
polyhexamethylene adipamide	3
polypropylene glycol	3
polyvinyl alcohol [alcotex 17f-h]	3
propane-1,2-diol	3
propargyl alcohol	3
pryidinium, 1-(phenylmethyl)-, ethyl methyl derivatives, chlorides	3
quaternary amine	3
quaternary ammonium compound	3
quaternary ammonium salts	3
sodium carboxymethylcellulose	3
sodium dichloro-s-triazinetrione	3
sodium mercaptobenzothiazole	3
squalene	3
sucrose	3
tebuthiuron	3
p-terphenyl	3
m-terphenyl	3
o-terphenyl	3
terpineol	3
tetrachloroethene	4
tetramethyl ammonium chloride	3
tetrasodium ethylenediaminetetraacetate	3
thiourea	3
tributyl phosphate	3
trichloroisocyanuric acid	3
trimethylbenzene	3
tripropylene glycol methyl ether	3
trisodium nitrilotriacetate	3
urea	3

References

1. New York State Department of Environmental Conservation. (2009, September*). Supplemental generic environmental impact statement on the oil, gas and solution mining regulatory program (draft).* Well permit issuance for horizontal drilling and high-volume hydraulic fracturing to develop the Marcellus Shale and other low-permeability gas reservoirs. Albany, NY: New York State Department of Environmental Conservation. Retrieved January 20, 2010, from ftp://ftp.dec.state.ny.us/dmn/download/OGdSGEISFull.pdf.
2. Veil, J. A., Puder, M. G., Elcock, D., & Redweik, R. J. (2004). *A white paper describing produced water from production of crude oil, natural gas, and coalbed methane.* Prepared for the U.S. Department of Energy, National Energy Technology Laboratory, contract W-31-109-ENG-38. Argonne, IL: Argonne National Laboratory. Retrieved January 20, 2011, from http://www.netl.doe.gov/technologies/oil-gas/publications/oil_pubs/prodwaterpaper.pdf.
3. URS Operating Services, Inc. (2010, August 20). *Expanded site investigation—Analytical results report. Pavillion area groundwater investigation*. Prepared for U.S. Environmental Protection Agency, contract PO No. EP-W-05-050. Denver, CO: URS Operating Services, Inc. Retrieved January 27, 2011, from http://www.epa.gov/region8/superfund/wy/pavillion/PavillionAnalyticalResultsReport.pdf.
4. Alpha Environmental Consultants, Inc., Alpha Geoscience, & NTS Consultants, Inc. (2009). *Issues related to developing the Marcellus Shale and other low-permeability gas reservoirs.* Prepared for the New York State Energy Research and Development Authority, contract nos. 11169, 10666, and 11170. Albany, NY: New York State Energy Research and Development Authority.

TABLE D3. NATURALLY OCCURRING SUBSTANCES MOBILIZED BY FRACTURING ACTIVITIES

Chemical	Common Valence States	Ref.
aluminum	III	1
antimony	V,III,-III	1
arsenic	V, III, 0, -III	1
barium	II	1
beryllium	II	1
boron	III	1
cadmium	II	1
calcium	II	1
chromium	VI, III	1
cobalt	III, II	1
copper	II, I	1
hydrogen sulfide	N/A	2
iron	III, II	1
lead	IV, II	1
magnesium	II	1
molybdenum	VI, III	1
nickel	II	1
radium (226)	II	2
radium (228)	II	2
selenium	VI, IV, II, 0, -II	1
silver	I	1
sodium	I	1
thallium	III, I	1
thorium	IV	2
tin	IV, II, -IV	1
titanium	IV	1
uranium	VI, IV	2
vanadium	V	1
yttrium	III	1
zinc	II	1

References

1. Sumi, L. (2005). *Our drinking water at risk: What EPA and the oil and gas industry don't want us to know about hydraulic fracturing*. Durango, CO: Oil and Gas Accountability Project/Earthworks. Retrieved January 21, 2011, from http://www.earthworksaction.org/pubs/DrinkingWaterAtRisk.pdf.
2. Sumi, L. (2008). *Shale gas: Focus on the Marcellus Shale*. Durango, CO: Oil and Gas Accountability Project/Earthworks. Retrieved January 21, 2011, from http://www.earthworksaction.org/pubs/OGAPMarcellusShaleReport-6-12-08.pdf.

APPENDIX E: ASSESSING MECHANICAL INTEGRITY

In relation to hydrocarbon production, it is useful to distinguish between the internal and external mechanical integrity of wells. Internal mechanical integrity is concerned with the containment of fluids within the confines of the well. External mechanical integrity is related to the potential movement of fluids along the wellbore outside the well casing.

A well's mechanical integrity can be determined most accurately through a combination of data and tests that individually provide information, which can then be compiled and evaluated. This appendix provides a brief overview of the tools used to assess mechanical well integrity.

CEMENT BOND TOOLS

The effectiveness of the cementing process is determined using cement bond tools and/or cement evaluation tools. Cement bond tools are acoustic devices that produce data (cement bond logs) used to evaluate the presence of cement behind the casing. Cement bond logs generally include a gamma-ray curve and casing collar locator; transit time, which measures the time it takes for a specific sound wave to travel from the transmitter to the receiver; amplitude curve, which measures the strength of the first compressional cycle of the returning sound wave; and a graphic representation of the waveform, which displays the manner in which the received sound wave varies with time. This latter presentation, the variable density log, reflects the material through which the signal is transmitted. To obtain meaningful data, the tool must properly calibrated and be centralized in the casing to obtain data that is meaningful for proper evaluation of the cement behind the casing.

Other tools available for evaluating cement bonding use ultrasonic transducers arranged in a spiral around the tool or in a single rotating hub to survey the circumference of the casing. The transducers emit ultrasonic pulses and measure the received ultrasonic waveforms reflected from the internal and external casing interfaces. The resulting logs produce circumferential visualizations of the cement bonds with the pipe and borehole wall. Cement bonding to the casing can be measured quantitatively, while bonding to the formation can only be measured qualitatively. Even though cement bond/evaluation tools do not directly measure hydraulic seal, the measured bonding qualities do provide inferences of sealing.

The cement sheath can fail during well construction if the cement fails to adequately encase the well casing or becomes contaminated with drilling fluid or formation material. After a well has been constructed, cement sheath failure is most often related to temperature- and pressure-induced stresses resulting from operation of the well (Ravi et al., 2002). Such stresses can result in the formation of a microannulus, which can provide a pathway for the migration of fluids from high-pressure zones.

TEMPERATURE LOGGING

Temperature logging can be used to determine changes that have taken place in and adjacent to injection/production wells. The temperature log is a continuous recording of temperature versus depth. Under certain conditions the tool can be used to conduct a flow survey, locating points of inflow or

outflow in a well; locate the top of the cement in wells during the cement curing process (using the heat of hydration of the cement); and detect the flow of fluid and gas behind the casing. The temperature logging tool is the oldest of the production tools and one of the most versatile, but a highly qualified expert must use it and interpret its results.

Noise Logging

The noise logging tool may have application in certain conditions to detect fluid movement within channels in cement in the casing/borehole annulus. It came into widespread application as a way to detect the movement of gas through liquid. For other flows, for example water through a channel, the tool relies on the turbulence created as the water flows through a constriction that creates turbulent flow. Two advantages of using the tool are its sensitivity and lateral depth of investigation. It can detect sound through multiple casings, and an expert in the interpretation of noise logs can distinguish flow behind pipe from flow inside pipe.

Pressure Testing

A number of pressure tests are available to assist in determining the internal mechanical integrity of production wells. For example, while the well is being constructed, before the cement plug is drilled out for each casing, the casing should be pressure-tested to find any leaks. The principle of such a "standard pressure test" is that pressure applied to a fixed-volume enclosed vessel, closed at the bottom and the top, should remain constant if there are no leaks. The same concept applies to the "standard annulus pressure test," which is used when tubing and packers are a part of the well completion.

The "Ada" pressure test is used in some cases where the well is constructed with tubing without a packer, in wells with only casing and open perforations, and in dual injection/production wells.

The tools discussed above are summarized below in Table E1.

TABLE E1. COMPARISON OF TOOLS USED TO EVALUATE WELL INTEGRITY

Type of Tool	Description and Application	Types of Data
Acoustic cement bond tools	Acoustic devices to evaluate the presence of cement behind the casing	• Gamma-ray curve • Casing collar locator: depth control • Transit time: time it takes for a specific sound wave to travel from the transmitter to the receiver • Amplitude curve: strength of the first compressional cycle of the returning sound wave • Waveform: variation of received sound wave over time • Variable density log: reflects the material through which the signal is transmitted
Ultrasonic transducers	Transmit ultrasonic pulses and measure the received ultrasonic waveforms reflected from the internal and external casing interfaces to survey well casing	• Circumferential visualizations of the cement bonds with the pipe and borehole wall • Quantitative measures of cement bonding to the casing • Qualitative measure of bonding to the formation • Inferred sealing integrity
Temperature logging	Continuous recording of temperature versus depth to detect changes in and adjacent to injection/production wells	• Flow survey • Points of inflow or outflow in a well • Top of cement in wells during the cement curing process (using the heat of hydration of the cement) • Flow of fluid and gas behind casing
Noise logging tool	Recording of sound patterns that can be correlated to fluid movement; sound can be detected through multiple casings	• Fluid movement within channels in cement in the casing/borehole annulus
Pressure tests	Check for leaks in casing	• Changes in pressure within a fixed-volume enclosed vessel, implying that leaks are present

References

Ravi, K., Bosma, M., & Gastebled, O. (2002, April 30-May 2). *Safe and economic gas wells through cement design for life of the well.* No. SPE 75700. Presented at the Society of Petroleum Engineers Gas Technology Symposium, Calgary, Alberta, Canada.

APPENDIX F: STAKEHOLDER-NOMINATED CASE STUDIES

This appendix lists the stakeholder-nominated case studies. Potential retrospective case study sites can be found in Table F1, while potential prospective case study sites are listed in Table F2.

TABLE F1. POTENTIAL RETROSPECTIVE CASE STUDY SITES

Formation	Location	Key Areas to be Addressed	Key Activities	Potential Outcomes	Partners
Bakken Shale	Killdeer and Dunn Co., ND	Production well failure during hydraulic fracturing; suspected drinking water aquifer contamination; surface waters nearby; soil contamination; more than 2,000 barrels of oil and fracturing fluids leaked from the well	Monitoring wells to evaluate extent of contamination of aquifer; soil and surface water monitoring	Determine extent of contamination of drinking water resources; identify sources of well failure	NDDMR-Industrial Commission, EPA Region 8, Berthold Indian Reservation
Barnett Shale	Alvord, TX	Benzene in water well			RRCTX, landowners, USGS, EPA Region 6
Barnett Shale	Azle, TX	Skin rash complaints from contaminated water			RRCTX, landowners, USGS, EPA Region 6
Barnett Shale	Decatur, TX	Skin rash complaints from drilling mud applications to land			RRCTX, landowners, USGS, EPA Region 6

Table continued on next page

Table continued from previous page

Formation	Location	Key Areas to be Addressed	Key Activities	Potential Outcomes	Partners
Barnett Shale	Wise/Denton Cos. (including Dish), TX	Potential drinking water well contamination; surface spills; waste pond overflow; documented air contamination	Monitor other wells in area and install monitoring wells to evaluate source(s)	Determine sources of contamination of private well	RRCTX, TCEQ, landowners, City of Dish, USGS, EPA Region 6, DFW Regional Concerned Citizens Group, North Central Community Alliance, Sierra Club
Barnett Shale	South Parker Co. and Weatherford, TX	Hydrocarbon contamination in multiple drinking water wells; may be from faults/fractures from production well beneath properties	Monitor other wells in area; install monitoring wells to evaluate source(s)	Determine source of methane and other contaminants in private water well; information on role of fracture/fault pathway from HF zone	RRCTX, landowners, USGS, EPA Region 6
Barnett Shale	Tarrant Co., TX	Drinking water well contamination; report of leaking pit	Monitoring well	Determine if pit leak impacted underlying ground water	RRCTX, landowners, USGS, EPA Region 6
Barnett Shale	Wise Co. and Decatur, TX	Spills; runoff; suspect drinking water well contamination; air quality impacts	Sample wells, soils	Determine sources of contamination of private well	RRCTX, landowners, USGS, EPA Region 6, Earthworks Oil & Gas Accountability Project
Clinton Sandstone	Bainbridge, OH	Methane buildup leading to home explosion			OHDNR, EPA Region 5

Table continued on next page

Table continued from previous page

Formation	Location	Key Areas to be Addressed	Key Activities	Potential Outcomes	Partners
Fayetteville Shale	Arkana Basin, AR	General water quality concerns			AROGC, ARDEQ, EPA Region 6
Fayetteville Shale	Conway Co., AR	Gray, smelly water			AROGC, ARDEQ, EPA Region 6
Fayetteville Shale	Van Buren or Logan Cos., AR	Stray gas (methane) in wells; other water quality impairments			AROGC, ARDEQ, EPA Region 6
Haynesville Shale	Caddo Parish, LA	Drinking water impacts (methane in water)	Monitoring wells to evaluate source(s)	Evaluate extent of water well contamination and if source is from HF operations	LGS, USGS, EPA Region 6
Haynesville Shale	DeSoto Parish, LA	Drinking water reductions	Monitoring wells to evaluate water availability; evaluate existing data	Determine source of drinking water reductions	LGS, USGS, EPA Region 6
Haynesville Shale	Harrison Co., TX	Stray gas in water wells			RRCTX, landowners, USGS, EPA Region 6
Marcellus Shale	Bradford Co., PA	Drinking water well contamination; surface spill of HF fluids	Soil, ground water, and surface water sampling	Determine source of methane in private wells	PADEP, landowners, EPA Region 3, Damascus Citizens Group, Friends of the Upper Delaware
Marcellus Shale	Clearfield Co., PA	Well blowout			PADEP, EPA Region 3

Table continued on next page

Table continued from previous page

Formation	Location	Key Areas to be Addressed	Key Activities	Potential Outcomes	Partners
Marcellus Shale	Dimock, Susquehanna Co., PA	Contamination in multiple drinking water wells; surface water quality impairment from spills	Soil, ground water, and surface water sampling	Determine source of methane in private wells	PADEP, EPA Region 3, landowners, Damascus Citizens Group, Friends of the Upper Delaware
Marcellus Shale	Gibbs Hill, PA	On-site spills; impacts to drinking water; changes in water quality	Evaluate existing data; determine need for additional data	Evaluate extent of large surface spill's impact on soils, surface water, and ground water	PADEP, landowner, EPA Region 3
Marcellus Shale	Hamlin Township and McKean Co., PA	Drinking water contamination from methane; changes in water quality	Soil, ground water, and surface water sampling	Determine source of methane in community and private wells	PADEP, EPA Region 3, Schreiner Oil & Gas
Marcellus Shale	Hickory, PA	On-site spill; impacts to drinking water; changes in water quality; methane in wells; contaminants in drinking water (acrylonitrile, VOCs)			PADEP, landowner, EPA Region 3
Marcellus Shale	Hopewell Township, PA	Surface spill of HF fluids; waste pit overflow	Sample pit and underlying soils; sample nearby soil, ground water, and surface water	Evaluate extent of large surface spill's impact on soils, surface water, and ground water	PADEP, landowners, EPA Region 3
Marcellus Shale	Indian Creek Watershed, WV	Concerns related to wells in karst formation			WVOGCC, EPA Region 3

Table continued on next page

Table continued from previous page

Formation	Location	Key Areas to be Addressed	Key Activities	Potential Outcomes	Partners
Marcellus Shale	Lycoming Co., PA	Surface spill of HF fluids	PADEP sampled soils, nearby surface water, and two nearby private wells; evaluate need for additional data collection to determine source of impact	Evaluate extent of large surface spill's impact on soils, surface water, and ground water	PADEP, EPA Region 3
Marcellus Shale	Monongahela River Basin, PA	Surface water impairment (high TDS, water availability)	Data exists on water quality over time for Monongahela River during ramp up of HF activity; review existing data	Assess intensity of HF activity	USACE, USGS, EPA Region 3
Marcellus Shale	Susquehanna River Basin, PA and NY	Water availability; water quality	Assess water use and water quality over time; review existing data	Determine if water withdrawals for HF are related to changes in water quality and availability	USGS may do a study here as well
Marcellus Shale	Tioga Co., NY	General water quality concerns			NYDEP, EPA Region 2, Earthworks
Marcellus Shale	Upshur Co., WV	General water quality concerns			WVOGCC, EPA Region 3
Marcellus Shale	Wetzel Co., WV, and Washington/ Green Cos., PA	Stray gas; spills; changes in water quality; several landowners concerned about methane in wells	Soil, ground water, and surface water sampling	Determine extent of impact from spill of HF fluids associated with well blowout and other potential impacts to drinking water resources	WVDEP, WVOGCC, PADEP, EPA Region 3, landowners, Damascus Citizens Group
Piceance Basin	Battlement Mesa, CO	Water quality and quantity concerns			COGCC, landowners, EPA Region 8

Table continued on next page

Table continued from previous page

Formation	Location	Key Areas to be Addressed	Key Activities	Potential Outcomes	Partners
Piceance Basin (tight gas sand)	Garfield Co., CO (Mamm Creek area)	Drinking water well contamination; changes in water quality; water levels	Soil, ground water, and surface water sampling; review existing data	Evaluate source of methane and degradation in water quality basin-wide	COGCC, landowners, EPA Region 8, Colorado League of Women Voters
Piceance Basin	Rifle, CO	Water quality and quantity concerns			COGCC, landowners, EPA Region 8
Piceance Basin	Silt, CO	Water quality and quantity concerns			COGCC, landowners, EPA Region 8
Powder River Basin (CBM)	Clark, WY	Drinking water well contamination	Monitoring wells to evaluate source(s)	Evaluate extent of water well contamination and if source is from HF operations	WOOGC, EPA Region 8, landowners
San Juan Basin (shallow CBM and tight sand)	LaPlata Co., CO	Drinking water well contamination, primarily with methane (area along the edge of the basin has large methane seepage)	Large amounts of data have been collected through various studies of methane seepage; gas wells at the margin of the basin can be very shallow	Evaluate extent of water well contamination and determine if HF operations are the source	COGCC, EPA Region 8, BLM, San Juan Citizens Alliance
Raton Basin (CBM)	Huerfano Co., CO	Drinking water well contamination; methane in well water; well house explosion	Monitoring wells to evaluate source of methane and degradation in water quality	Evaluate extent of water well contamination and determine if HF operations are the source	COGCC, EPA Region 8
Raton Basin (CBM)	Las Animas Co., CO	Concerns about methane in water wells			COGCC, landowners, EPA Region 8

Table continued on next page

Table continued from previous page

Formation	Location	Key Areas to be Addressed	Key Activities	Potential Outcomes	Partners
Raton Basin (CBM)	North Fork Ranch, Las Animas Co., CO	Drinking water well contamination; changes in water quality and quantity	Monitoring wells to evaluate source of methane and degradation in water quality	Evaluate extent of water well contamination and determine if HF operations are the source	COGCC, landowners, EPA Region 8
Tight gas sand	Garfield Co., CO	Drinking water and surface water contamination; documented benzene contamination	Monitoring to assess source of contamination	Determine if contamination is from HF operations in area	COGCC, EPA Region 8, Battlement Mesa Citizens Group
Tight gas sand	Pavillion, WY	Drinking water well contamination	Monitoring wells to evaluate source(s) (ongoing studies by ORD and EPA Region 8)	Determine if contamination is from HF operations in area	WOGCC, EPA Region 8, landowners
Tight gas sand	Sublette Co. WY (Pinedale Anticline)	Drinking water well contamination (benzene)	Monitoring wells to evaluate source(s)	Evaluate extent of water well contamination and determine if HF operations are the source	WOGCC, EPA Region 8, Earthworks

Within the scope of this study, prospective case studies will focus on key areas such as the full lifecycle and environmental monitoring. To address these issues, key research activities will include water and soil monitoring before, during, and after hydraulic fracturing activities.

TABLE F2. PROSPECTIVE CASE STUDIES

Formation	Location	Potential Outcomes	Partners
Bakken Shale	Berthold Indian Reservation, ND	Baseline water quality data, comprehensive monitoring and modeling of water resources during all stages of the HF process	NDDMR-Industrial Commission, University of North Dakota, EPA Region 8, Berthold Indian Reservation
Barnett Shale	Flower Mound/ Bartonville, TX	Baseline water quality data, comprehensive monitoring and modeling of water resources during all stages of the HF process	NDDMR-Industrial Commission, EPA Region 8, Mayor of Flower Mound
Marcellus Shale	Otsego Co., NY	Baseline water quality data, comprehensive monitoring and modeling of water resources during all stages of the HF process	NYSDEC; Gastem, USA; others TBD
Marcellus Shale	TBD, PA	Baseline water quality data, comprehensive monitoring and modeling of water resources during all stages of the HF process in a region of the country experiencing intensive HF activity	Chesapeake Energy, PADEP, others TBD
Marcellus Shale	Wyoming Co, PA	Baseline water quality data, comprehensive monitoring and modeling of water resources during all stages of the HF process	DOE, PADEP, University of Pittsburgh, Range Resources, USGS, landowners, EPA Region 3
Niobrara Shale	Laramie Co., WY	Baseline water quality data, comprehensive monitoring and modeling of water resources during all stages of the HF process, potential epidemiology study by Wyoming Health Department	WOGCC, Wyoming Health Department, landowners, USGS, EPA Region 8
Woodford Shale or Barnett Shale	OK or TX	Baseline water quality data, comprehensive monitoring and modeling of water resources during all stages of the HF process	OKCC, landowners, USGS, EPA Region 6

Acronym List

ARDEQ	Arkansas Department of Environmental Quality
AROGC	Arkansas Oil and Gas Commission
BLM	Bureau of Land Management
CBM	Coalbed methane
Co.	County
COGCC	Colorado Oil and Gas Conservation Commission
DFW	Dallas–Fort Worth
DOE	United States Department of Energy
EPA	United States Environmental Protection Agency
HF	Hydraulic fracturing
LGS	Louisiana Geological Survey
NDDMR	North Dakota Department of Mineral Resources
NYSDEC	New York Department of Environmental Conservation
OHDNR	Ohio Department of Natural Resources
OKCC	Oklahoma Corporation Commission
PADEP	Pennsylvania Department of Environmental Protection
RRCTX	Railroad Commission of Texas
TBD	To be determined
TCEQ	Texas Commission on Environmental Quality
USACE	United States Army Corps of Engineers
USGS	United States Geological Survey
VOC	Volatile organic compound
WOGCC	Wyoming Oil and Gas Conservation Commission
WVDEP	West Virginia Department of Environmental Protection
WVOGCC	West Virginia Oil and Gas Conservation Commission

APPENDIX G: FIELD SAMPLING AND ANALYTICAL METHODS

Field samples and monitoring data associated with hydraulic fracturing activities are collected for a variety of reasons, including to:

- Develop baseline data prior to fracturing.
- Monitor any changes in drinking water resources during and after hydraulic fracturing.
- Identify and quantify environmental contamination that may be associated with hydraulic fracturing.
- Evaluate well mechanical integrity.
- Evaluate the performance of treatment systems.

Field sampling is important for both the prospective and retrospective case studies discussed in Chapter 7. In retrospective case studies, EPA will take field samples to determine the cause of reported drinking water contamination. In prospective case studies, field sampling and monitoring provides for the identification of baseline conditions of the site prior to drilling and fracturing. Additionally, data will be collected during each step in the oil or natural gas drilling operation, including hydraulic fracturing of the formation and oil or gas production, which will allow EPA to monitor changes in drinking water resources as a result of hydraulic fracturing.

The case study site investigations will use monitoring wells and other available monitoring points to identify (and determine the quantity of) chemical compounds relevant to hydraulic fracturing activities in the subsurface environment. These compounds may include the chemical additives found in hydraulic fracturing fluid and their reaction/degradation products, as well as naturally occurring materials (e.g., formation fluid, gases, trace elements, radionuclides, and organic material) released during fracturing events.

This appendix first describes types of samples (and analytes associated with those samples) that may be collected throughout the oil and natural gas production process and the development and refinement of laboratory-based analytical methods. It then discusses the potential challenges associated with analyzing the collected field samples. The appendix ends with a summary of the data analysis process as well as a discussion of the evaluation of potential indicators associated with hydraulic fracturing activities.

FIELD SAMPLING: SAMPLE TYPES AND ANALYTICAL FOCUS

Table G1 lists monitoring and measurement parameters for both retrospective and prospective case studies. Note that samples taken in retrospective case studies will be collected after hydraulic fracturing has occurred and will focus on collecting evidence of contamination of drinking water resources. Samples taken for prospective case studies, however, will be taken during all phases of oil and gas production and will focus on improving EPA's understanding of hydraulic fracturing activities.

TABLE G1. MONITORING AND MEASUREMENT PARAMETERS AT CASE STUDY SITES

Sample Type	Case Study Site	Parameters
Surface and ground water (e.g., existing wells, new wells) Soil/sediments, soil gas	Prospective and retrospective (collect as much historical data as available)	• General water quality (e.g., pH, redox, dissolved oxygen) and water chemistry parameters (e.g., cations and anions) • Dissolved gases (e.g., methane) • Stable isotopes (e.g., Sr, Ra, C, H) • Metals • Radionuclides • Volatile and semi-volatile organic compounds, polycyclic aromatic hydrocarbons • Soil gas sampling in vicinity of proposed/actual hydraulic fracturing well location (e.g., Ar, He, H_2, O_2, N_2, CO_2, CH_4, C_2H_6, C_2H_4, C_3H_6, C_3H_8, iC_4H_{10}, nC_4H_{10}, iC_5H_{12})

Flowback and produced water	Prospective	• General water quality (e.g., pH, redox, dissolved oxygen, total dissolved solids) and water chemistry parameters (e.g., cations and anions)
		• Metals
		• Radionuclides
		• Volatile and semi-volatile organic compounds, polycyclic aromatic hydrocarbons
		• Sample fracturing fluids (time series sampling)
		  ○ Chemical concentrations
		  ○ Volumes injected
		  ○ Volumes recovered

Drill cuttings, core samples	Prospective	• Metals • Radionuclides • Mineralogic analyses

Table G1 indicates that field sampling will focus primarily on water and soil samples, which will be analyzed for naturally occurring materials and chemical additives used in hydraulic fracturing fluid, including their reaction products and/or degradates. Drill cuttings and core samples will be used in laboratory experiments to analyze the chemical composition of the formation and to explore chemical reactions between hydraulic fracturing fluid additives and the hydrocarbon-containing formation.

Data collected during the case studies are not restricted to the collection of field samples. Other data include results from mechanical integrity tests and surface geophysical testing. Mechanical well integrity can be assessed using a variety of tools, including acoustic cement bond tools, ultrasonic transducers, temperature and noise logging tools, and pressure tests (see Appendix E). Geophysical testing can assess geologic and hydrogeologic conditions, detect and map underground structures, and evaluate soil and rock properties.

Field Sampling Considerations

Samples collected from drinking water taps or treatment systems will reflect the temperature, pressure, and redox conditions associated with the sampling site and may not reflect the true conditions in the subsurface, particularly in dissolved gas concentrations. In cases where dissolved gases are to be analyzed, special sampling precautions are needed. Because the depths of hydraulic fracturing wells can exceed 1,000 feet, ground water samples will be collected from settings where the temperature and

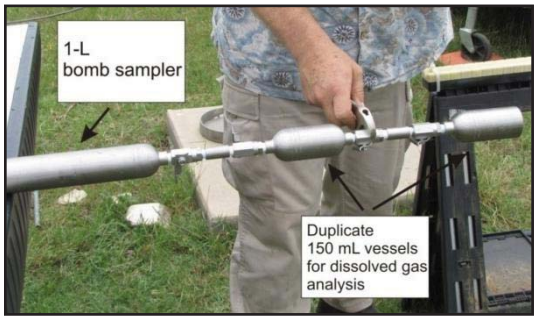


FIGURE G1. BOMB SAMPLER

pressure are significantly higher than at the surface. When liquid samples are brought to the surface, decreasing pressure can lead to off-gassing of dissolved gases (such as methane) and to changes in redox potential and pH that can lead to changes in the speciation and solubility of minerals and metals. Therefore, the sampling of water from these depths will require specialized sampling equipment that maintains the pressure of the formation until the sample is analyzed. One possible approach for this type of sampling is to employ a bomb sampler (shown in Figure G1) with a double-valve configuration that activates a series of stainless steel sampling vessels to collect pressurized ground water in one sampling pass.

Development and Refinement of Laboratory-Based Analytical Methods

The ability to characterize chemical compounds related to hydraulic fracturing activities depends on the ability to detect and quantify individual constituents using appropriate analytical methods. As discussed in Chapter 6, EPA will identify the chemical additives used in hydraulic fracturing fluids as well as those found in flowback and produced water, which may include naturally occurring substances and reaction/degradation products of fracturing fluid additives. The resulting list of chemicals will be analyzed for existing analytical methods. Where analytical methods exist, detailed information will be compiled on detection limits, interferences, accuracy, and precision. In other instances, standardized analytical methods may not be readily available for use on the types of samples generated by hydraulic fracturing activities. In these situations, a prioritization strategy informed by risk, case studies, and experimental and modeling investigations will be used to develop analytical methods for high-priority chemicals in relevant environmental matrices (e.g., brines).

The sampling and analytical chemistry requirements depend on the specific goals of the field investigation (e.g., detection, quantification, toxicity, fate and transport). Sample types may include formulations of hydraulic fracturing fluid systems, water samples (e.g., ambient water, flowback, and produced water), drilling fluids, soil, and solid residues. In many cases, samples may reflect the presence of multiple phases (gas-liquid-solid) that impact chemical partitioning in the environment. Table G2 briefly discusses the types of analytical instrumentation that can be applied to samples collected during field investigations (both retrospective and prospective case studies).

TABLE G2. OVERVIEW OF ANALYTICAL INSTRUMENTS THAT CAN BE USED TO IDENTIFY AND QUANTIFY CONSTITUENTS ASSOCIATED WITH HYDRAULIC FRACTURING ACTIVITIES

Type of Analyte	Analytical Instrument(s)	MDL Range*
Volatile organics	GC/MS: gas chromatograph/mass spectrometer GC/MS/MS: gas chromatograph/mass spectrometer/ mass spectrometer	0.25–10 µg/L
Water-soluble organics	LC/MS/MS: liquid chromatograph/mass spectrometer/mass spectrometer	0.01–0.025 µg/L
Unknown organic compounds	LC/TOF: liquid chromatograph/time-of-flight mass spectrometer	5 µg/L
Metals, minerals	ICP: inductively coupled plasma	1–100 µg/L
	GFAA: graphite furnace atomic absorption	0.5–1 µg/L
Transition metals, isotopes	ICP/MS: inductively coupled plasma/mass spectrometer	0.5–10 µg/L
Redox-sensitive metal species, oxyanion speciation, thioarsenic speciation, etc.	LC/ICP/MS: liquid chromatograph/inductively coupled plasma/mass spectrometer	0.5–10 µg/L
Ions (charged elements or compounds)	IC: ion chromatograph	0.1–1 mg/L

*The minimum detection limit, which depends on the targeted analyte.

POTENTIAL CHALLENGES

The analysis of field samples collected during case studies is not without challenges. Two anticipated challenges are discussed below: matrix interference and the analysis of unknown chemical compounds.

MATRIX INTERFERENCE

The sample matrix can affect the performance of the analytical methods being used to identify and quantify target analytes; typical problems include interference with the detector signal (suppression or amplification) and reactions with the target analyte, which can reduce the apparent concentration or complicate the extraction process. Some potential matrix interferences are listed in Table G3.

TABLE G3. EXAMPLES OF MATRIX INTERFERENCES THAT CAN COMPLICATE ANALYTICAL APPROACHES USED TO CHARACTERIZE SAMPLES ASSOCIATED WITH HYDRAULIC FRACTURING

Type of Matrix Interference	Example Interferences	Potential Impacts on Chemical Analysis
Chemical	• Inorganics: metals, minerals, ions • Organics: coal, shale, hydrocarbons • Dissolved gases: methane, hydrogen sulfide, carbon dioxide • pH • Oxidation potential	• Complexation or co-precipitation with analyte, impacting extraction efficiency, detection, and recovery • Reaction with analyte changing apparent concentration • Impact on pH, oxidation potential, microbial growth • Impact on solubility, microbial growth
Biological	• Bacterial growth	• Biodegradation of organic compounds, which can change redox potential, or convert electron acceptors (iron, sulfur, nitrogen, metalloids)
Physical	• Pressure and temperature • Dissolved and suspended solids • Geologic matrix	• Changes in chemical equilibria, solubility, and microbial growth • Release of dissolved minerals, sequestration of constituents, and mobilization of minerals, metals

Some gases and organic compounds can partition out of the aqueous phase into a non-aqueous phase (already present or newly formed), depending on their chemical and physical properties. With the numbers and complex nature of additives used in hydraulic fracturing fluids, the chemical composition of each phase depends on partitioning relationships and may depend on the overall composition of the mixture. The unknown partitioning of chemicals to different phases makes it difficult to accurately determine the quantities of target analytes. In order to address this issue, EPA has asked for chemical and physical properties of hydraulic fracturing fluid additives in the request for information sent to the nine hydraulic fracturing service providers.

Analysis of Unknown Chemical Compounds

Once injected, hydraulic fracturing fluid additives may maintain their chemical structure, partially or completely decompose, or participate in reactions with the surrounding strata, fluids, gases, or microbes. These reactions may result in the presence of degradates, metabolites, or other transformation products, which may be more or less toxic than the parent compound and consequently increase or decrease the risks associated with hydraulic fracturing formulations. The identification and quantification of these products may be difficult, and can be highly resource intensive and time-consuming. Therefore, the purpose of each chemical analysis will need to be clearly articulated to ensure that the analyses are planned and performed in a cost-effective manner.

Data Analysis

The data collected by EPA during retrospective case studies will be used to determine the source and extent of reported drinking water contamination. In these cases, EPA will use different methods to investigate the sources of contamination and the extent to which the contamination has occurred. One important method to determine the source and migration pathways of natural gas is isotopic

fingerprinting, which compares both the chemical composition and the isotopic compositions of natural gas. Although natural gas is composed primarily of methane, it can also include ethane, propane, butane, and pentane, depending on how it is formed. Table G4 illustrates different types of gas, the constituents, and the formation process of the natural gas.

TABLE G4. TYPES OF NATURAL GASES, CONSTITUENTS, AND PROCESS OF FORMATION

Type of Natural Gas	Constituents	Process of Formation
Thermogenic gas	Methane, ethane, propane, butane, and pentane	Geologic formation of fossil fuel
Biogenic gas	Methane and ethane	Methane-producing microorganisms chemically break down organic material

Thermogenic light hydrocarbons detected in soil gas typically have a well-defined composition indicative of reservoir composition. Above natural gas reservoirs, methane dominates the light hydrocarbon fraction; above petroleum reservoirs, significant concentrations of ethane, propane, and butane are found (Jones et al., 2000). Also, ethane, propane, and butane are not produced by biological processes in near-surface sediments; only methane and ethylene are products of biodegradation. Thus, elevated levels of methane, ethane, propane, and butane in soil gas indicate thermogenic origin and could serve as tracers for natural gas migration from a reservoir.

The isotopic signature of methane can also be used to delineate the source of natural gas migration in retrospective case studies because it varies with the formation process. Isotopic fingerprinting uses two parameters—$\delta^{13}C$ and δD—to identify thermogenic and biogenic methane. These two parameters are equal to the ratio of the isotopes $^{13}C/^{12}C$ and D/H, respectively. Baldassare and Laughrey (1997), Schoell (1980, 1983), Kaplan et al. (1997), Rowe and Muehlenbachs (1999), and others have summarized values of $\delta^{13}C$ and δD for methane, and their data show that it is often possible to distinguish methane formed from biogenic and thermogenic processes by plotting $\delta^{13}C$ versus δD. Thus, the isotopic signature of methane recovered from retrospective case study sites can be compared to the isotopic signature of potential sources of methane near the contaminated site. Isotopic fingerprinting of methane, therefore, could be particularly useful for determining if the methane is of thermogenic origin and in situations where multiple methane sources are present.

In prospective case studies, EPA will use the data collected from field samples to (1) provide a comprehensive picture of drinking water resources during all stages in the hydraulic fracturing water lifecycle and (2) inform hydraulic fracturing models, which may then be used to predict impacts of hydraulic fracturing on drinking water resources.

Evaluation of Potential Indicators of Contamination

Natural gas is not the only potential chemical indicator for gas migration due to hydraulic fracturing activities: Hydrogen sulfide, hydrogen, and helium may also be used as potential tracers. Hydrogen sulfide is produced during the anaerobic decomposition of organic matter by sulfur bacteria, and can be found in varying amounts in sulfur deposits, volcanic gases, sulfur springs, and unrefined natural gas and

petroleum, making it a potential indicator of natural gas migration. Hydrogen gas (H_2) and helium (He) are widely recognized as good fault and fracture indicators because they are chemically inert, physically stable, and highly insoluble in water (Klusman, 1993; Ciotoli et al., 1999 and 2004). For example, H_2 and He have been observed in soil gas at values up to 430 and 50 ppmv respectively over the San Andreas Fault in California (Jones and Pirkle, 1981), and Wakita et al. (1978) has observed He at a maximum concentration of 350 ppmv along a nitrogen vent in Japan. The presence of He in soil gas is often independent of the oil and gas deposits. However, since He is more soluble in oil than water, it is frequently found at elevated concentrations in soil gas above natural gas and petroleum reservoirs and hence may serve as a natural tracer for gas migration.

EPA will use the data collected from field samples to identify and evaluate other potential indicators of hydraulic fracturing fluid migration into drinking water supplies. For example, flowback and produced water have higher ionic strengths (due to large concentrations of potassium and chloride) than surface waters and shallow ground water and may also have different isotopic compositions of strontium and radium. Although potassium and chloride are often used as indicators of flowback or produced water, they are not considered definitive. However, if the isotopic composition of the flowback or produced water differs significantly from those of nearby drinking water resources, then isotopic ratios could be sensitive indicators of contamination. Recent research by Peterman et al. (2010) lends support for incorporating such analyses into this study. Additionally, DOE NETL is working to determine if stable isotopes can be used to identify Marcellus flowback and produced water when commingled with surface waters or shallow ground water. EPA also plans to use this technique to evaluate contamination scenarios in the retrospective case studies and will coordinate with DOE on this aspect of the research.

References

Baldassare, F. J., & Laughrey, C. D. (1997). Identifying the sources of stray methane by using geochemical and isotopic fingerprinting. *Environmental Geosciences*, *4*, 85-94.

Ciotoli, G., Etiope, G., Guerra, M., & Lombardi, S. (1999). The detection of concealed faults in the Ofanto basin using the correlation between soil-gas fracture surveys. *Tectonophysics*, *299*, 321-332.

Ciotoli, G., Lombardi, S., Morandi, S., & Zarlenga, F. (2004). A multidisciplinary statistical approach to study the relationships between helium leakage and neotectonic activity in a gas province: The Vasto basin, Abruzzo-Molise (central Italy). *The American Association of Petroleum Geologists Bulletin*, *88*, 355-372.

Jones, V. T., & Pirkle, R. J. (1981, March 29-April 3). *Helium and hydrogen soil gas anomalies associated with deep or active faults*. Presented at the American Chemical Society Annual Conference, Atlanta, GA.

Jones, V. T., Matthews, M. D., & Richers, D. M. (2000). Light hydrocarbons for petroleum and gas prospecting. In M. Hale (Ed.), *Handbook of Exploration Geochemistry* (pp. 133-212). Elsevier Science B.V.

Kaplan, I. R., Galperin, Y., Lu, S., & Lee, R. (1997). Forensic environmental geochemistry—Differential of fuel-types, their sources, and release time. *Organic Geochemistry*, *27*, 289-317.

Klusman, R. W. (1993). *Soil gas and related methods for natural resource exploration.* New York, NY: John Wiley & Sons.

Peterman, Z. E., Thamke, J., & Futa, K. (2010, May 14). *Strontium isotope detection of brine contamination of surface water and groundwater in the Williston Basin, northeastern Montana*. Presented at the GeoCanada Annual Conference, Calgary, Alberta, Canada.

Rowe, D., & Muehlenbachs, K. (1999). Isotopic fingerprinting of shallow gases in the western Canadian sedimentary basin—Tools for remediation of leaking heavy oil wells. *Organic Geochemistry*, *30*, 861-871.

Schoell, M. (1980). The hydrogen and carbon isotopic composition of methane from natural gases of various origin. *Geochimica et Cosmochimica Acta*, *44*, 649-661.

Schoell, M. (1983). Genetic characteristics of natural gases. *American Association of Petroleum Geologists Bulletin*, *67*, 2225-2238.

Wakita, H., Fujii, N., Matsuo, S., Notsu, K., Nagao, K., & Takaoka, N. (1978, April 28). Helium spots: Caused by diapiric magma from the upper mantle. *Science*, *200*(4340), 430-432.

APPENDIX H: MODELING

It is standard practice to evaluate and model complex environmental systems as separate components, as can be the case with water operations associated with hydraulic fracturing. For example, system components can be classified based on media type, such as water body models, ground water models, watershed models, and waste unit models. Additionally, models can be chosen based on whether a stochastic or deterministic representation is needed, solution types (e.g., analytical, semi-analytical or numerical), spatial resolution (e.g., grid, raster, or vector), or temporal resolution (e.g., steady-state or time-variant).

For a holistic systems approach, it is important to evaluate how the components interact with each other, and how the entire system responds. This integration is often achieved by either loosely or tightly coupling individual system components with fully integrated complete system models available.

Modeling will be important in both case studies and scenario evaluations. The prospective case studies provide an opportunity to test our level of understanding by comparing model performance to field observations. This understanding will help justify the use of specific models for hypothesis testing during the retrospective studies. Finally, demonstrated understanding provides the foundation for predicting system response under future scenarios.

CASE STUDIES

PROSPECTIVE CASE STUDIES

Application and testing of models will be integrated into the prospective case studies. By collecting characterization data prior to hydraulic fracturing, baseline conditions can be determined and used to generate the mathematically required initial conditions for the model. The modeling team will participate in planning the field effort in order to generate the specific types of data required. From this starting point, the ability of the models to represent hydraulic fracturing operations can be evaluated by comparing initial-to-final conditions in the model with those generated from field sampling.

For example, from a ground water modeling perspective, various aspects of the hydraulic fracturing process can be investigated, including:

- The pressure pulse resulting from fracturing.
- Potential indicators of well construction faults.
- The flow and composition of the flowback and produced water.
- Possible early time impacts to water supply wells.

Ground water modeling for prospective case studies may match a site conceptual model that is expected to include the following geologic elements:

- Shale beds located at depths of 1,000 feet or greater.
- Aquifers consisting of heterogeneous geologic formations.
- Unconsolidated, consolidated, and fractured consolidated materials.

- Possible presence of abandoned and improperly sealed wells.

Subsurface transport is expected to include:

- Flow of reactive chemical species.
- Potential importance of temperature and pressure effects.
- Mixtures of inorganic and organic chemicals.
- Two-phase flow of water and gas.

The sites are expected to require:

- Simulation in three dimensions, although some simple questions are expected to be answerable by one- or two-dimensional analyses.
- Time-dependent simulations in which the time scales include short times for chemical reaction and long times for transport to drinking water wells.
- Site-, region-, and basin-scale evaluations.

The simulation of a hydraulic fracturing operation shares many characteristics with certain types of petroleum reservoir simulations. As a consequence, the modeling studies may be computationally intensive. Specific research questions will be developed for each aspect of the hydraulic fracturing case study. From these and site data, a conceptual model will be developed for model application. An appropriately chosen model can then be used in answering the research question. Following this process ensures that the level of complexity of the model will be appropriate but not excessive.

Retrospective Case Studies

Modeling can play an important role in the testing of hypotheses of cause and effect. The forensic studies will take the step-wise and progressive strategy, starting with simple conceptualizations and adding complexity as data and understanding supports.

Scenario Testing

While the scenarios will be initially approached through separate evaluations of the different water operations (e.g., water acquisition, chemical mixing, well injection, flowback and produced water, wastewater treatment and waste disposal), full systems evaluations will require integrated systems modeling.

Modeling Tools

The types of models to be used in this study may include:

Multi-phase and multi-component ground water models. Members of the TOUGH family of models developed at Lawrence Berkeley National Laboratory can be used to simulate the flow and transport phenomena in fractured zones, where geothermal and geochemical processes are active, where permeability changes, and where phase-change behavior is important. These codes been adapted for problems requiring capabilities that will be also needed for hydraulic fracturing simulation: multiphase

and multi-component transport, geothermal reservoir simulation, geologic sequestration of carbon, geomechanical modeling of fracture activation and creation, and inverse modeling.

Single-phase and multi-component ground water models. These include the finite difference solutions, such as represented by the USGS Modular Flow (MODFLOW) and its associated transport codes, including Modular Transport 3D-Multispecies (MT3DMS) or the related Reactive Transport 3D (RT3D), and the finite element solutions, such as the Finite Element Subsurface Flow Model (FEFLOW), and others semi-analytical solutions (e.g., GFLOW and TimML). Various chemical and/or biological reactions can be integrated into the advective ground water flow models to allow the simulation of reaction flow and transport in the aquifer system. For a suitably conceptualized system consisting of single-phase transport of water-soluble chemicals, these models have potential for supporting hydraulic fracturing assessments.

Watershed models. EPA has experience with the well-established watershed management models SWAT (semi-empirical, vector-based, continuous in time) and HSPF (semi-physics-based, vector-based, continuous in time). A number of innovative watershed models are under development, including GBMM (semi-physics based, gridded, continuous in time) and VELMA (semi-empirical, gridded, continuous in time). The watershed models will play an important role in modeling water acquisition.

Waterbody models. The well-established EPA model for representing water quality in rivers and reservoirs is Water Quality Analysis Simulation Program (WASP). EPA has invested in Environmental Fluid Dynamics Code (EFDC) for a more detailed representation of hydrodynamics in water bodies.

Alternative futures models. Alternative futures analysis involves three basic components (Baker et al., 2004): (1) characterize the current and historical landscapes in a geographic area, and the trajectory of the landscape to date; (2) develop two or more alternative "visions" or scenarios for the future landscape that reflect varying assumptions about land and water use and the range of stakeholder viewpoints; and (3) evaluate the likely effects of these landscape changes and alternative futures on things people care about (e.g., valued endpoints). Fortunately for this project, EPA has conducted alternative futures analysis for much of the landscape of interest for this project. The EPA Region 3 Chesapeake Bay Program futures scenarios extrapolate to 2030 for a region that covers much of the Marcellus shale play. The EPA ORD Futures Midwest Landscape study includes a future landscape for 2022 for a region that covers Colorado and North Dakota. We currently do not have an EPA futures coverage for the Barnett Shale play.

Integrated modeling systems. The EPA has led a multi-agency development of the Framework for Risk Analysis in Multimedia Environmental Systems (FRAMES) platform for integrated multi-media, multi-component, multi-receptor risk assessment. FRAMES is currently being applied to the mountaintop mining issues in West Virginia in cooperation with EPA Region 3. Other platforms available for water resources evaluations include the DHI Mike SHE. Research continues at the University of Waterloo on the integrated ground water/surface water three-dimensional simulator HydroGeoSphere. Full, integrated modeling is beyond the scope of this research plan, but may play an important role in future hydraulic fracturing investigations.

CALIBRATION AND UNCERTAINTY IN MODEL APPLICATIONS

Hydraulic fracturing models will be calibrated with data to show that they simulate the changes from the pre- and post-hydraulic fracturing of the formation; this provides the minimum testing of the model. Where possible, it is strongly desired to test the calibration of the models using a second data set. For example, initial gas production data can be used to calibrate the model, while data collected later should be used to test the calibration.

All model parameters are uncertain because of measurement approximation and error, uncharacterized point-to-point variability, reliance on estimates, and imprecise scale-up from laboratory measurements. Model outputs are subject to uncertainty, even after model calibration (e.g., Tonkin and Dougherty, 2008). Thus, environmental models do not possess generic validity (Oreskes et al., 1994), but the application is critically dependent on choices of input parameters which are subject to the uncertainties described above. Proper application of models requires acknowledgement of uncertainties, which can lead to best scientific credibility for the results and by extension the Agency (see Oreskes, 2003).

The accomplishment of this task is dependent on the complexity of the simulation model, the time available, and the computer resources available. At one extreme, where the models are very compute-time extensive (as expected for the full hydraulic fracturing simulation), it may only be possible to explore a limited number of plausible alternative parameter sets. For more simple models a variant of Monte Carlo simulation could be used to generate many alternate results that could be analyzed statistically to present a formal probability of a result.

Some available tools include the Design Analysis Kit for Optimization and Terascale Applications (DAKOTA) and Computer Codes for Universal Sensitivity Analysis, Calibration, and Uncertainty Evaluation (UCODE-2005); Parameter Estimation (PEST) and iTOUGH2 could be used for suitably conceptualized problems.

References

Baker, J. P., Hulse, D. W., Gregory, S. V., White, D., van Sickle, J., Berger, P. A., Dole, D., & Schumaker, N. H. (2004). Alternative futures for the Willamette River Basin, Oregon. *Ecological Applications*, *14*(2), 313-324.

Oreskes, N. K., Shrader-Frechette, K., & Belitz, K. (1994, February 4). Verification, validation, and confirmation of numerical models in the earth sciences. *Science*, *263*(5147), 641-646.

Oreskes, N. K. (2003). The role of quantitative models in science. In C. D. Canham, J. J. Cole, & W. K. Lauenroth (Eds.), *Models in ecosystem science* (pp. 13-31). Princeton, NJ: Princeton University Press.

Tonkin, M., & Dougherty, J. (2009). Efficient nonlinear predictive error variance for highly parameterized models. *Water Resources Research*, *45.*

GLOSSARY

Abandoned well: A well that is no longer in use, whether dry, inoperable, or no longer productive.[1]

Aerobic: Life or processes that require, or are not destroyed by, the presence of oxygen.[2]

Anaerobic: A life or process that occurs in, or is not destroyed by, the absence of oxygen.[2]

Analyte: A substance or chemical constituent being analyzed.[3]

Aquiclude: An impermeable body of rock that may absorb water slowly, but does not transmit it.[4]

Aquifer: An underground geological formation, or group of formations, containing water. A source of ground water for wells and springs.[2]**Aquitard:** A geological formation that may contain ground water but is not capable of transmitting significant quantities of it under normal hydraulic gradients.[2]

Assay: A test for a specific chemical, microbe, or effect.[2]

Biocide: Any substance the kills or retards the growth of microorganisms.[5]

Biodegradation: The chemical breakdown of materials under natural conditions.[2]

Casing: Pipe cemented in the well to seal off formation fluids and to keep the hole from caving in.[1]

Coalbed: A geological layer or stratum of coal parallel to the rock stratification.

Flowback water: 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. Both the process and the returned water are commonly referred to as "flowback."[6]

Fluid leakoff: The process by which injected fracturing fluid migrates from the created fractures to other areas within the hydrocarbon-containing formation.

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]

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]

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-laden gelled fluid into subsurface rock formations in order to improve flow into a wellbore.[1]

Hydraulic fracturing water lifecycle: The lifecycle 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.

Impoundment: A body of water or sludge confined by a dam, dike, floodgate, or other barrier.[2]

Mechanical integrity: An injection well has mechanical integrity if: (1) there is no significant leak in the casing, tubing, or packer (internal mechanical integrity) and (2) there is no significant fluid movement into an underground source of drinking water through vertical channels adjacent to the injection wellbore (external mechanical integrity).[7]

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 is methane.[1]

Naturally occurring radioactive materials: All radioactive elements found in the environment, including long-lived radioactive elements such as uranium, thorium, and potassium and any of their decay products, such as radium and radon.

Play: A set of oil or gas accumulations sharing similar geologic and geographic properties, such as source rock, hydrocarbon type, and migration pathways.[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.[8]

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.[9]

Prospective case study: 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 EPA to evaluate changes in water quality over time and to assess the fate and transport of chemical contaminants.

Public water system: A system for providing the public with water for human consumption (through pipes or other constructed conveyances) that has at least 15 service connections or regularly serves at least 25 individuals.[10]

Redox (oxidation-reduction) reaction: A chemical reaction involving transfer or electrons from one element to another.[3]

Residential well: A pumping well that serves one home or is maintained by a private owner.[5]

Retrospective case study: A study of sites that have (or have had) active hydraulic fracturing practices, with a focus on sites with reported instances of drinking water resource contamination or other impacts

in areas where hydraulic fracturing has already occurred. These studies will use existing data and possibly field sampling, modeling, and/or parallel laboratory investigations to determine the likelihood that reported impacts are due to hydraulic fracturing activities.

Shale: A fine-grained sedimentary rock composed mostly of consolidated clay or mud. Shale is the most frequently occurring sedimentary rock.[9]

Source water: Operators may withdraw water from surface or ground water sources themselves or may purchase it from suppliers.[6]

Subsurface: Earth material (as rock) near but not exposed at the surface of the ground.[11]

Surface water: All water naturally open to the atmosphere (rivers, lakes, reservoirs, ponds, streams, impoundments, seas, estuaries, etc.).[2]

Tight sands: A geological formation consisting of a matrix of typically impermeable, non-porous tight sands.

Total dissolved solids (TDS): All material that passes the standard glass river filter; also called total filterable residue. Term is used to reflect salinity.[2]

Turbidity: A cloudy condition in water due to suspended silt or organic matter.[2]

Underground injection well: A steel- and concrete-encased shaft into which hazardous waste is deposited by force and under pressure.[2]

Underground source of drinking water (USDW): An aquifers currently being used as a source of drinking water or capable of supplying a public water system. USDWs have a TDS content of 10,000 milligrams per liter or less, and are not "exempted aquifers."[2]

Vadose zone: The zone between land surface and the water table within which the moisture content is less than saturation (except in the capillary fringe) and pressure is less than atmospheric. Soil pore space also typically contains air or other gases. The capillary fringe is included in the vadose zone.[2]

Water table: The level of ground water.[2]

References

1. Oil and Gas Mineral Services. (2010). *Oil and gas terminology*. Retrieved January 20, 2011, from http://www.mineralweb.com/library/oil-and-gas-terms.
2. U.S. Environmental Protection Agency. (2006). *Terms of environment: Glossary, abbreviations and acronyms*. Retrieved January 20, 2011, from http://www.epa.gov/OCEPAterms/aterms.html.
3. Harris, D. C. (2003). *Quantitative chemical analysis.* Sixth edition. New York, NY: W. H. Freeman and Company.

4. Geology Dictionary. (2006). *Aquiclude.* Retrieved January 30, 2011, from http://www.alcwin.org/Dictionary_Of_Geology_Description-136-A.htm.
5. Webster's New World College Dictionary. (1999). Fourth edition. Cleveland, OH: Macmillan USA.
6. New York State Department of Environmental Conservation. (2009, September). *Supplemental generic environmental impact statement on the oil, gas and solution mining regulatory program (draft). Well permit issuance for horizontal drilling and high-volume hydraulic fracturing to develop the Marcellus Shale and other low-permeability gas reservoirs*. Albany, NY: New York State Department of Environmental Conservation, Division of Mineral Resources, Bureau of Oil & Gas Regulation. Retrieved January 20, 2011, from ftp://ftp.dec.state.ny.us/dmn/download/OGdSGEISFull.pdf.
7. U. S. Environmental Protection Agency. (2010). *Glossary of underground injection control terms.* Retrieved January 19, 2011, from http://www.epa.gov/r5water/uic/glossary.htm#ltds.
8. Ground Water Protection Council & ALL Consulting. (2009, April). *Modern shale gas development in the United States: A primer.* Contract DE-FG26-04NT15455. Prepared for the U.S. Department of Energy, Office of Fossil Energy and National Energy Technology Laboratory. Retrieved January 20, 2011, from http://www.netl.doe.gov/technologies/oil-gas/publications/EPreports/Shale_Gas_Primer_2009.pdf.
9. U.S. Department of the Interior. *Bureau of Ocean Energy Management, Regulation and Enforcement: Offshore minerals management glossary*. Retrieved January 20, 2011, from http://www.mms.gov/glossary/d.htm.
10. U. S. Environmental Protection Agency. (2010.) *Definition of a public water system.* Retrieved January 30, 2011, from http://water.epa.gov/infrastructure/drinkingwater/pws/pwsdef2.cfm.
11. Merriam-Webster's Dictionary. (2011). *Subsurface*. Retrieved January 20, 2011, from http://www.merriam-webster.com/dictionary/subsurface.

Recycled/Recyclable
Printed with vegetable-based ink on paper that contains a minimum of 50% post-consumer fiber and is processed chlorine free.

EPA/600/D-11/001/February 2011/www.epa.gov/research

United States
Environmental Protection
Agency

PRESORTED STANDARD
POSTAGE & FEES PAID
EPA
PERMIT NO. G-35

Office of Research and Development (8101R)
Washington, DC 20460

Official Business
Penalty for Private Use
$300