



Gastem USA

*Designing a Water Quality
Program*

Designing a Water Quality Program

- Goal
- Design
- Challenges
- Limitations
- Future



Lake Otsego, Cooperstown, NY

Water Quality Program Overview

Baseline Water Testing

Establish ambient water quality

Establish introduced water quality

Frac fluid Testing

Establish chemical composition of potential contaminants

Establish Tracer Parameter(s)

Water Quality Monitoring

Establish the effectiveness of Best Management Practices

Monitor ambient water for potential impacts

Goal

- Best Management Practices



Mats used to diminish environmental impact

- Environmental Stewardship

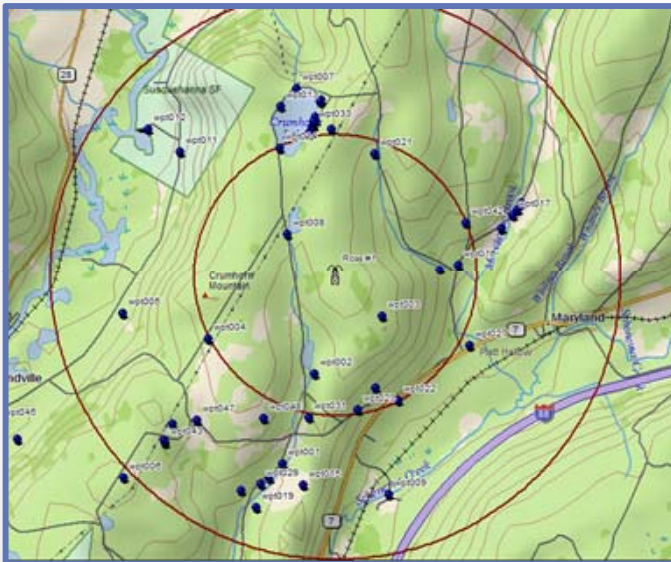


Ross Well Site, Maryland, NY

Monitoring for potential impacts to surface and ground water

Study Design

Establish Area of Interest



Establish list of analytes to be sampled –Water Quality Parameters

- Dissolved methane, propane and ethane
- Volatile Organic Compounds
- Glycols
- pH
- Conductivity
- Chloride
- Alkalinity
- Sulfate
- Total Dissolved Solids
- Total Suspended Solids
- Calcium
- Magnesium
- Sodium
- Potassium
- Iron
- Manganese
- Arsenic
- Barium
- Chromium
- Lead
- Lithium
- Strontium

Document... document

Write out plan

- Establish DQO, QA/QC
- Resample residential wells after hydraulic fracture of the Utica Shale for water quality parameters
- RESULTS: Compare monitoring results to baseline database to see if goals are met



DRAFT

Ross Surface and Ground Water
Quality Baseline Study
&
Ongoing Water Quality Monitoring and
Assessment
Phase I: Utica Shale Stimulation

Gastem USA Ross No. 1 Well Site
Maryland, New York

Summary: This report documents the water quality baseline study and the ongoing data monitoring to assess the effect of a low volume hydraulic fracturing of the Utica Shale on ambient water quality at Gastem's Ross No. 1 natural gas exploration well.

12/10/2010



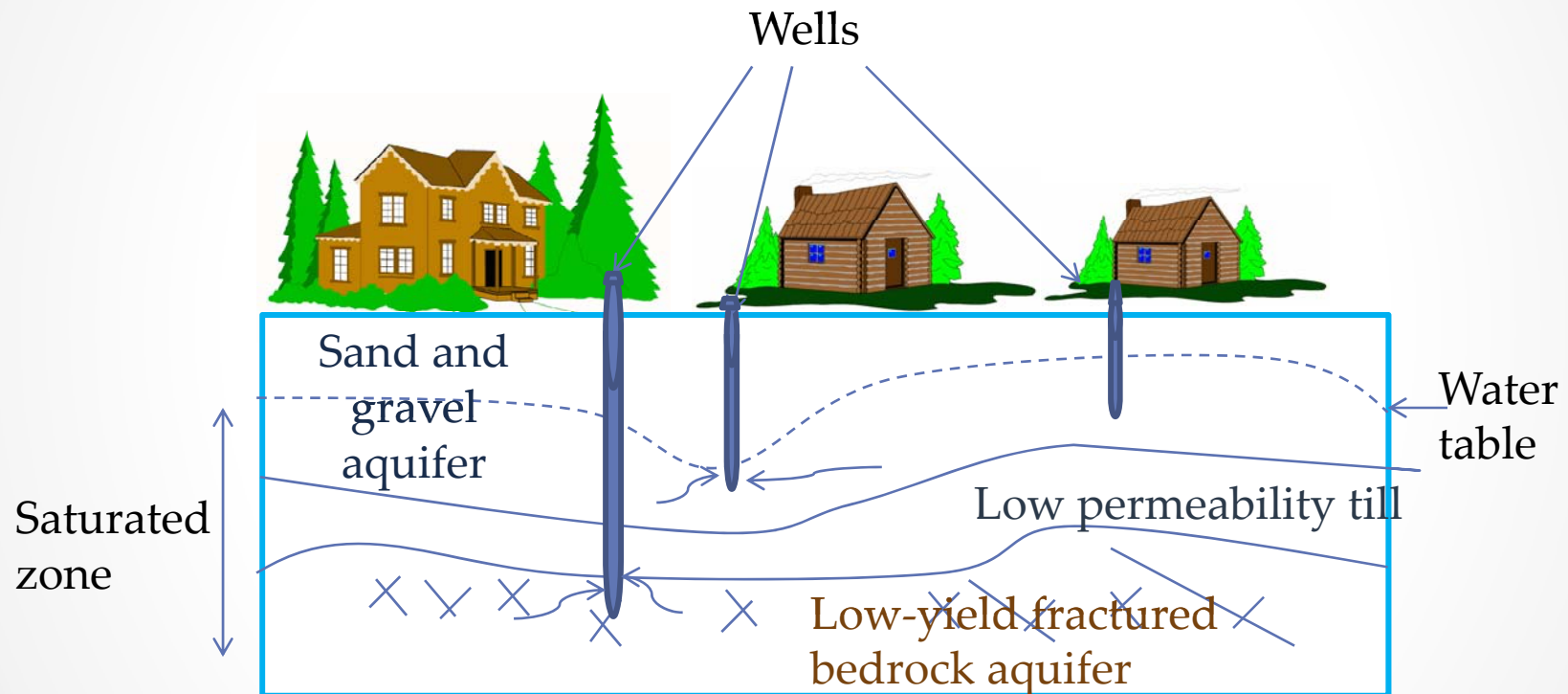
Challenges

Site-specific variability

- additives
 - ❖ Develop an understanding on the specific additive formulations used for the specific target formations (Marcellus, Utica)
- baseline water quality
 - ❖ Characterize regional water quality
 - ❖ Select chemical tracer/fingerprint

Variability Baseline Water Quality

- ❖ Characterize region-wide groundwater quality



Different water source in aquifer = variable water quality

Select Chemical Fingerprint

- **Chemical tracers**
 - Introduced tracers
(Utica Shale Stimulation)
- Flowback =
Combination additives
+ produced water



- **Natural Tracers**
(Brine, mercury, lead, arsenic, organic acids, hydrocarbons, poly aromatic hydrocarbons volatile, and semi-volatile organic compounds)

Introduced Chemical Tracers



Advantages

- Powerful fingerprint
- Easily explained
- Already present in flowback

Disadvantages

- Site specific
 - ❖ Look for trends in available results
- Tedious looking for data on flow back components
 - ❖ Find time proven tracers

Types of Potential Tracers in Shale flowback

- Organic
 - Modest concentrations
 - Most less than 1 ppm
- Inorganic
 - Higher Concentrations
 - Potassium & Chlorides

ANALYTES	RESIDENTIAL		FLOWBACK
	WATER WELLS (before)	WATER WELLS (after)	ADDITIVES IN FLUID
Non X-VOC	Non detect	Non detect	Ethylene glycol 35 mg/L
SVOC	Non detect	Non detect	Acetone 13 µg/L
X-VOCs	Non detect	Non detect	Chloromethane 8.0 µg/L
Potassium	0.27-0.97mg/L	0.23-0.98mg/L	61.6 mg/L
Chlorides	0-69 mg/l	1.1-84 mg/l	5070 mg/l

Selecting Tracers

	K ⁺	Cl ⁻
Ease of detection in field		X
Ease of detection in laboratory	X	X
Non-reactive with water	X	X
Low Sorption	X	X
Availability in Frac Fluid	X	X
Background interference		Road salt

Chloride

Fate and Transport extensively studied: Conservative tracer (no retardation reactions, only advection and dispersion), most mobile, present in high concentrations.

What Next?

- Introduced water analysis
- Point of injection mixture analysis
- Chemical transformations, fate and transport of organic compounds in frac fluid



Designing a Water Quality Program for Shale Exploration

Uni Blake
Majitox for Gastem USA

The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Introduction

Protecting water quality is the key objective of developing a comprehensive water quality monitoring program. The design of an effective program requires characterizing and understanding all the chemical variables associated with the ambient water resources and the natural gas well site. This includes characterizing the: (1) quality of the surrounding water resources before any natural gas exploration activity starts (establishing a baseline), (2) additives used in hydraulic fracturing, (3) flowback fluids, and (4) ambient water after hydraulic fracturing activities. The combination of the above information is crucial when it comes to delineating and differentiating potential contaminations that may occur as a result of hydraulic fracturing.

Project Goals

There is concern about the potential contamination of surface and ground water primarily by the additives used in the hydraulic fracturing process and secondarily by the flowback from the well after the frac job is completed. The flowback contains some additives, salts, metals and organic compounds. Understanding the exact nature of these chemical streams is important especially when it comes to selecting indicator parameters that can be used to trace sources or track a contamination plume.

Project Design

Gastem USA designed a water quality monitoring program for use at the Ross Well site in Maryland, NY.

1. A sampling and analysis plan which incorporated quality assurance and quality control protocols was written to ensure that the data collected was accurate, precise, representative and complete.
2. A two mile radius centered at the Ross Well site was established as the area of interest. This region was determined to have the greatest potential of being impacted by activities at the well site because of proximity.
3. Analytical data from flowback fluid studies was gathered to aid in the development of the monitoring program (Hayes, 2009, Clark, 2009). This data was instrumental in selecting potential sentinel indicators and chemical tracers for potential contamination caused by hydraulic fracturing.

4. Water samples were collected at the surface and ground water (private wells) locations and tested for general water quality indicators and for other parameters that are associated with natural gas exploration and development activities. See Table 3.
5. The Well underwent hydraulic fracturing in the fall of 2008. Day one flowback water was sampled and analyzed. This water contained mostly additives and their chemically transformed constituents.
6. Water samples from the area of concern were collected for a twelve months following the hydraulic fracturing of the Shale.

Table 3. Parameters Tested in Surface Water and Residential Wells

• Dissolved methane, propane and ethane	• Volatile Organic Compounds
• Glycols	• pH
• Conductivity	• Chloride
• Alkalinity	• Sulfate
• Total Dissolved Solids	• Total Suspended Solids
• Calcium	• Magnesium
• Sodium	• Potassium
• Iron	• Manganese
• Arsenic	• Barium
• Chromium	• Lead
• Lithium	• Strontium

Challenges

There were challenges faced when developing the Shale water monitoring.

- Variability in baseline water quality: Residential water wells vary in depth and aquifer location. This variability has an impact on the concentrations of natural constituents found in the groundwater. It is known that drinking water wells located close to natural gas deposits may contain elevated levels of BTEX, methane, and strontium (Lesage et al., 1997). Gastem found that some wells had detectable levels of methane, and some had constituents that exceeded local water quality standards. This variability has an impact on creating a representative baseline water quality database. *Solution: A team of stakeholders in Otsego County are working on developing a program that will characterize groundwater quality.*
- Additives. Additive selection depends on the nature of each frac job, type of well, depth of the well, and the company performing the hydraulic fracturing. *Solution: Comparing fracturing fluids collected during the stimulation of various target formations to determine if the variability has an appreciable impact.*
- Chemical fate and transport. Fate and transport mechanisms of the potential contaminants have the ability to change the distribution and concentrations of the contaminants in the soil and groundwater. *Solution: Literature search on reported fate*

and transport models of the potential indicator parameters to determine their suitability as indicators.

Selecting Chemical Tracers

Specific indicator parameters can help overcome some of the challenges faced when developing a monitoring program. There are different types of chemical tracers and fingerprints that have been recommended to monitor potential chemical migration in hydraulic fracturing.

- Isotopes
- Frac Fluid Constituents
- Added Chemical Tracers

Frac Fluid Constituents as Unique Tracers

In Gastem’s water quality monitoring program, frac fluid constituents were used as indicators of potential migration. The process of identifying indicator parameters in potential groundwater contamination is a complex problem because there are both natural and anthropogenic sources of chemically similar contaminants. However, because of flowback aging studies, it is possible to determine which constituents are anthropogenic and which are natural. Table 4, summarizes the constituents that were selected based in their available concentrations in the flowback fluids.

Table 4. Selected Flowback Constituents

Detected Constituents (Highest concentration to Lowest)	Indicator Potential	Source	Notes
Inorganic anions			
Strontium	N	Natural	
Lithium	N	Natural	
Sodium	N	Natural	
Calcium	N	Natural	
Potassium	Y	Natural/Added	
Organics			
Toluene	N	Natural	
Ethylene Glycol	N	Added	Biodegrades rapidly
Inorganic cations			
Chlorides	Y	Natural/Added	

Results

Table 5. Comparison of Select Parameters from Utica Shale Stimulation Results

ANALYTES	RESIDENTIAL WATER WELLS (before)	RESIDENTIAL WATER WELLS (after)	ADDITIVES IN FLUID
Non X-VOC	Non detect	Non detect	Ethylene glycol* 35 mg/L
SVOC	Non detect	Non detect	Acetone* 13 mg/L
X-VOCs	Non detect	Non detect	Chloromethane* 8.0 mg/L
Potassium	0.27-0.97mg/L	0.23-0.98mg/L	61.6 mg/L
Chlorides	0-69 mg/l	1.1-84 mg/l	5070 mg/l

*highest concentration parameter in the chemical group

Indicator parameters selected

Chlorides: Chloride's fate and transport has been extensively studied; as a conservative solute, chloride is commonly used in groundwater transport and plume monitoring studies (barber, 1992). It is modeled using advection and dispersion. However, chlorides are not necessarily unique to hydraulic fracturing. Chlorides are found in the formation brine solutions, and are also used in the region for de-icing road surfaces in concentrations high enough to impact groundwater (Godwin, 2003).

Potassium: Potassium has also served as an indicator in groundwater studies. It is highly soluble and not likely to precipitate. It is found in appreciable concentrations. It is used in well drilling activities as a clay stabilizer. If high levels of chloride are detected in the field in a water resource, and if elevated potassium can be confirmed, then the probability increases that there has been migration of frac fluid.

Table 6. Selected Indicator Parameters

	K ⁺	Cl ⁻
Ease of detection in field		X
Ease of detection in laboratory	X	X
Non-reactive with water	X	X
Low Sorption	X	X
Availability in Frac Fluid	X	X
Background interference	K-bentonite from the Utica Shale	Road salt

Conclusion

The possibility exists for potential migration indicators to be drawn from the field of additives used in hydraulic fracturing. The right choices can be a demonstrative and powerful tool. However, deciphering which constituent(s) can serve as a sentinel tracers and which other

constituents can serve as confirmation tracers requires meticulous data review. The process includes understanding the chemical additives used, and the chemical processes that occur as a result of mixing at the surface and downhole.

Study Limitations: (1) Impact of produced water is not included within the scope of the study, since is generally understood that produced water does not contain significant concentrations additives (Hayes, 2009), (2) water quality contribution of the introduced supply water, and (3) site specific fate and transport information of organic constituents were not reviewed intensively.

Future: A comprehensive study to determine a potential organic confirmation tracer.

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