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)

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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.

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[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

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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	

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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

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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

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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

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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

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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	

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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

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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

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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	

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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

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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

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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

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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[methylenephosphonic] 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

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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.
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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

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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.
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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

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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

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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

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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

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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

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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

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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

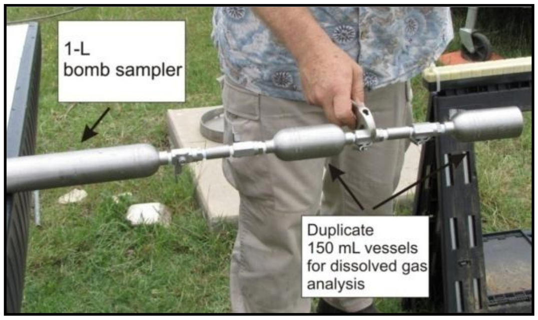

FIGURE G1. BOMB SAMPLER

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.

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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.

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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]

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