



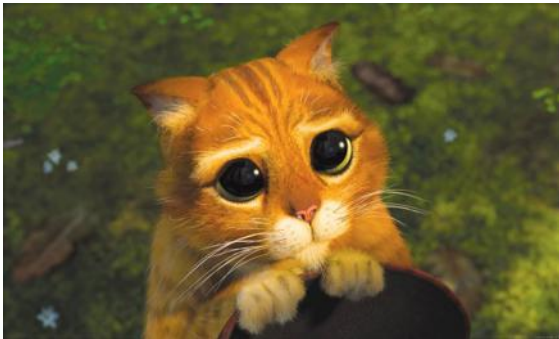
chemistry
matters

*making environmental
data meaningful*

“Fracking Up” Drinking Water?

Court D. Sandau, PhD, PChem
Watertech 2012 – Banff, AB

Introduction



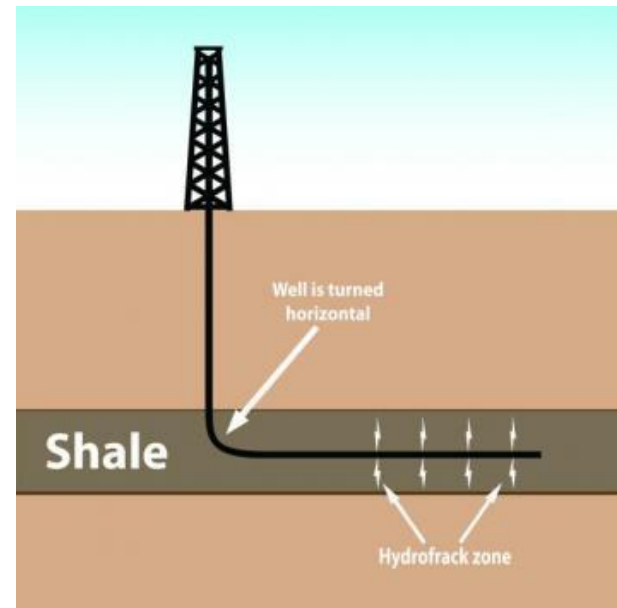
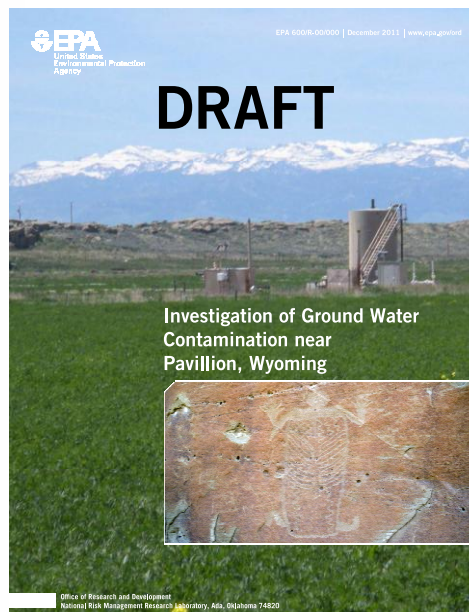


Recent Headlines



December 8, 2011

EPA says fracking likely polluted Wyoming aquifer





Recent Headlines

AP Associated Press

December 15, 2011

**Marcellus firm pays \$93K for fouling
Clearfiled County Stream**

CALGARY SINCE 1882 HERALD



January 17, 2012

**Regulators say hydraulic fracturing may have
caused oil spill on farm near Innisfail**



Recent Headlines

The Gazette



April 3, 2012

Tighter shale-gas exploration rules recommended

CALGARY HERALD



April 5, 2012

Quebec bans any fracking pending studies



Recent Headlines

THE VANCOUVER SUN

February 6, 2012

Most Canadians oppose natural-gas 'fracking'

In B.C., 67 per cent support moratorium on controversial extraction method in shale deposits

FINANCIAL POST



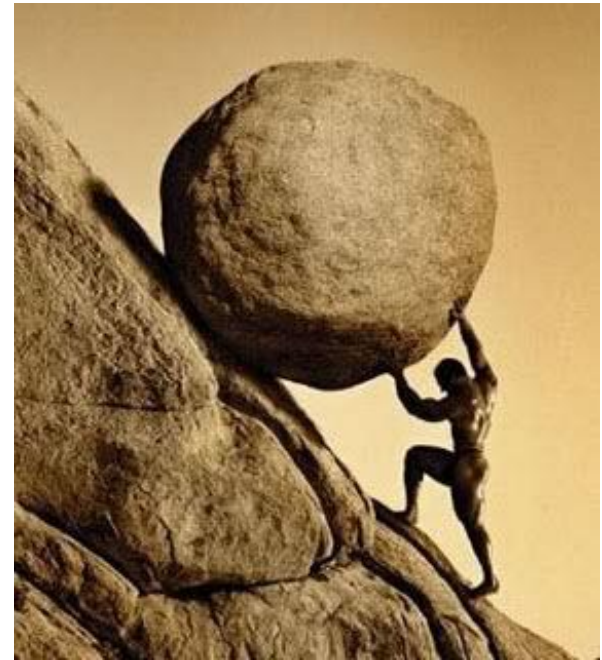
December 12, 2011

Encana slams EPA's Wyoming fracking finding



Dealing with Landowner Claims

- Landowners with O&G knowledge can take advantage
- Guilty until proven innocent
- Insufficient data and lack of information on fluids is problematic

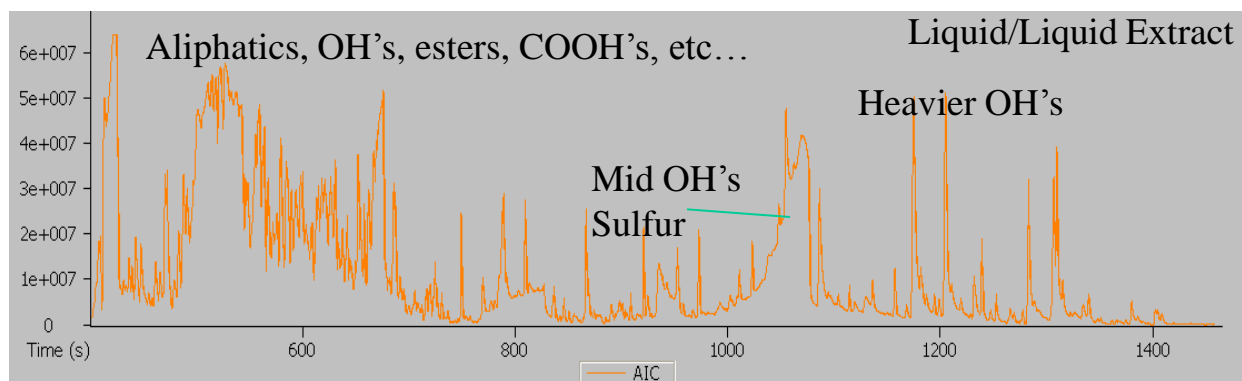
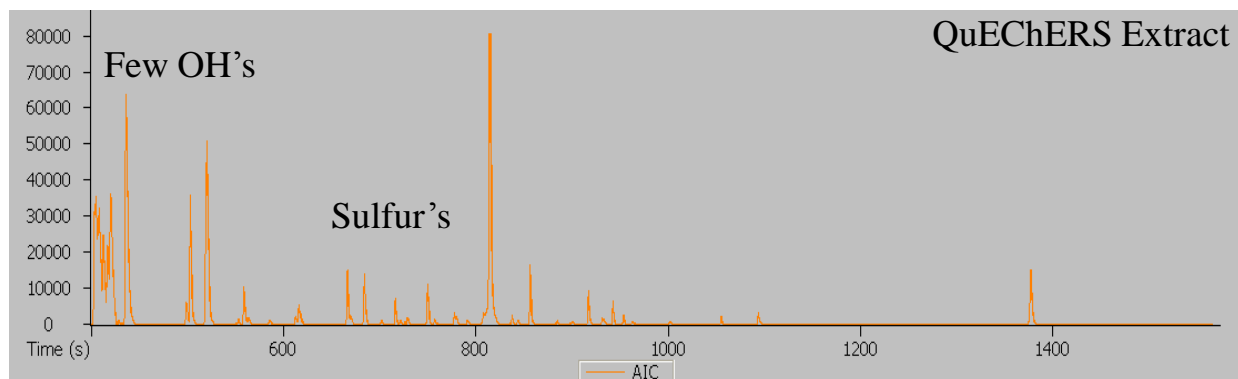




Methods for Identifying Fluids

- Frack fluids are complex!
- Over 1000 compounds identified in fluid below
- Analyzed by GC-TOF-MS

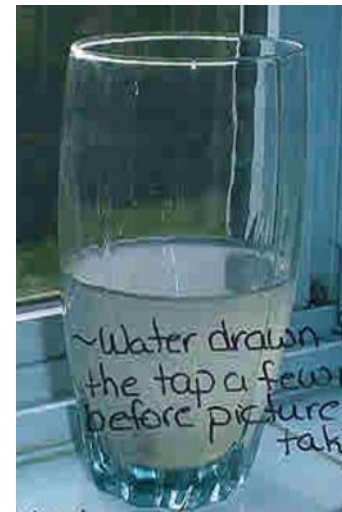
*Courtesy of Frank Dorman PhD,
Penn State University*





Case Study

- November – baseline water well sampling
- January – CBM well drilling completed
- February – fracking begins (1.4 km away from landowner's home)
- Early March – fracking complete
- End of March – residential water complaint



Case Study



- June to July – client hired consultant to collect water samples for analysis
 - Eight ‘untargeted’ sampling events
 - Routine analysis – CBM package
 - Some samples sent to Health Unit for analysis
 - July – fibrous (non-soluble) material reported in water – sent to a petrology lab





Results from Preliminary Work

- Toluene found in water well
- Several exceedances of 'natural' components
 - Turbidity, TDS, Total Fe, Total Mn, Na
- White fibrous material identified as:

“TRIOXANE!”



Symptoms: (includes breakdown into formaldehyde)

Nausea	Vomiting	Headaches	Dizziness	Pain in mouth	Difficulty Urinating
Convulsions	Coma	Genotoxic	Fetotoxic	Death	



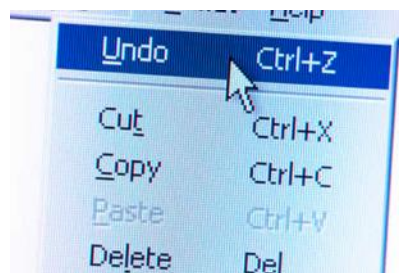
Case Study

- July – preliminary results reported to landowner and regulators
- August – brought onto case, might go legal
- August – regulator involvement begins

Let's Review



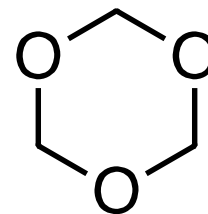
Next Thought?





Data Review

- Fibrous material cannot be Trioxane
- Solubility too high



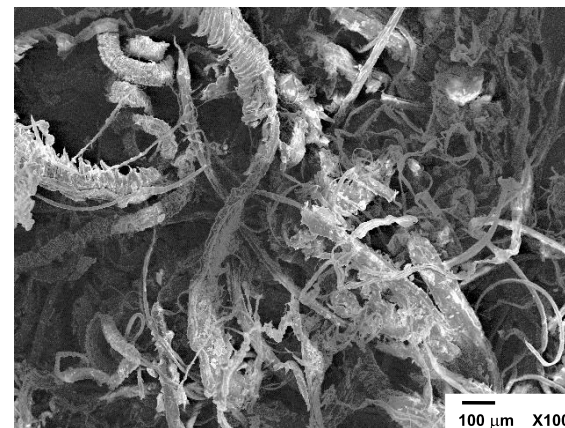
Trioxane

MW: 90.08 g/mol

Solubility: 17.2 g/100 mL

White crystalline solid

Inherent toxicity

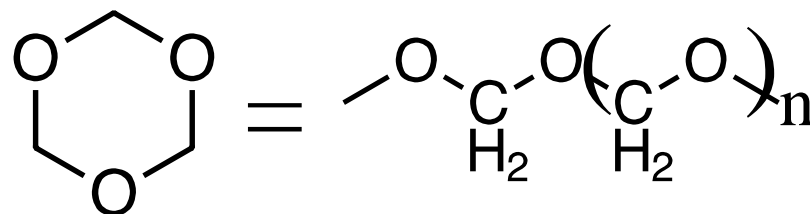
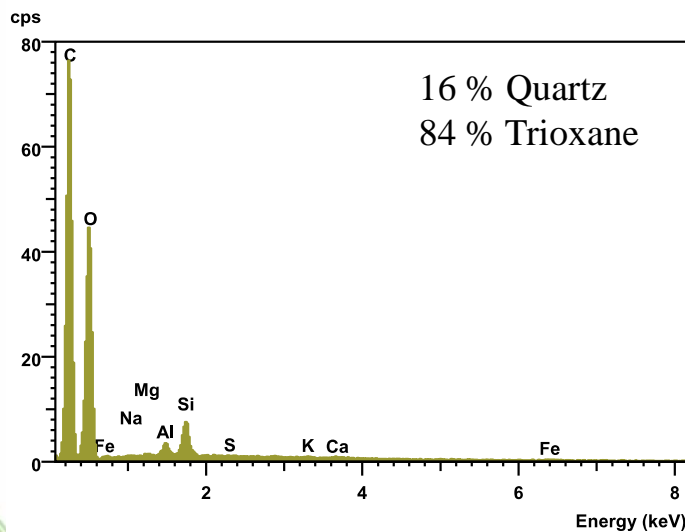


Data Review



- Petrology lab should not be determining source
 - XRD/XES not specific enough
 - Used elemental identification
- Trioxane dissolves in acid and base, this material did not

Elemental Spectrograph



Polyacetal by FTIR



Developed a More Formalized Approach

- Routine analysis does not help for frack fluids
- What should be looked for?
 - Look at MSDS and find target compounds
- Determined an approach
 - Legal sample water wells and surface water
 - Camera for well integrity & well cleaning
 - Legal sampling water wells and surface water



Useless MSDS Information

Frack Fluid 1

2. COMPOSITION/INFORMATION ON INGREDIENTS

No hazardous materials are contained in this product.

Frack Fluid 2

2. COMPOSITION/INFORMATION ON INGREDIENTS

COMPONENT	CAS#	% BY WEIGHT
Secondary Alcohol	Proprietary	Proprietary
Essential Oils	Proprietary	Proprietary
Alcohols	Proprietary	Proprietary
Alkyl Alkoxyate	Proprietary	Proprietary
Organic Polyol	Proprietary	Proprietary

- Frack company not very forth coming
- Assured us that they do not use Trioxane
- Reluctantly supplied samples



Determining Analytical Program and Results of Investigation

Product Name	Ingredients	%	Related Analysis	Water Sample Results
Product 1	Proprietary	Unknown	Alkanolamine	Not Detected
Product 2	Potassium Metaborate	Trade Secret	Routine water chemistry	No Indication of Impact
	Potassium Hydroxide	0.1 to 25	Routine water chemistry	No Indication of Impact
	Ethylene Glycol	0.1 to 25	Glycol screen	Not Detected
Product 3	No hazardous materials are contained in this product	Unknown	N/A	N/A
Product 4	Secondary Alcohol	Proprietary	Alcohol screen	Not Detected
	Essential Oils	Proprietary	VOCs / TEHs/ Mineral Oil and Grease	Not Detected
	Alcohols	Proprietary	Alcohol screen	Not Detected
	Alkyl Alkoxylate	Proprietary	VOCs / TEHs	Low levels of toluene detected in main well, source identified (next slide)
	Organic Polyol	Proprietary	Glycol / Alcohol screen	Not Detected

Routine Testing /Additional Parameters	CBM	N/A	N/A	Routine Water Chemistry, BTEX, F1-F2, Coliforms, Metals, PAH's Dissolved Polyacetal and Trioxane	No Concern, stable pre and post conditions Trioxane not detected
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Legal Sampling

- Legal sampling important
- Data can stand scrutiny of litigation proceedings (if necessary)
- Process documents integrity of sampling procedures as well as of the samples



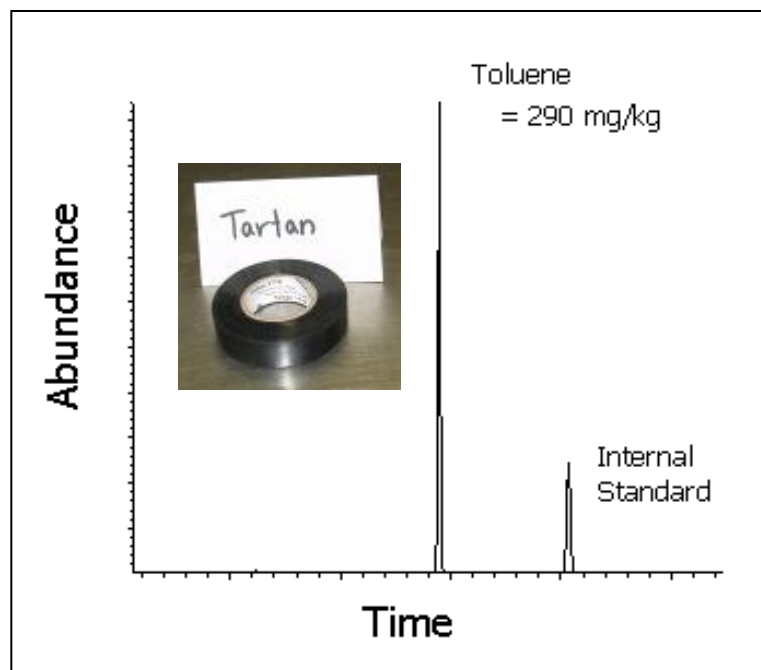


Sampling Events

- Regulators wanted to take independent samples to analyze themselves
- Sampling over long weekend, regulator left landowner with sample bottles!!
- Legally defensible?



Field Notes & Documentation



Experimental Procedure

- 200mL of HPLC water and ~2.0g of tape, were sonicated together for 1 hour
- 5mL of the tape extracts was analyzed for BTEX
- Using the exact tape mass, the concentration of toluene was calculated to be 290 mg/kg



- *Field notes*
- *Observations from experiment*

Conclusions



- Investigations can go sideways quickly – hire the right consultant to take to completion
- Frack fluid composition needs to be available to client
- Analyze for appropriate, targeted analytes
 - Routine parameters not sufficient
 - Target most soluble, most mobile, and highest concentration components





Conclusions

- Trioxane was a polymer, likely the pump breaking down
- Toluene from electrical tape on pump
- No constituents from frack fluids detected in water samples
- Remaining analytes within normal limits
 - Better characterization of well water would have helped



Results

- Too much 'bad' data
- Timing of poor water quality still coincidence to fracking?
- Settled with landowners





Questions?

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