United States Environmental Protection Agency

Technical Roundtables on EPA's Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources

CHEMICAL MIXING

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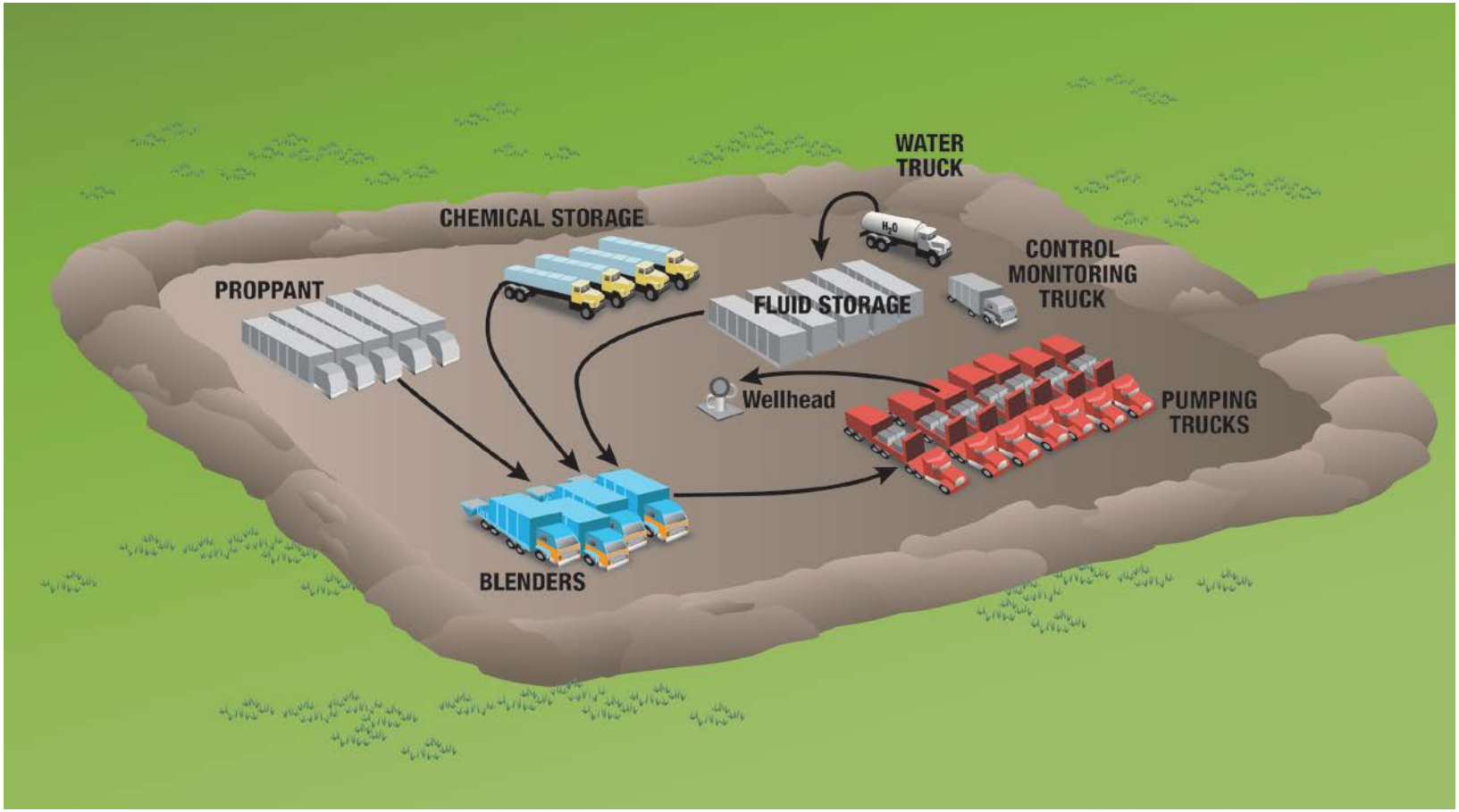
Chemical Mixing



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

Chemical Mixing Research Projects

Secondary Research Questions	Applicable Research Projects
1. What are the identities and volumes of chemicals used in hydraulic fracturing fluids, and how might this composition vary at a given site and across the country?	Literature Review Service Company Analysis FracFocus Analysis Analytical Method Development
2. What are the chemical, physical, and toxicological properties of hydraulic fracturing chemical additives?	Toxicity Assessment
3. What is currently known about the frequency, severity, and causes of spills of hydraulic fracturing fluids and additives?	Literature Review Spills Database Analysis Service Company Analysis Well File Review
4. If spills occur, how might hydraulic fracturing chemical additives contaminate drinking water resources?	Literature Review Case Studies (Dunn County, ND; Bradford County, PA; Wise County, TX)

Analysis of Existing Data

United States Environmental Protection Agency

Data Sources

Literature Review
Existing papers and reports, focusing on peer-reviewed literature

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- Chemicals used in fluids along with their environmental fate and transport
- Spills of HF fluids and chemical additives

Service Company Analysis
Information about HF operations provided by nine service companies

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- Chemicals used in HF fluids
- Spills of HF fluids and chemical additives

Spills Database Analysis
Database compiled by EPA containing data on surface spills of hydraulic fracturing fluids and wastewaters

→

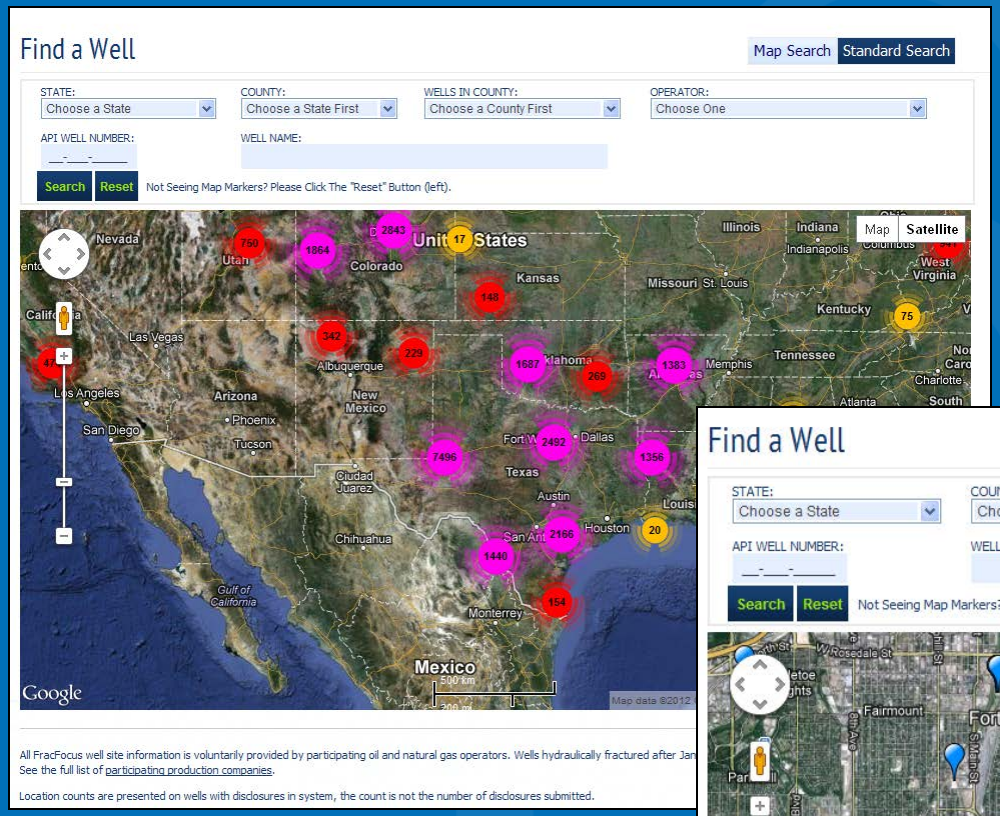
Spill information from National Response Center database, Five state databases (CO, NM, NY, PA, TX), and data from nine service companies

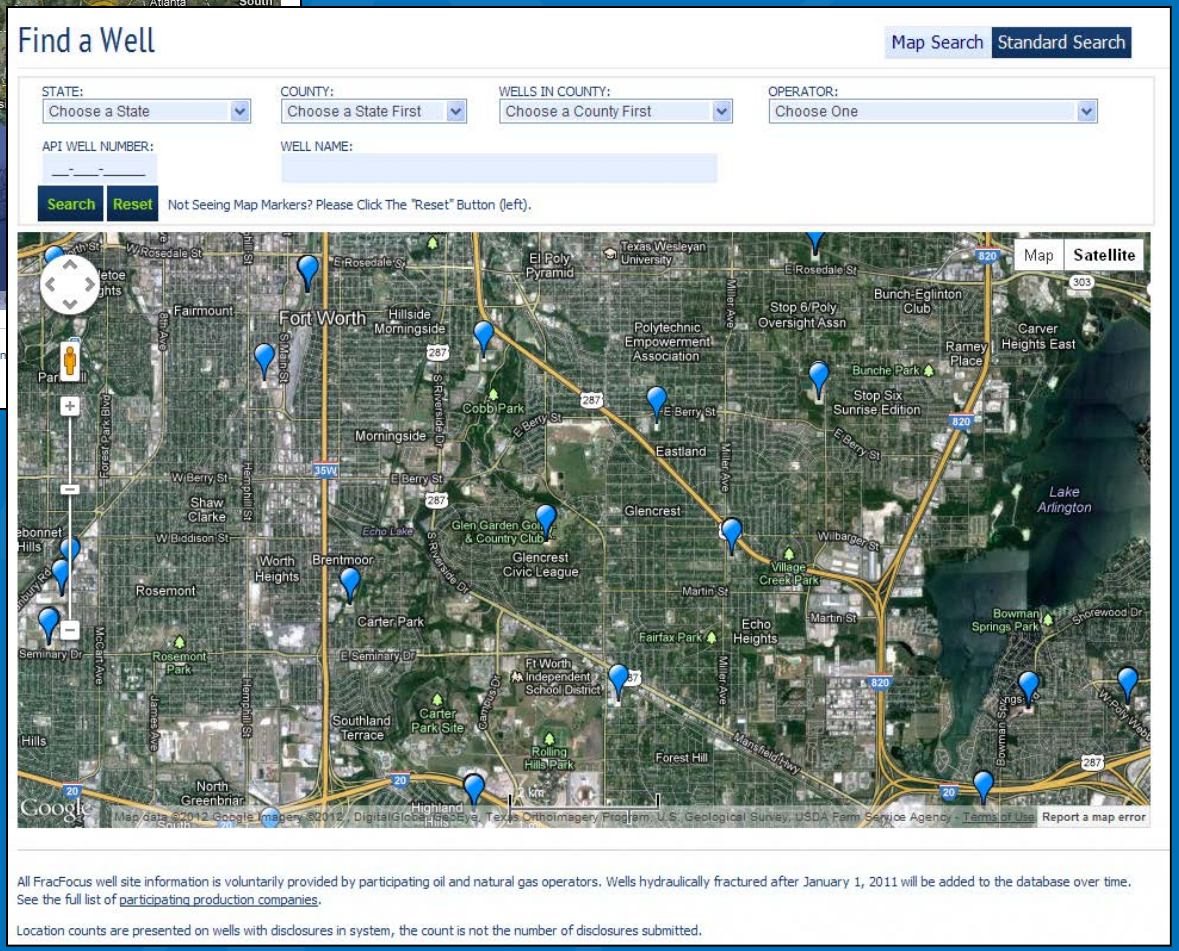
Anticipated Data

Analysis of Existing Data

Data Sources	Anticipated Data
Well File Review Well-specific records provided by nine oil and gas operators	Spill data for **333** wells hydraulically fractured in 2009 and 2010
FracFocus Analysis National Registry for chemicals used in hydraulic fracturing	Reported chemicals with frequency, amounts, and geographic location of usage

FracFocus





Office of Research and Development

FracFocus

Hydraulic Fracturing Fluid Product Component Information Disclosure

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

Mockup for discussion purposes only

Hydraulic Fracturing Fluid Composition:

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

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

* Total Fluid Volume sources may include fresh water, produced water, and/or recycled water, or other fluids such as propane
** Information is based on the maximum potential for concentration and thus the total may be over 100%
*** Name of company or individual that requested proprietary status under a state or federal law
N/A means Not applicable
Proprietary means a chemical that is non disclosable under a state or federal law protecting confidential business information or trade secrets.

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

Sample disclosure provided by the Ground Water Protection Council

Analysis of Existing Data

RESEARCH PROGRESS:

- Literature review is underway.
- Data has been collected from spills database, service companies, oil and gas operators, FracFocus.
- Databases have been developed.
- Data review and analysis is underway.

NEXT STEPS:

- Perform analyses to address research questions.
- Determine how best to summarize confidential business information.

Toxicity Assessment

OBJECTIVE:

To gather existing data regarding toxicity associated with the chemicals found in hydraulic fracturing fluids and wastewaters to support future risk screening and assessments.

APPROACH:

- Identify chemicals reportedly used in hydraulic fracturing.
  - ❑ Chemicals found in hydraulic fracturing fluids
  - ❑ Chemicals found in flowback and produced water
- Identify physicochemical properties of chemicals.
- Identify available toxicity reference values (cancer and noncancer).
- Conduct Quantitative Structure-Activity Relationship (QSAR) modeling to predict potential toxicity.

Toxicity Assessment

RESEARCH PROGRESS:

- Preliminary list of chemicals in hydraulic fracturing fluid and/or flowback and produced water
  - ~1100 unique chemical substances
  - ~800 chemicals with chemical structures
  - ~400 chemicals with physicochemical properties
- Calculating physicochemical properties based on chemical structures
- Developing the Toxicity Reference Value Spreadsheet
  - Integrated Risk Information System
  - Provisional Peer-Reviewed Toxicity Values
  - Agency for Toxic Substances and Disease Registry
  - State authoritative values
  - Other
- Calculating Lowest Observed Adverse Effect Levels using QSAR models

Toxicity Assessment Example

Chemical Name	Health-Based Values		Regulatory Values
	Noncancer	Cancer	
	IRIS RfD (mg/kg-day)	IRIS Oral Slope Factor (mg/kg-day)	MCL (mg/L)
Benzene	0.004	0.015-0.055	0.005
Toluene	0.08	N/A	1
Ethylbenzene	0.1	N/A	0.7
Xylenes (total)	0.2	N/A	10

IRIS: EPA Integrated Risk Information System
RfD: Reference Dose
MCL: Regulatory Maximum Contaminant Level under the Safe Drinking Water Act
N/A: insufficient data available

Toxicity Assessment

NEXT STEPS:

- Identify additional state-based reference value data sources.
- Complete QSAR modeling to predict potential toxicity of chemicals without authoritative toxicity reference values.

Analytical Methods Development

OBJECTIVE:

To improve selected methods so that they provide necessary detection and quantitation limits in complex matrices.

APPROACH:

- Select methods for adaptation and development based on considerations such as:
  - Frequency of occurrence in fracturing fluids and wastewaters
  - Existence and performance of methods for analytes of interest
  - Mobility in the environment
  - Availability of instrumentation/detection systems

Analytical Methods Development

APPROACH (Cont.):

- Develop method
  - ❑ Identify/select base method
  - ❑ Conduct QA/QC round of testing
  - ❑ Modify method, if appropriate
- Verify method
- Validate method

Analytical Methods Development

RESEARCH PROGRESS:

- Currently working on:
  - Glycols and related compounds
  - Acrylamide
  - Ethoxylated alcohols
  - Disinfection byproducts
  - Radionuclides
  - Metals

NEXT STEPS:

- Verify and validate identified methods

Questions for Discussion

1) As hydraulic fracturing companies change their formulations and go "green," what are the trends in chemical usage (e.g., are they using less of a given compound, using more of a given compound; what are the new chemicals)?

2) What tracers are used in hydraulic fracturing? What are the trends in tracer use and identity? What are the detection methods and detection limits for the tracers?