Chemical Disclosure Programs for Hydraulic Fracturing Fluids: *Challenges for Environmental Laboratories*

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CHEMICAL DISCLOSURE

Chemical Disclosure for Hydraulic Fracturing Fluids

- Hydraulic Fracturing has been successful used for over 60 years
  - Oil and Natural Gas Wells, both vertical and horizontal
  - Water Wells
- Many of the concerns about hydraulic fracturing have centered on the desire to know what chemicals are used in the process

Chemical Disclosure for Hydraulic Fracture Fluids

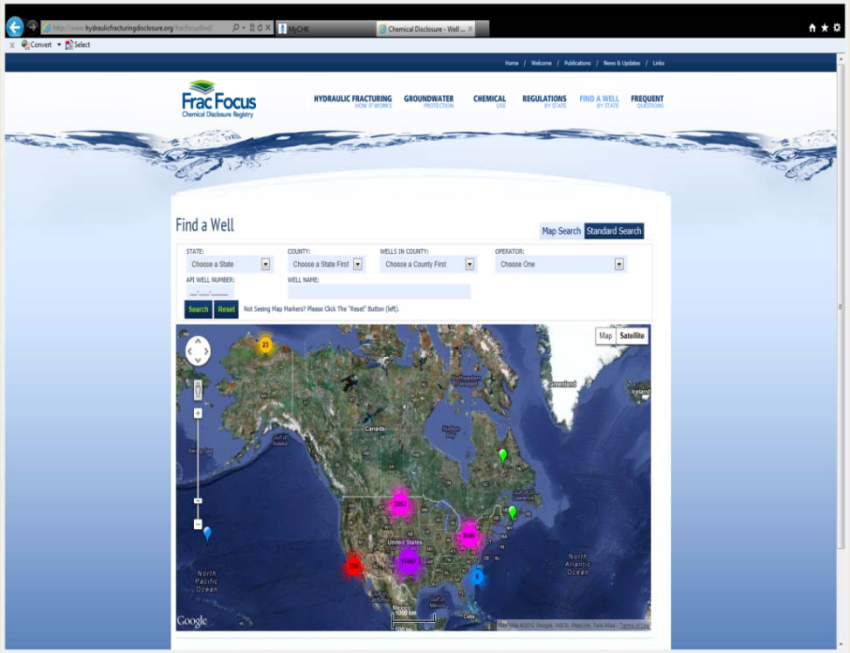
- Voluntary and regulatory efforts have been implemented to address these concerns
  - Intent is to provide the public readily accessible information about the chemicals being used to fracture wells
  - Generally based on information available from the Material Safety Data Sheet (MSDS) available for the product
    - MSDS is required by the OSHA Hazard Communication Standard
    - OSHA established thresholds for product ingredient reporting
    - Provisions for some products to remain proprietary
  - Some critics have called for "full" disclosure

FracFocus

- Voluntary Program
  - www.fracfocus.org
- Operated by Groundwater Protection Council and Interstate Oil and Gas Compact Commission
- Being utilized by state regulatory agencies
  - Several states, including Texas, Oklahoma, Colorado, Louisiana, and New Mexico, require its use
  - Several states are considering utilizing the registry to meet chemical disclosure regulations

FracFocus Chemical Disclosure Registry

- Over 20,000 disclosures have been voluntarily posted since February, 2011
- The "Find A Well" feature is used to search for wells by name, location, etc.
- For each well, the output contains information regarding location, products used and volumes used, and concentrations in the hydraulic fracturing fluid
- Has provisions for non-MSDS listed chemicals to be posted as well



Hydraulic Fracturing Fluid Product Component Information Disclosure

Fracture Date:	3/4/2012
State:	LOUISIANA
County:	SABINE
API Number:	1708522353
Operator Name:	CHESAPEAKE
Well Name and Number:	EVANS 26-10-14 1H
Longitude:	-93.76859
Latitude:	31.817183
Long/Lat Projection:	NAD27
Production Type:	GAS
True Vertical Depth (TVD):	11,831
Total Water Volume (gal)*:	4,412,982

Hydraulic Fracturing Fluid Composition:

Trade Name	Supplier	Purpose	Ingredients	Chemical Abstract Service Number (CAS #)	Maximum Ingredient Concentration in Additive (% by Mass)**	Maximum Ingredient Concentration in HF Fluid (% by Mass)**	Comments
Fresh Water		Carrier/Base Fluid				85.20813%	
Premium White		Proppant	Crystalline Silica (Quartz Sand, Silicon Dioxide)	014808-60-7	100.00%	8.65919%	
PRC Premium		Proppant	Crystalline Silica (Quartz Sand, Silicon Dioxide)	014808-60-7	98.00%	5.34021%	
			Phenol/Formaldehyde Resin	009003-35-4	5.00%	0.27246%	
			Hexamethylenetetramine (Hexamine)	000100-97-0	1.00%	0.05449%	
15 hcl	TRICAN	Acid	Water	007732-18-5	85.00%	0.03545%	
			Hydrochloric Acid	007647-01-0	15.00%	0.00626%	
FORMIC ACID	TRICAN	Acid	Formic Acid	000064-18-6	85.00%	0.00060%	
			Water	007732-18-5	15.00%	0.00011%	
LAI-20	TRICAN	Corrosion Inhibitor	Methanol (Methyl Alcohol)	000067-56-1	40.00%	0.00033%	
			Propargyl Alcohol (2-Propynol)	000107-19-7	8.00%	0.00007%	
FEAC-30	TRICAN	Iron Control Agent	Acetic Acid	000064-19-7	60.00%	0.00013%	
			Water	007732-18-5	60.00%	0.00013%	
			Citric Acid	000077-92-9	30.00%	0.00007%	
Gyptron T-390	CHAMPION	Scale Inhibitor	Ethoxylated Nonylphenol	N/A	10.00%	0.00095%	
			Methanol (Methyl Alcohol)	000067-56-1	10.00%	0.00095%	
Bactron K-139	CHAMPION	Anti-Bacterial Agent	Quaternary Ammonium Compound	068424-85-1	10.00%	0.00179%	
			Ethanol	000064-17-5	5.00%	0.00089%	
			Glutaraldehyde (Pentanediol)	000111-30-8	5.00%	0.00089%	

WG-111L	TRICAN	Gelling Agent	Petroleum Distillate Hydrotreated Light	064742-47-8	60.00%	0.19832%	
			Polysaccharide blend	N/A	60.00%	0.19832%	
WXB-77	TRICAN	Cross Linker	Petroleum Distillate Hydrotreated Light	064742-47-8	60.00%	0.09151%	
			Ulexite (Borate Salt)	001319-33-1	60.00%	0.09151%	
FR-12 (Anionic Acrylamide)	TRICAN	Friction Reducer	Petroleum Distillate Hydrotreated Light	064742-47-8	60.00%	0.07067%	
			Copolymer of Acrylamide and Sodium Acrylate	025987-30-8	40.00%	0.04711%	
			Quaternary Ammonium Chloride (Ammonium Chloride)	012125-02-9	2.00%	0.00236%	
WBO-8	TRICAN	Breaker	Sodium Bromate	007789-38-0	100.00%	0.01170%	
S-15 (Surfactant)	TRICAN	Surfactant	Alcohol Alkoxylate	TRADE SECRET	20.00%	0.00001%	
			Methanol (Methyl Alcohol)	000067-56-1	20.00%	0.00001%	
Additional Ingredients Not Listed on MSDS							
PRC Premium, Premium White		Proppant	No Non-MSDS Listed Components	NOT AVAILABLE			
			Non-MSDS Components Not Provided by Supplier	NOT PROVIDED			
Bactron K-139, Gyptron T-390	CHAMPION	Anti-Bacterial Agent, Scale Inhibitor	Sodium Chloride	007647-14-5			
			Sodium Glycolate	002836-32-0			
			Tetrasodium Ethylenediaminetetraacetate	000064-02-8			
			Water	007732-18-5			
15 hcl, FEAC-30, FORMIC ACID, FR-12 (Anionic Acrylamide), LAI-20, S-15 (Surfactant), WBO-8, WG-111L, WXB-77	TRICAN	Acid, Breaker, Corrosion Inhibitor, Cross Linker, Friction Reducer, Gelling Agent, Iron Control Agent, Surfactant	Alcohol Ethoxylate Surfactants	TRADE SECRET			
			Guar Gum	009000-30-0			
			Modified Bentonite (Organophillic Clay)	068953-58-2			
			Modified Thiourea Polymer	068527-49-1			
			n-Olefin	TRADE SECRET			
			Propylene Carbonate	000108-32-7			
			Sorbitan Trioleate	026266-58-0			
			Water	007732-18-5			

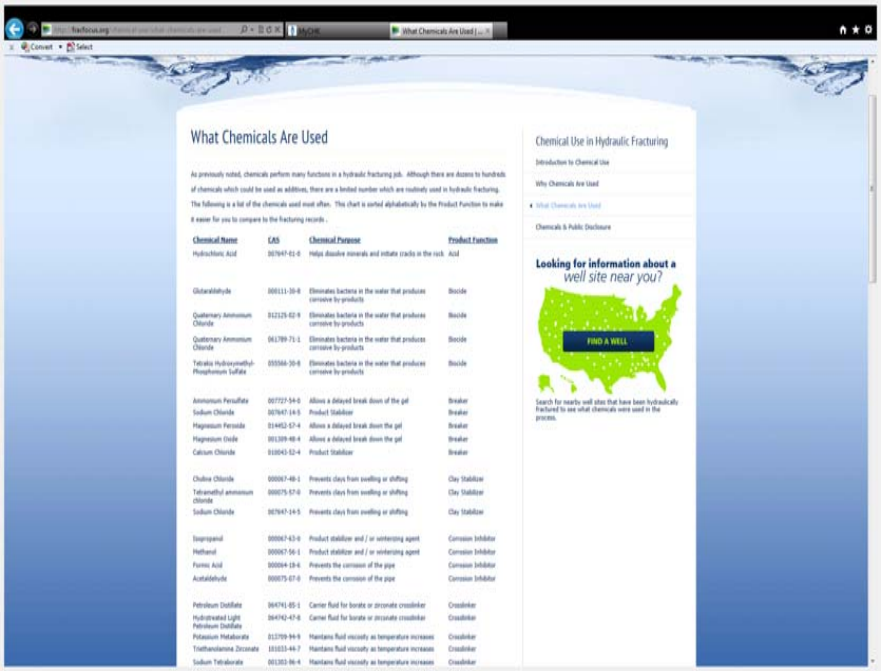
* Total Water Volume sources may include fresh water, produced water, and/or recycled water

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

"Additional Ingredients Not Listed on MSDS" component information were obtained directly from the supplier. As such, the Operator is not responsible for inaccurate and/or incomplete information. Any questions regarding the content of this information should be directed to the supplier who provided it.

Ingredient information for chemicals subject to 29 CFR 1910.1200(i) and Appendix D are obtained from suppliers Material Safety Data Sheets (MSDS)

Other Information in FracFocus



- Other information is available, such as
  - Chemical list
    - Less than 50 chemicals are most often used in hydraulic fracturing
  - Links to OSHA and EPA Chemical Fact Sheets
  - Regulations by State
  - Frequent Questions

CHALLENGES FOR ENVIRONMENTAL LABORATORIES

Challenges for Environmental Laboratories

- Requests for analysis of environmental media for hydraulic fracture fluid components are expected to increase
  - Environmental media: air, ground water, surface water, and soil
  - Other media: produced formation water, hydraulic fracture fluid flowback, and waste materials
- Some advocates are requesting analyses of all components in a hydraulic fracture fluid in pre-drilling sampling programs

Challenges for Environmental Laboratories

- Analysis for Parameters without Regulatory Agency Approved Methods
- Achieving Lower Reporting Limits
- Method Selection
- Matrix Interferences for Produced Water
- Reporting Tentatively Identified Compounds (TICs)

Analysis of Parameters without Regulatory Agency Approved Methods

- Environmental laboratories have the expertise needed to develop or adapt analytical methods for the range of compounds not typically included in regulatory agency approved analytical methods
  - Polymers
    - Cellulose-based polymers
    - Co-polymers of acrylamide and sodium acrylate
  - Antimicrobials
    - Tetrakis hydroxymethyl phosphonium sulfate
  - Emerging compounds
    - Synthetic acids

Analysis of Parameters without Regulatory Agency Approved Methods

- Identification of appropriate indicator parameters
  - Surrogates for breakdown, reaction products, or metabolites
    - Nitrogen series -- amide-based polymers
    - Chloride -- hydrochloric acid or potassium chloride
  - Use of surrogates or indicator compounds
    - Cost-effects
    - No new methods or modifications to existing methods needed
  - Communication with regulatory agencies and the general public

Analysis of Parameters without Regulatory Agency Approved Methods

- Documentation of Accuracy of Non-traditional Methods
  - Methods are available from non-environmental laboratory sources, e.g. product testing, cooling tower, etc.
  - Example:
    - Surface release of hydraulic fracture fluid
    - Fluid contained a specific quaternary ammonium compound
      - Direct analytical method was not available
    - Colorimetric direct binary complex method designed for swimming pools and cooling towers was adapted for use
    - Interferences: calcium, iron, polyacrylic acid, and sodium lauryl sulfate – all of which were present
    - Provided sufficient information to determine presence/absence and an estimate of concentration

Challenges for Environmental Laboratories

- Analysis for Parameters without Regulatory Agency Approved Methods
- Achieving Lower Reporting Limits
  - Case Study: Glycols/Alcohols
    - Groundwater from Domestic Water Wells
  - Reporting Estimated Values
- Method Selection
- Matrix Interferences for Produced Water
- Reporting Tentatively Identified Compounds (TICs)

Case Study: Glycols and Alcohols in Ground Water

- Study One

Compound	Method Reporting Limit	Ground Water Evaluative Criteria
Ethylene Glycol	10 mg/L	14 mg/L
1,2-Propylene Glycol	10 mg/L	310 mg/L
1-Propanol	10 mg/L	0.1 mg/L
Tetraethylene Glycol	10 mg/L	NA
Triethylene Glycol	10 mg/L	60 mg/L
2-Butoxyethanol	10 mg/L	0.150 mg/l
Isopropyl Alcohol	0.050 mg/L	3 mg/L
Ethanol	0.100 mg/L	NA
Propargyl Alcohol	10 mg/L	0.031 mg/L
Methanol	10 mg/L	0.780 mg/L

- Study Two
  - Initial method reporting limit for five glycols – 100 mg/L

- Two studies of ground water from domestic water wells
  - Two laboratories – similar reporting limit issues
  - Method reporting limit generally exceeded the selected evaluative criteria for tap water
  - Data was essentially useless for evaluation of potential health concerns

Reporting Estimated Values

- Some laboratories report a significant percentage of results as "J" qualified or estimated values
  - Example: Groundwater from 15 domestic water wells
    - 50 percent of data for sulfate, total dissolved solids (TDS), and pH were estimated values
    - No excess chloride, TDS or turbidity issues
    - Many of the volatile organics were reported as "J" values which were at or below the method reporting limit
      - Re-analysis of the samples showed all of the "J" values were actually below the reporting limit
- For groundwater from domestic water wells, laboratories should strive to report only non-qualified results

Challenges for Environmental Laboratories

- Analysis for Parameters without Regulatory Agency Approved Methods
- Achieving Lower Reporting Limits
- Method Selection
- Matrix Interferences for Produced Water
- Reporting Tentatively Identified Compounds (TICs)

Method Selection

- Methods need to be selected with care and consideration for the type of sample being analyzed
  - Need to be aware of potential matrix interferences
  - Use of methods which result in elevated reporting limits provides data that are relatively meaningless
  - Need to understand the inherent biases and differences between analytical methods for the same parameter
    - Explanations for differences in the results
    - Understand conditions for which one method is preferable to another
    - Assist the client in choosing the most appropriate method

Examples of Method Selection Issues

- Method Selection Issues
  - Bromide
    - USEPA Method 300.0/301.0 (anions by ion chromatography)
      - Method reporting limit – 0.1 to 5.0 mg/L
      - Most typical reporting limit for groundwater data on thousands of baseline samples – 1 mg/L
      - Data is essentially useless – need reporting limit of 0.1 mg/L
  - Radium-226 and Radium-228
    - USEPA Methods 901.1 and 903.0/904.0 were used on groundwater samples from domestic water wells
    - Analytical results between the two methods were generally inconsistent

Comparison of Analytical Results for Two Methods for Radium 226 and Radium 228

Parameter	Method	Units	Sample Number				
			1	2	3	4	5
Well A							
Ra-226	E901.1	pCi/L	31 +/- 15	14 U +/- 12	27 +/- 14	2.2 U +/- 8.7	33 +/- 15
Ra-226	E903.0	pCi/L	6.37 +/- 0.85	3.00 +/- 0.80	3.2 U +/- 2.7	2.0 +/- 1.1	28.5 +/- 9.2
Ra-228	E901.1	pCi/L	53 +/- 17	18 U +/- 15	18 U +/- 14	19 U +/- 12	24 U +/- 14
Ra-228	E904.0	pCi/L	10.6 +/- 1.3	3.0 +/- 1.1	3.6 U +/- 3.8	0.8 U +/- 1.9	55 +/- 14
Well B							
Ra-226	E901.1	pCi/L	18 U +/- 15	5 U +/- 11	26 +/- 12	-10 U +/- 370	44 +/- 16
Ra-226	E903.0	pCi/L	7.41 +/- 0.93	0.23 +/- 0.12	5.5 +/- 3.1	1.19 U +/- 0.98	3.4 +/- 1.1
Ra-228	E901.1	pCi/L	10 U +/- 15	11 U +/- 16	28 +/- 15	3 U +/- 11	33 +/- 17
Ra-228	E904.0	pCi/L	8.6 +/- 1.2	0.11 U +/- 0.20	2.8 U +/- 3.5	0.5 U +/- 2.0	2.4 U +/- 1.7

U – not detected

Challenges for Environmental Laboratories

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Matrix Interferences for Produced Formation Water

- Laboratories need to be better prepared to deal with the matrix interferences that are inherent to the highly saline nature of produced formation water
- Example: Evaluation of produced formation water for glycol compound as indicator of presence of hydraulic fracture fluid
  - USEPA Method 8015
    - Insufficiently robust to overcome matrix issues in produced water
      - Elevated concentrations of inorganic salts
    - Method reporting limits: 10 to 50 mg/L
  - USEPA Method 8270
    - More robust for larger glycols, e.g. glycol ethers
    - For lighter glycols, insufficient to provide meaningful reporting limits
  - USEPA Method 8321
    - Appear to be capable of lower reporting limits
    - Common glycols used in hydraulic fracture fluids co-elute

Challenges for Environmental Laboratories

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- Reporting Tentatively Identified Compounds (TICs)

Reporting Tentatively Identified Compounds (TICs)

- Public concern regarding hydraulic fracturing include questions regarding air emissions
  - Increasing demand for air toxics evaluations around oil and gas exploration and production sites
  - USEPA Method TO-15 is most commonly used
    - Method focuses on 97 volatile organic compounds regulated by the Clean Air Act Amendments of 1990
      - Does not include several of the volatile compounds which can be associated with oil and gas exploration, including fuel combustion in vehicles and equipment
      - Several of the compounds are typically reported as TICs, e.g. trimethylbenzenes
- Need to expand capabilities to specifically identify these compounds

Environmental Laboratories Should …

- Develop new or modifications to EPA methods
  - More adequately handle salt and other matrix interferences
  - Provide lower reporting limits for specific glycols and alcohols
  - Achieve lower reporting limits for bromide in groundwater
- Reach out to product laboratories to identify additional methods which can be used for polymers, surfactants, biocides, etc.
- Bring new methods or method modifications to the appropriate regulatory agencies for approval

Environmental Laboratories Should …

- Expand and improve capabilities for compound identification
  - Identify the most commonly encountered TICs for EPA Method TO-15
  - Prepare to more accurately identify and quantitate these compounds
- Reduce the reporting of "J" qualified data, especially for general water quality parameters
- Communicate with clients, regulatory agencies, and the general public

QUESTIONS?

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