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Evaluation of Volatile and Semi-Volatile Organic Compounds Potentially Associated with the Gas Shale Fracturing Process in the Fayetteville and Marcellus Shale

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Abstract

With the recent growth of the natural gas industry coupled with technological advancements, gas shale fracturing has become an effective and highly profitable method for natural gas production. Unlike conventional natural gas extraction which may require vertical fracturing, gas shale fracturing relies on a method known as horizontal fracturing to remove gas trapped within the impermeable facies. Compared to vertical fracturing, horizontal fracturing requires larger amounts of fluids to be injected downhole under high pressure. These fracturing fluids can contain high concentrations of petroleum hydrocarbons with known adverse health effects. Due to the large volumes used, the potential for groundwater contamination has caused concern in the public. In this study, groundwater quality was evaluated in regions associated with gas shale fracturing. Groundwater samples were collected from 15 shallow aquifer wells at varying depths in areas near gas shale fracturing sites in north-central Arkansas. Samples were also collected from 7 groundwater monitoring wells in proposed gas shale production areas in New York State. Concentrations of volatile (VOC) and semi-volatile (SVOC) organic compounds in groundwater samples, including gasoline range organics (GRO) and diesel range organic (DRO), were analyzed using gas chromatography.

This study also investigated flowback water quality from both horizontally and vertically fractured wells. Flowback water is water that returns to the surface within 14 days of the initial fracturing event. Flowback data made available by the Shale Network were collected using geographic information systems (GIS). Flowback sample analytes of interest were DRO and GRO compounds. These samples came from gas shale fracturing wells located within the Marcellus Shale region in Pennsylvania and West Virginia.

Noticeable patterns were present in DRO and GRO flowback data. Flowback water results showed differences between horizontally and vertically fractured well DRO patterns. Vertically fractured wells showed a sharp decrease in DRO concentrations following fracture events. Horizontally fractured wells exhibited a peak in loading when flowback water shifted to produced water. This pattern suggests the method of completion has a large effect on DRO loading. GRO loadings appeared to not be effected by the method of completion. A horizontally fractured well and vertically fractured well within 16km showed similar loading patterns. GRO data suggest factors such as geographic location, may be responsible for VOC loading trends.

VOCs and SVOCs were present at detectable levels in groundwater samples. Average concentration of GROs in groundwater samples collected from wells in Arkansas was 14.7±13.0 µg/L. Monterey CF was the only New York site with GROs above the detection limit, with a mean concentration of 11.4±3.1 µg/L. Concentrations of GROs in New York were found to be statistically lower compared to Arkansas locations ($P = 0.042$). DRO concentrations in groundwater samples collected from Arkansas ranged from non-detect to 4.48±0.81 mg/L. DROs were detected in two groundwater samples collected from New York State. DRO concentrations in New York groundwater samples were found to be statistically lower compared to samples collected in Arkansas ($P = 0.029$). Results from this study also support that methane was detected in 10 out of 22 groundwater samples from Arkansas and New York State. The average concentration for the 6 groundwater samples collected in Arkansas with detectable levels of methane was 0.05±0.06 mg/L. Methane was detected in groundwater samples collected from four sites in New York State. However, no statistical difference was found between New York and Arkansas samples. A relationship between the distances of Arkansas groundwater samples to gas shale fracturing operations was not found for any measured organics.

Evaluation of Volatile and Semi-Volatile Organic Compounds Potentially Associated with the Gas Shale Fracturing Process in the Fayetteville and Marcellus Shale

by

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Flowback data were provided by the Shale Network in collaboration with the Marcellus Shale Coalition, and the Gas Technology Institute. Groundwater samples were collected by the University of Arkansas for Medical Sciences, and the United States Geological Survey.

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1. Introduction

The United States has seen a rapid increase in total natural gas reserves. This increase has been driven primarily by the development of shale gas. Advancements in technology now permit previously unattainable shale gas resources to be utilized, doubling the United States gas reserves and, increasing natural gas production by ~28% since 2006 (EIA, 2013). This increase in natural gas will have a large economic effect on the United States. It is expected that the United States will become an exporter of natural gas by 2020 and reach “energy independence” by 2035 (EIA, 2013).

In order to develop these shale gas reserves, a process known as hydraulic fracturing is utilized. Hydraulic fracturing is a process used in the extraction of underground resources to increase oil, natural gas and, water production rates when these resources are located in rock formations with a naturally low permeability (King, 2012). During the hydraulic fracturing process, water is injected at high pressures to increase pore pressure. As the pore pressure is increased the total normal stress is reduced causing a reduction in the formations shear strength (Davies et al., 2013). The reduction in shear strength leads to a fracture event. As more fractures develop, the permeability of the formation increases allowing for increased production rates (Davies et al., 2013). Hydraulic fracturing can be broken down into two methods, vertical fracturing and horizontal fracturing. After the fracturing event is complete, injection waters return to the surface as flowback water (Hayes, 2009). This flowback period lasts for the first 14 days (Hayes, 2009). After is point the composition of the waters changes to produced waters. Produced waters are waters that occur naturally in the rock formation (Hayes, 2009).

Shale gas reservoirs can range anywhere from 1,500-6,000m underground and are often deposited in thin layers that cover vast areas (King, 2012). This condition limits the economic viability of vertical fracturing as a method of extraction. Horizontal fracturing, often referred to as high volume fracturing, is the preferred method for removing natural gas from shale facies. During the fracturing process, chemical additives which include petroleum hydrocarbons are used to decrease the fracture time and, increase the efficiency of the fracture event (Davies et al., 2013). Of these additives 25% are considered carcinogens and over 75% may have negative effects on sensory organs, respiratory function and, gastrointestinal systems (Colborn et al., 2011). Another, 40-50% may interfere with brain, nervous system and, cardiovascular health, and 37% may affect the endocrine system (Colborn et al., 2011). Due to the adverse health effects, there has been concern over the possibility of fracturing fluids being introduced to groundwater systems (Colborn et al., 2011). For this reason, there has been an increase in research aimed at establishing a potential link between water quality and hydraulic fracturing.

The majority of these studies have focused on inorganic anions in groundwater. Compounds traditionally chosen are conservative ions, which have inherently different properties than organic constituents. Inorganics are typically chosen as analytes of interest because formation waters, which occur naturally within the facies, have high concentrations of salts (Boyer et al., 2011). Therefore, the interaction with formation waters stimulated by gas shale fracturing could potentially contaminate potable groundwaters with elevated concentrations of salts (Boyer et al., 2011). However, chemical additives are injected downhole in waters which have chloride concentrations several orders of magnitude lower than formation waters (Hayes, 2009). Therefore, using inorganic analytes as indicators of contamination focuses primarily on events that occur after the fracturing process is completed. This is not the most effective method to account for contamination that may result from the injection waters. Using this approach, contamination that occurs before the fracturing fluid is introduced to formation waters may go unnoticed.

Studies have been conducted to examine organic contaminants associated with gas shale fracturing in groundwater. A recent study performed by the U.S. EPA examined two deep monitoring wells in Pavillion, Wyoming near hydraulic fracturing operations (Gross et al., 2013). The U.S. EPA preliminary report concluded that fracturing fluid migrated from the nearby target formation to the aquifer above (Gross et al., 2013). Within this aquifer, they found high levels of glycols, alcohols and, methane believed to originate from hydraulic fracturing (Gross et al., 2013). Methane is the one of the more commonly studied hydrocarbon contaminants in gas shale fracturing. Jackson et al. (2013) observed a relationship between elevated methane concentrations and the distance to the nearest gas shale fracturing well. Methane can have different origins and as a result the compound to have different isotopes. Two common sources of methane in groundwater are created by biogenic or thermogenic processes (King, 2012). Thermogenic methane is formed deep below the Earth’s surface due to the breakdown of organic materials under high temperature in conditions expected for a shale containing natural gas (King, 2012). Biogenic methane is produced near the Earth’s surface due to the decay of organic materials by microorganisms (King, 2012). Biogenic methane can be found in groundwaters in areas that not associated with shale plays. It is difficult to draw conclusions about the source of methane without isotopic analysis (King, 2012).

Few studies have considered petroleum hydrocarbons when investigating groundwater contamination related to gas shale fracturing (Gross et al., 2013). However, petroleum hydrocarbons are present throughout the entire fracturing process making them an important contaminant to consider (Hayes, 2009). Shale gas is unique in its composition and is considered a wet gas, meaning it contains a variety of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) that range from C_1-C_{32}. Two major petroleum hydrocarbon groups within this range are gasoline range organics (GROs), which range from C_6-C_{10}, and diesel range organics (DROs), which range from C_{10}-C_{32}. Several of these organic compounds are also present in the injection fluids (Hayes, 2009). Benzene, toluene, ethylbenzene and xylene (BTEX) are petroleum hydrocarbons that are of particular interest since they have been associated with adverse health effects (Gross et al., 2013). BTEX compounds may be added to the injection fluids but can also occur naturally in formation waters (Gross et al., 2013). A recent study found that surface spills of produced water from the fracturing process may result in BTEX compounds above maximum containment levels (MCLs) (Gross et al., 2013). To my knowledge there has not been a study that quantifies the loadings of petroleum hydrocarbons throughout the fracturing process.

Previous research has assumed that the concentration of fracturing additives remains consistent throughout the flowback period regardless of the rate of return. Therefore, it was thought that regardless of the flow of returning up hole the concentration of additives will not change. If an increase in the concentration of these chemicals occurs, it is therefore due to inputs from the formation waters (Hayes, 2009). When assessing the impact that horizontal fracturing has on organic contaminant patterns, compared to vertical fracturing, it is important to consider the loading. Loading values account for flow rate, as well as the concentration of the contaminant. The flow rate up hole is higher in the initial days following the fracture compared to weeks afterward. In this thesis, I have quantified petroleum hydrocarbon loadings at key points during the fracturing process. Data from two horizontally fractured and two vertically fractured wells within the Marcellus Shale region were obtained via the Shale Network database.

Using these data, I compared two methods of completion, horizontal and vertical fracturing, to determine important differences in organic loading. Simultaneously, I identified trends within key petroleum hydrocarbons groups. A major objective of this thesis was to determine what hydrocarbon trends are present in flowback water and the factors that may influence these trends. This was done by observing the organic loadings of key constituents such as GROs and DROs. The results from this thesis will be helpful for future researchers when evaluating questions concerning the risk of groundwater contamination, as well as when considering remediation options in the event of a spill.

In this thesis I also address the question of whether the potential for groundwater contamination associated with horizontal gas shale fracturing is greater than vertical gas fracturing. Horizontal gas shale fracturing requires a larger volume of water and takes longer to complete. Therefore, it is possible that there may be a greater risk for the potential of groundwater contamination. This question was addressed by comparing organic contaminant data from groundwater wells located in two separate shale plays. Fifteen groundwater wells located in the Fayetteville shale within close distance to horizontally drilled and fractured sites were compared to locations in the Marcellus shale in regions that have only experienced vertical fracturing and have not yet utilized shale gas resources. The object of this analysis was to determine if hydrocarbon concentrations differ in an area with horizontal fracturing compared to an area with vertical fracturing. Data were used to determine if hydrocarbon concentrations are influenced by the distance to the nearest gas shale fracturing site.

2. Literature Review

2.1 Water Sources Associated with Gas Shale Fracturing:

During a typical hydraulic fracturing event, 1 to 4 million gallons of water is needed for the successful completion of the well (Hayes, 2009). Vertical wells use approximately 1 million gallons, while horizontal wells require 3-4 million gallons (Hayes, 2009). This water is pumped at high pressure downhole where it is combined with additives, such as friction reducers to ensure a successful fracture (Hayes, 2009). These waters are referred to as injection waters (Hayes, 2009). Once fracturing is complete, the pressure is released and the direction of fluid flow is reversed. At this point approximately 25% of the injection water flows to the surface and is removed over a period of several days (Haluszczak, 2013). The injection water that reaches the surface within the first two weeks is known as flowback water (Haluszczak, 2013). This water contains high concentrations of oils and greases along with soluble organics. The organics that have accumulated downhole are both volatile and semi-volatile (Hayes, 2009). During the drilling and fracturing process, water is produced along with the natural gas. This water, known as produced water, is composed of naturally occurring formation waters and moves through the wellhead along with the gas (Haluszczak, 2013). Produced water reaches the surface after the initial two-week period and continues to flow until the well is capped (Haluszczak, 2013). Both produced and flowback waters are stored on-site in tanks or pits before they undergo treatment, disposal, or recycling (American Petroleum Institute, 2009).

2.2 Fracture Design:

When discussing the fate and transport of hydrocarbons in relation to gas shale fracturing, it is important to fully understand the processes both before and after the hydraulic fracturing event. Although each well has unique characteristics, general practices are commonly used.

2.2.1 Well Design

Modern gas shale fracturing wells vary in depth and width depending on location. Wells include safety parameters that are designed to protect non-oil zones from the injection and flowback fluids that contain petroleum hydrocarbons (US Environmental Protection Agency, 2011). These wells must be protected from natural forces such as subsidence which may accompany the fuel removal (US Environmental Protection Agency, 2011). This is achieved by using a casing, which is a steel pipe used to line the inside of the wellbore. The casing is protected by creating a “casting string”. A casing string is composed of jointed casting which is then run downhole (American Petroleum Institute, 2009). This system provides a barrier between the fracturing waters and fresh water systems. Proper sealing of casings creates a vertical and horizontal hydraulic barrier (US Environmental Protection Agency, 2011). They also serve as pathways for injection and flowback waters to reach the surface. The American Petroleum Institute (API) standards for these casings vary based on location and can be found in Specification 5CT (American Petroleum Institute, 2009).

Regardless of direction of the well, horizontal or vertical, the casing process occurs over many phases. The first phase begins with the outside barrier with the largest diameter being created, as shown in Figure 1.

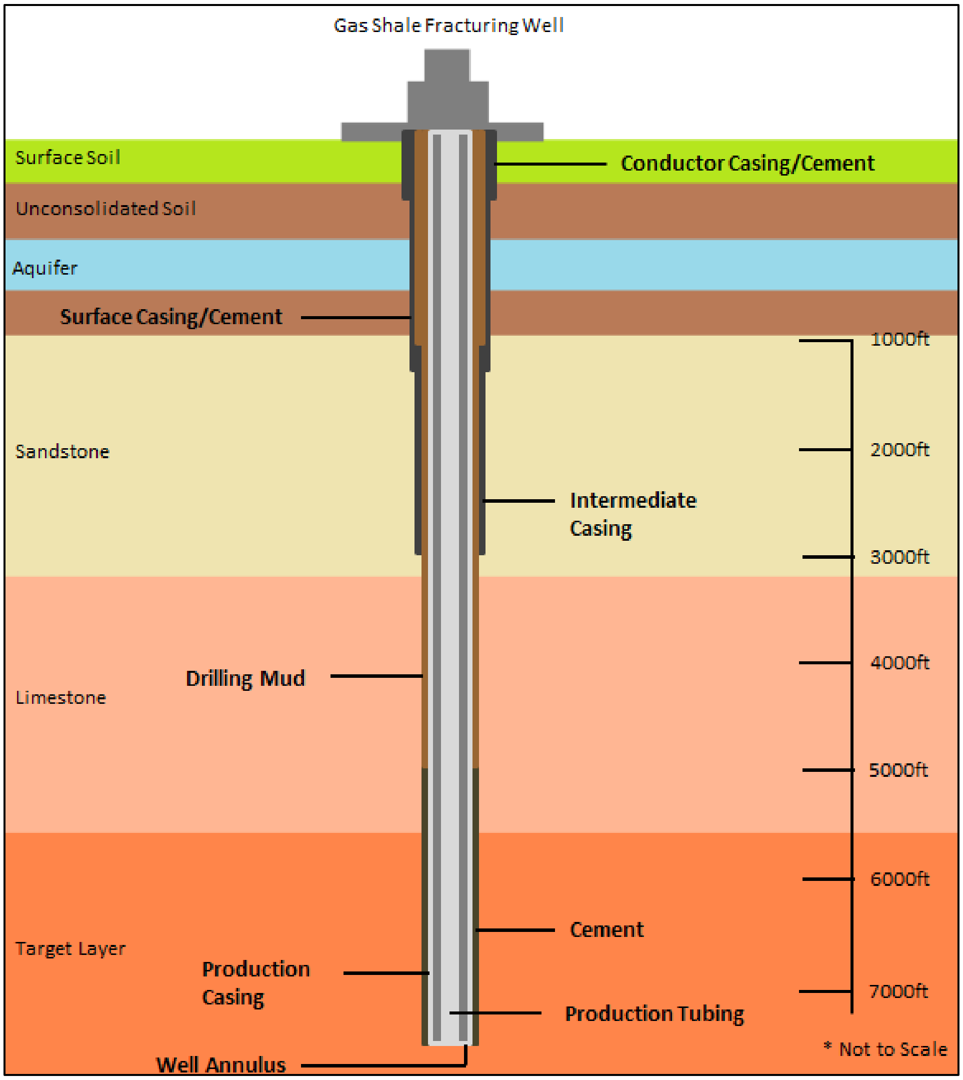


Figure 1: Typical fracturing well design.

During this phase the conductor casing is set, which prevents the well from collapsing into the wellbore (American Petroleum Institute, 2009). Once this casing is set, drilling may begin inside the casing string until it is below the groundwater zone. The surface casing is then run downhole, where cement is used to fill the annulus. The annulus makes up the space between the drilled hole and the outer wall of the pipe, as shown in Figure 1 (American Petroleum Institute, 2009). This casing extends 500 to 1,500ft deep depending on the location. The casing is then flushed with fresh waters until the cement returns to the surface. This process, known as "circulation" ensures that cement fills the annulus space, eliminating the pathway between fracturing fluids and groundwater aquifers (American Petroleum Institute, 2009). Not all states require this step, Arkansas, for example only requires a certain depth of circulation depending on the casing type. The surface casing serves as the primary boundary between groundwater and the hydraulic fracturing waters, thus, making the surface casing a crucial potential pathway for organic pollutants (American Petroleum Institute, 2009). Once the surface casing is completed, the wellbore can then be drilled to the next zone where an intermediate casing is constructed (American Petroleum Institute, 2009). This casing is also not mandatory but serves to protect other valuable resources such as coal (American Petroleum Institute, 2009). From this point, the wellbore is drilled to completion where a production casing set into place using the same method as the surface casing (American Petroleum Institute, 2009). The production casing serves as a secondary form of protection isolating the flowback waters from groundwater aquifers (American Petroleum Institute, 2009).

2.2.2 Chemical Design

When performing the hydraulic fracturing process, the maximum achievable downhole pump rate is desired. This pump rate ensures the efficient transfer of energy which maximizes the degree of fracturing (Fontaine et al., 2008). Pressure loss, caused by tubular friction, results in reduced downhole pumping rates (Fontaine et al., 2008). The reduced rate decreases flow velocity decreasing energy transfer to the fractures, leading to a lower carrying capacity of proppant which is used to keep fractures open (Fontaine et al., 2008). In order to achieve this maximum downhole pump rate, fracturing waters may contain several compounds including organic hydrocarbons, which serve as friction reducers, crosslinkers, gelling agents, etc. (Fontaine et al., 2008). The addition of chemical additives to hydraulic fracturing waters helps maximize the effectiveness of the fractures. These chemicals act to ensure the maximum amount of gas produced from the well is reached. Concentrations of these additives vary depending on the local geology and well characteristics. The most common chemicals present in injection waters can be found in Table 1.

Table 1. Common chemicals included in the hydraulic fracturing phase (FracFocus, 2014).

Function	**Compound**
Acid	Hydrochloric Acid
Biocide	TetrakisHydroxymethyl-Phosphonium Sulfate
Biocide	Glutaraldehyde
Biocide	Quaternary Ammonium Chloride
Breaker	Ammonium Persulfate
Breaker	Sodium Chloride
Breaker	Magnesium Peroxide
Breaker	Magnesium Oxide
Breaker	Calcium Chloride
Clay Stabilizer	Choline Chloride
Clay Stabilizer	Tetramethyl Ammonium Chloride
Clay Stabilizer	Sodium Chloride
Corrosion Inhibitor	Isopropanol
Corrosion Inhibitor	Methanol
Corrosion Inhibitor	Formic Acid
Corrosion Inhibitor	Acetaldehyde
Crosslinker	Petroleum Distillate
Crosslinker	Hydrotreated Light Petroleum Distillate
Crosslinker	Potassium Metaborate
Crosslinker	TriethanolamineZirconate
Crosslinker	Sodium Tetraborate
Crosslinker	Boric Acid
Crosslinker	Zirconium Complex
Crosslinker	Borate Salts
Crosslinker	Ethylene Glycol
Crosslinker	Methanol
Friction Reducer	Polyacrylamide
Friction Reducer	Petroleum Distillate

Friction Reducer	Hydrotreated Light Petroleum Distillate
Friction Reducer	Methanol
Friction Reducer	Ethylene Glycol
Gelling Agent	Guar Gum
Gelling Agent	Petroleum Distillate
Gelling Agent	Hydrotreated Light Petroleum Distillate
Gelling Agent	Methanol
Gelling Agent	Polysaccharide Blend
Gelling Agent	Ethylene Glycol
Iron Control	Citric Acid
Iron Control	Acetic Acid
Iron Control	Thioglycolic Acid
Iron Control	Sodium Erythorbate
Non-Emulsifier	Lauryl Sulfate
Non-Emulsifier	Isopropanol
Non-Emulsifier	Ethylene Glycol
pH Adjuster	Sodium Hydroxide
pH Adjuster	Potassium Hydroxide
pH Adjuster	Acetic Acid
pH Adjuster	Sodium Carbonate
pH Adjuster	Potassium Carbonate
Scale Inhibitor	Copolymers of Acrylamide and Sodium Acrylate
Scale Inhibitor	Sodium Polycarboxylate
Scale Inhibitor	Phosphonic Acid Salt
Surfactant	Lauryl Sulfate
Surfactant	Ethanol
Surfactant	Naphthalene
Surfactant	Methanol
Surfactant	Isopropyl Alcohol
Surfactant	2-Butoxyethanol

The relative composition of these fracturing materials is summarized in Table 2.

Table 2: Composition of hydraulic fracturing waters (King, 2008).

Volumetric Composition of a Fracturing Fluid

Component	Percent (%) by Volume
Water and sand	99.51
Surfactant	0.085
KCl	0.06
Gelling agent	0.056
Scale inhibitor	0.043
pH adjusting agent	0.011
Breaker	0.01
Crosslinker	0.007
Iron control	0.004
Corrosion inhibiter	0.002
Biocide	0.001
Acid	0.123
Friction reducer	0.088

Each of these chemicals completes unique tasks during the hydraulic fracturing phase. Proppant acts to keep fractures open after the pressure is reduced (King, 2008). Gelling agents help initiate the fracture and act to carry the proppant (King, 2008). Friction reducer is used to decrease the friction pressure as water flows through the pipe during periods of high pumping rates (King, 2008). Biocide serves as a disinfectant and limits the growth of microbes that interfere with the fracturing process. Microbes can destroy the gelled fracturing fluids and, in some cases produce hydrogen sulfide within the reservoir (King, 2008). These microbes are introduced from varying sources, such as the injection water, proppant, and polymers. Surfactants or non-emulsifiers are used to lower the surface tension among liquids in the fracturing fluid in order to prevent emulsions (King, 2008). Naphthalene is a common carrier fluid that is used to transport the surfactant (FracFocus, 2014). Breaker mixtures are often used to create to delay in the breakdown of the gelling agents. (FracFocus, 2014). Scale inhibitor limits the formation of mineral scale precipitates from forming and the associated blockage of piping and tubing (King, 2008). Hydrochloric acid (HCl) dissolves minerals, helping create fissures in the rock by reducing the pressure need to create the initial fissure (King, 2008). Corrosion inhibitor mixtures prevent the corrosion of pipes during the fracturing process (King, 2008). Due to the geology of many wells, iron controls are needed to prevent the precipitation of metal oxides. Since fracture injection fluids are exposed to high temperatures crosslinkers may be used. These mixtures are added to ensure that fluid viscosity remains constant as temperature increases (FracFocus, 2014). A pH adjuster is often added to maintain the effectiveness of many chemical components, such as crosslinkers, during the fracturing phase (FracFocus, 2014). Many of these agents are carried by petroleum distillate and hydrotreated light petroleum distillate (FracFocus, 2014). Methanol and ethylene glycol are commonly used in the gelling agent mixtures for product stabilization and/or winterization (FracFocus, 2014). More information on chemical additives can be found in Appendix A.

Table 3: Amount of additives used during hydraulic fracturing events (Hayes, 2009).

Component	Vertical Fracture Fluid (gal)	Horizontal Fracture Fluid (gal)
Surfactant	85000	340000
KCl	60000	240000
Gelling agent	56000	224000
Scale inhibitor	43000	172000
pH adjusting agent	11000	44000
Breaker	10000	40000
Crosslinker	7000	28000
Iron control	4000	16000
Corrosion inhibiter	2000	8000
Biocide	1000	4000
Acid	123000	492000
Friction reducer	88000	352000

The amount of each chemical added typically for a vertical and horizontal fracturing is summarized in Table 3. Horizontal fracturing frequently requires a larger amount of water which results in the larger volumes of chemical additives.

2.3 Geology:

In this thesis, I discuss two of the largest shale plays in the United States, the Marcellus and Fayetteville shale. In order to compare the two plays, it is important to understand their origins.

2.3.1 Marcellus Shale

The Marcellus shale is a Devonian shale located in western central New York that extends southwest into Virginia (Figure 2).

Figure 2. Map of Marcellus Shale (ALL Consulting, 2008).

Large portions of the shale are located in New York, Pennsylvania, Ohio and, West Virginia (Myers, 2012). The Marcellus Shale is highly organic black shale with a naturally low permeability (Soeder et al., 2009) This shale accumulated 380 million years ago during the middle Devonian on the continental crust in a shallow seaway with a depth of under 200 meters. At this time, Gondwana was moving towards the Laurentia at a rapid rate. This resulted in thrust faulting that lead to crustal thickening in the highland edge on the continent (Harper, 1999). This loading caused the Appalachian Basin seabed to sink. As the seabed sank the thickening of the Laurentia created a bend in the continental margin visible in Figure 3 (Harper, 1999).

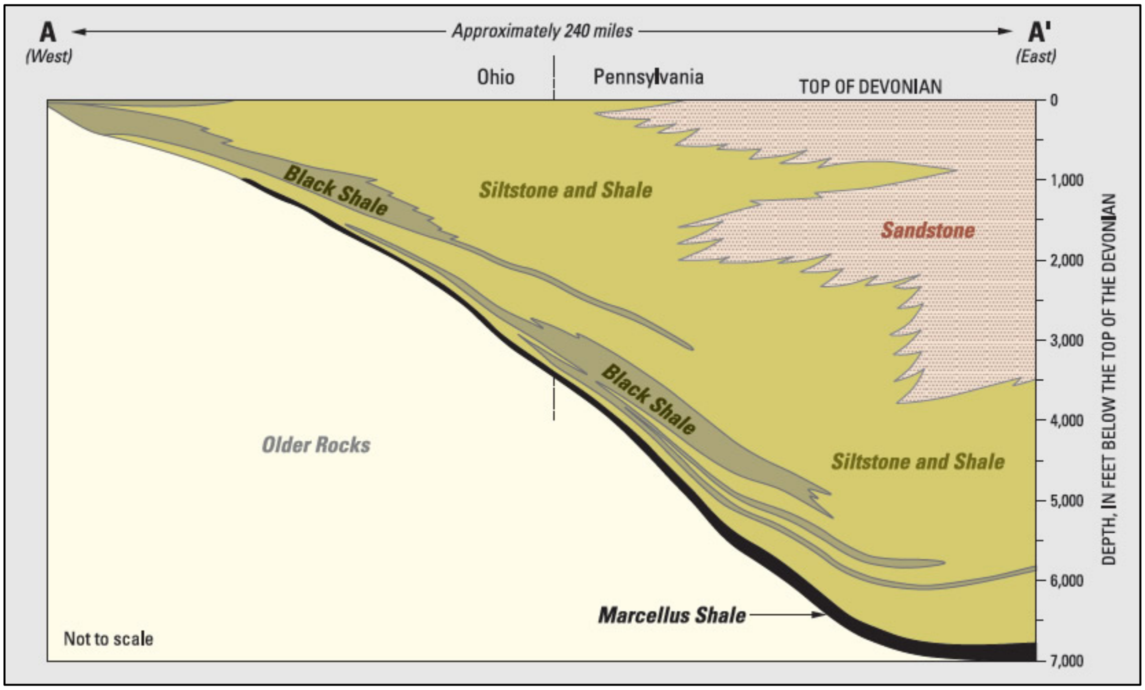


Figure 3. West to east line of section A-A' of Middle and Upper Devonian rocks in the Appalachian Basin. The Marcellus Shale is the lowest unit in the sequence (Soeder et al., 2009).

A stratigraphic column which includes the Marcellus Shale ranging from Ohio to Northwestern New York is shown in Figure 4.

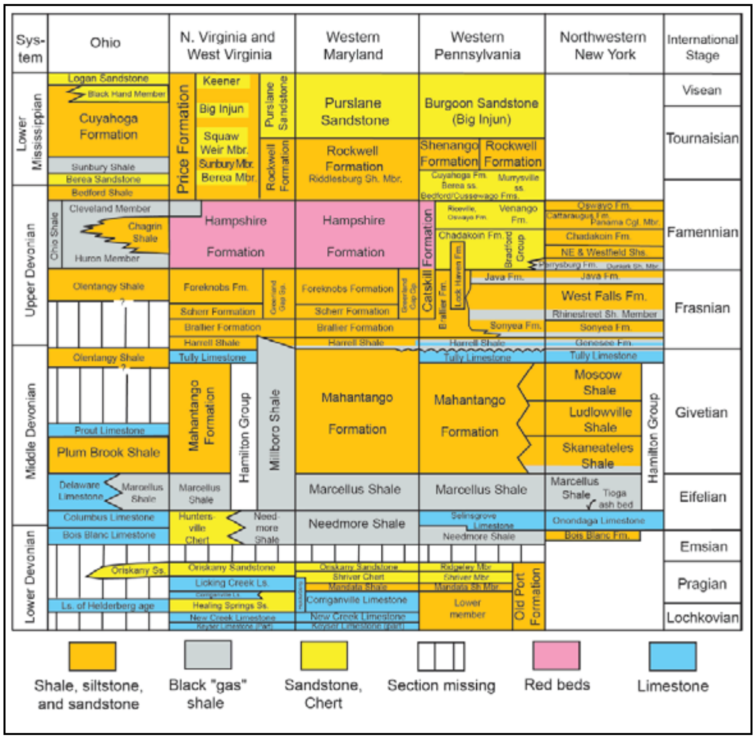


Figure 4: Stratigraphic column, showing the position of the Marcellus shale (Milici, 2006).

The Appalachian Basin sank past the pycnocline which separates warm oxygenated water from cold oxygen-deficient water in the ocean (Harper, 1999). A thrust loading episode then caused a low period of sediment flux, favoring the accumulation of rock with a high concentration of total organic carbon (TOC) (Soeder et al., 2009). River channels then began to deposit clastic sediments at a faster rate, depositing gray shale overtop of the black shale. Thrust loading caused this process to be repeated eight times over 20 million years (Ver Straeten, 1995). Before the collision of Gondwana and Laurentia, a high sedimentation rate existed. Under standard conditions, seawater was expelled from the fine grain shales during the burial process (Ver Straeten, 1995). Due to the high sedimentation rate, water was unable to be expelled. This high water content limited the compressibility of the shale and reduction of pore size. This action led to compaction disequilibrium, which was responsible for the high fluid pressure in the Marcellus Shale (Ver Straeten, 1995). As burial continued, temperature and pressure increased until the “oil window” was reached. The oil window occurs when oil and gas are created from the organic matter; this process usually requires an increase in pore space (Ver Straeten, 1995). Since the Marcellus formation did not expand during the burial, the production of oil and gas lead to an increase in pore pressure. This process created micro-cracks around organic matter particles which eventually lead to the creation of joints (Ver Straeten, 1995). The initial fracturing existed only in the Marcellus and other black shales, along the plane of bedding following the microscopic strength anisotropy generated by the initial compaction (Ver Straeten, 1995). During the initial hydrocarbon generation, Gondwana was slipping past Laurentia causing continental stress filed in the Appalachian Basin. This stress field controlled the production gas in some of the horizontal wells without any stimulation (Ver Straeten, 1995).

Around 290 million years ago Gondwana spun clockwise around New York driving it into the Laurentia creating the foreland fold-thrust belts of the Appalachians (Ver Straeten, 1995). This event started the Alleghanian Orogeny. During this time, the Marcellus shale was further buried. The fluid pressure continued to build creating fractures in the shale that formed large gas chimneys with heights near 50 meters (Ver Straeten, 1995). These gas reserves are now targeted by gas shale fracturing operations.

2.3.2 Fayetteville Shale

Fayetteville shale, shown in Figure 5 is a black, fissile, clay shale located in northern Arkansas, and was deposited in the Late Mississippian (McFarland, 2004).

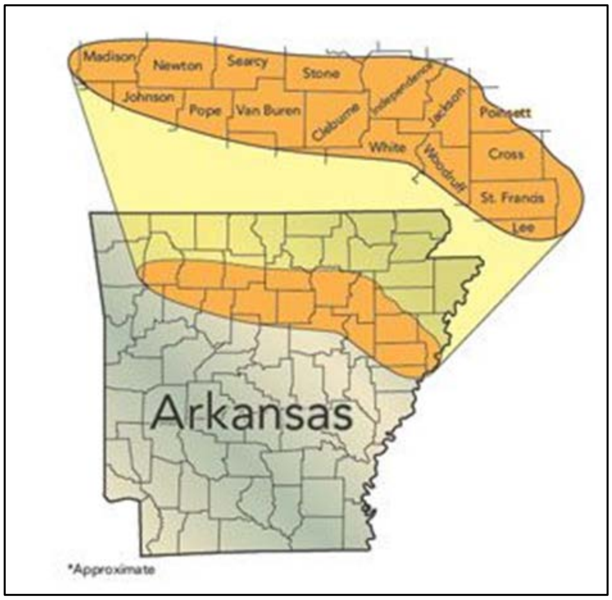


Figure 5: Map of Fayetteville Shale in Arkansas (http://www.ogj.com/unconventional-resources/fayetteville-play-map.html).

The Fayetteville shale ranges from 10 to 400 feet thick (McFarland, 2004). This region was subjected to relatively shallow continental shelf depositional patterns. The Fayetteville shale is a marine shale that was deposited with southward trending descending ramp in the northern Arkansas region (McFarland, 2004). Similar to the Marcellus shale, it is overlain by limestone (Arthur et al., 2008). This overlaying layer, known as the Pitkin Limestone, (Figure 6) is a fine to course grained oolitic biolistic limestone (Arthur et al., 2008). The Batesville Sandstone is the lower boundary which is composed of flaggy, fine to course grained sandstone, with some thin shale (Arthur et al., 2008).

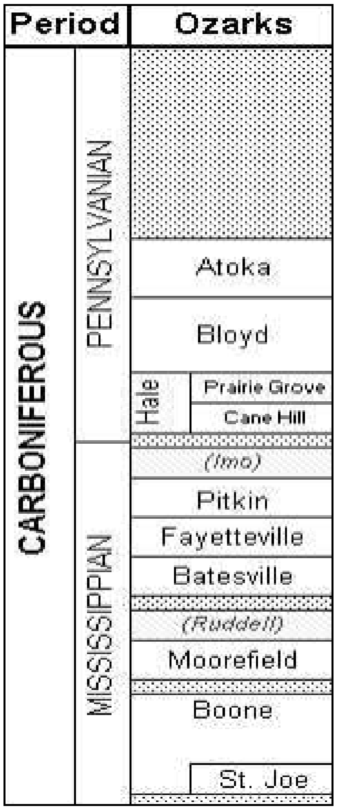


Figure 6: Stratigraphic column, showing the position of the Fayetteville Shale (McFarland, 2004).

The Fayetteville shale thickens towards the north-northeast section of the outcrop. Shale formations, such as the Cane Hill and Atoka shale, above the Fayetteville prevent the exchange of fluids between Fayetteville production waters and groundwater (Arthur et al., 2008). Drilling began in this region in 2001 with two wells, and in 7 years the number of wells developed reached 481 (Arthur et al., 2008). The annual cumulative production of this region went from 101 MMcf in 2004 to 89,168 MMcf in 2007 (Arthur et al, 2008). The producing zone ranges from 50 to 550 feet and wells range from 1,500 to 6,500 feet deep (Arthur et al., 2008).

2.4 <u>“Typical” Marcellus Shale Hydraulic Fracturing Job Using Fayetteville Shale Techniques:</u>

When comparing two separate regions it is important to discuss their geologic similarities as well as differences, and how these differences affect the fracturing process. This well was drilled by Guardian Exploration in 2007 in Potter County, New York using borrowed techniques from the Fayetteville shale. The Marcellus shale region began at a depth of 5220ft and extended to 5310ft (Fontaine et al., 2008). The well was cased with a casing that has a working pressure rating of 6700 psi. The formation was fractured between 5255ft and 5301ft (Fontaine et al., 2008). The Onondaga lime facies provides a lower boundary for the formation. There was no confining unit for upward fracture growth (Fontaine et al., 2008). This well was perforated in the lowermost portion of the organic rich section in the formation, a common practice in Marcellus shale region (Fontaine et al., 2008). Breakdown of this zone was achieved at a pumping rate of 10 BPM. In order to be broken down after the main fracturing event, the upper sections were then perforated in water (Fontaine et al., 2008). Spot acid was added after ~50 minutes to increase the perforations in the uppermost layers (Fontaine et al., 2008). The result of the acid addition can be seen in Figure 7.

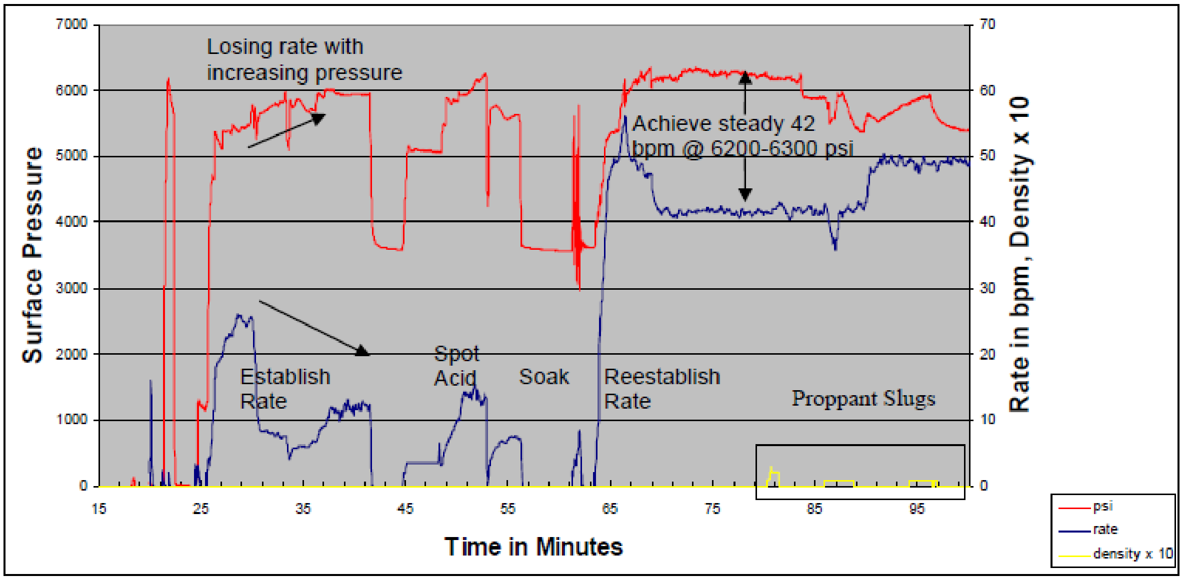


Figure 7. Result of spot acid treatment on surface pressure in the early stages of slickwater fracture in Marcellus shale at Potter County, PA (Fontaine et al., 2008).

The acid soak increased the pumping rate; however the pressure was still near the pressure limit set for the well casing (Fontaine et al., 2008). This is important to recognize as well casing failures are a main source of groundwater contamination. It was determined that the high perforated friction may have been caused by competing fractures, causing the high treatment pressure (Fontaine et al., 2008). In order to lower the pressure, proppant was introduced at 80 minutes. This large volume of proppant worked to lower the treatment pressure to 5500psi while increasing the pump rate to the optimal rate of 50 BPM (Fontaine et al., 2008). Many injections of proppant are used to increase the flow of gas from the fractures. This field study demonstrated that similar methods used to fracture Fayetteville shale are effective in the Marcellus shale region due to similar geologic characteristics. It is important to remember, however, that shales are not uniform and differences in mineralogy, crystalline structure, and other properties can vary significantly among regions (Fontaine et al., 2008).

2.5 Sources and Potential Pathways for Contaminants:

When discussing the possibility of groundwater contamination from organic compounds during the gas shale fracturing process, it is important to identify potential sources and pathways of contamination. A study performed in 2011, analyzed the common sources of water pollution in Ohio related to gas shale fracturing within the Marcellus shale region (Kell, 2011). During the period of 1983-2007, 185 groundwater contamination incidents affecting 184 private wells were reported (Kell, 2011). Drilling and completion failures (40%), orphaned wells (22%), production related (21%) and, waste disposal related issues (14%) were the most common pathways of contamination (Figure 8; Kell, 2011).

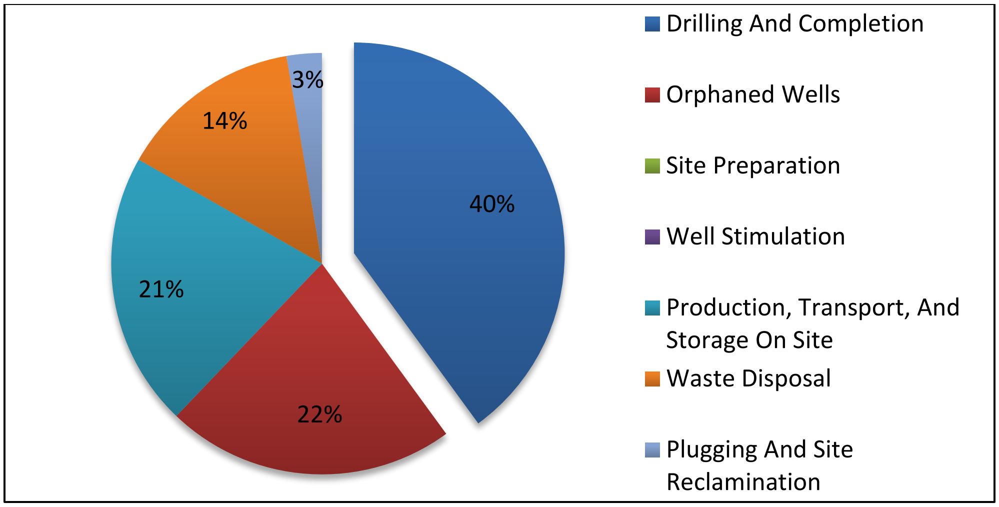


Figure 8: Gas shale fracturing incidents leading to groundwater contamination (Data from Kell, 2011).

The drilling and completion stage involves the casing process, which acts as a barrier separating hydraulic fracturing fluids and groundwater. Sixty-three of the drilling and completion stage incidents were caused by improperly engineered or non-maintained reserve pits (Kell, 2011). The reserve pit is constructed in order to contain the cutting and fluids that are circulated out during the drilling process. These pits often contain formation waters as well as crude oil (Kell, 2011). Eleven of the incidents occurred before the protective casing was installed (Kell, 2011). Production related issues occur when produced water flows to the surface of the well and are stored in tanks on site (Kell, 2011). Thirty-nine of the production incidents occurred due to leaky storage tanks, distribution lines, and produced water pits (Kell, 2011). Waste disposal issues occur when the produced waters are shipped off site for treatment (Kell, 2011). Orphaned wells refer to wells that have been abandoned after the gas shale fracturing process without being capped properly and do not have a legally responsible party (Kell, 2011).

It has been suggested that the process of hydraulic fracturing may create fractures that provide potential pathways to groundwater aquifers. This fracturing would reduce the transport time of these fluids through the geologic overburden and create a pathway between fracture waters and groundwater. In 2012, Myers developed a model using MODFLOW that suggests that the hydraulic fracturing process may increase preferential flow through natural fractures. This would result in hydraulic fracturing fluids potentially reaching ground water aquifers several years after the fracturing event (Myers, 2012). There has never been a confirmed case of groundwater contamination from this pathway (Kell, 2011).

2.6 Contaminant Fate and Transport:

As mentioned earlier, petroleum hydrocarbons are frequently used in hydraulic fracturing fluids and have the potential to reach groundwater aquifers (Kell, 2011). Due to this, it is important to understand the fate and transport of these compounds, along with how they interact with other constituents in the fracturing fluid. Accidental releases of petroleum hydrocarbons are one of the most common causes of groundwater contamination (Kao et al., 2008). These spills are difficult to remediate because residual amounts of petroleum hydrocarbons exist as non-aqueous-phase liquids within pore spaces and fractures of groundwater aquifers (Kao et al., 2008). This allows the residual stores of hydrocarbons to slowly leach into groundwater (Kao et al., 2008). As discussed earlier, petroleum hydrocarbons are often accompanied by other organic compounds in fracturing fluid. These compounds may affect the degradation and transport of the petroleum hydrocarbons.

One example of an organic compound that interferes with the degradation of petroleum hydrocarbons is ethanol. Petroleum hydrocarbons are frequently accompanied by ethanol in hydraulic fracturing fluids. Compared to the hydrophobic petroleum products, ethanol demonstrates hydrophilic characteristics (Powers et al., 2001). The preferential partitioning of ethanol into aqueous phase can create composition and volume of the aqueous phase over time, increasing the effective solubility of the petroleum products (Powers et al., 2001). Ethanol will be biodegraded at a much faster rate than other petroleum products. Preferential degradation of ethanol over BTEX has been seen under both anaerobic and aerobic environments (Powers et al., 2001). This biodegradation may cause low dissolved oxygen (DO) levels due to microbial activity in groundwater aquifers. Therefore, the presence of ethanol may affect the fate of petroleum products.

A contaminant group of great concern associated with hydraulic fracturing fluids is BTEX. Kao et al. (2008) conducted a large field study to evaluate the fate of BTEX compounds at a petroleum spill site. They found that natural attenuation caused the greatest reduction in BTEX concentrations in groundwater (Kao et al., 2008). This reduction in concentration was achieved through a mixture of physical, chemical, and biological processes. Low concentrations in DO were observed along with high carbon dioxide (CO_2), indicating a zone of natural bioremediation (Kao et al., 2008). This study site was exposed to a large biosparging operation, where oxygen was added to the groundwater system. During this time, the breakdown of hydrocarbons shifted from anaerobic to aerobic decomposition. A significant decrease in petroleum hydrocarbons was observed, demonstrating that aerobic decomposition is the dominant form of decay of these compounds in groundwater systems (Kao et al., 2008).

3. Methods

3.1 Flowback Data

3.1.1 Study Sites

Data from flowback sites that experienced hydraulic fracturing were provided by the Shale Network in collaboration with the Marcellus Shale Coalition and the Gas Technology Institute (Hayes, 2009). Data were recovered using GIS software HydroDesktop 1.6.13 (Ames et al., 2012). Four well locations in the Marcellus shale region were chosen based on availability of complete data. Three sampling sites were in Pennsylvania (Figure 9) while one site was located in West Virginia (Figure 10).

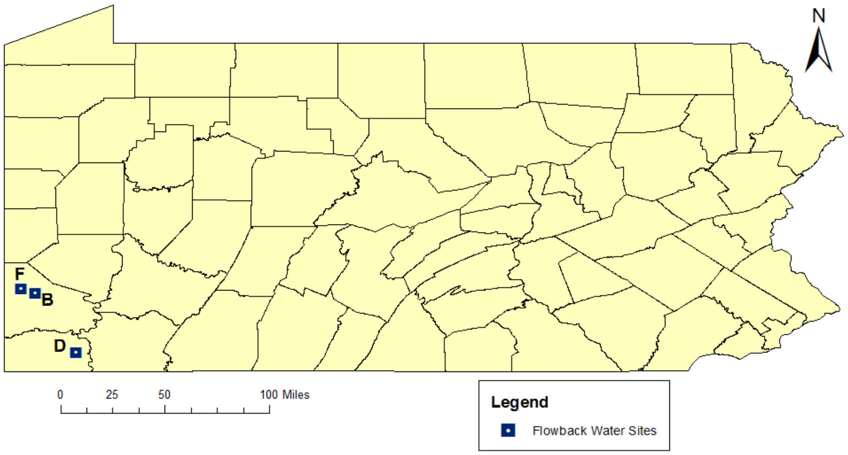


Figure 9: Location of Pennsylvania flowback water sites.

Figure 10: Location of West Virginia flowback water site.

3.1.2 Sampling Procedure

At each flowback location, gas well completion was done via hydraulic fracturing. Locations A (WV) and B (PA) were fractured using vertical fracturing methods. Locations D and F (PA) were fractured using a horizontal method (Table 4).

Table 4: Volume of fracturing fluid used at flowback sites.

	Well Type	Total Volume of Fracturing Fluid Used (bbls)
A	Vertical	40046
B	Vertical	94216
D	Horizontal	21144
F	Horizontal	77995

Five samples from each well location were collected by the Gas Technology Institute in 2009. These samples were collected during different phases of the fracturing process. A baseline sample of fracturing fluid was taken prior to injection. Grab samples were then taken on days 1, 4, and 14 following the fracturing event. These samples were collected from either a frac tank or flowback impoundment. After 90 days, a sample was taken from the producing well. Quality control and quality assurance information can be found in Appendix B. Concentrations of analytes were converted into loadings by multiplying by the up hole flow. Loading values were recorded in units of g/day.

3.1.3 Analytical Methods

Samples were analyzed for VOCs in the GRO range and SVOCs in the DRO range. Samples were analyzed for VOCs using gas chromatography/mass spectrometry (GCMS) following EPA method SW846-8260B. Samples were analyzed for SVOCs components by GCMS following EPA method SW846-8070C. The collected data were analyzed using SigmaPlot 12.5 (Systat Software, San Jose, CA) to identify statically significant regression trends.

3.2 Groundwater Data

3.2.1 Study Sites

Fifteen groundwater wells were sampled across Arkansas (Figure 11) in the Fayetteville shale region. These wells were located in a region that has been horizontally fractured for the purpose of gas shale extraction.

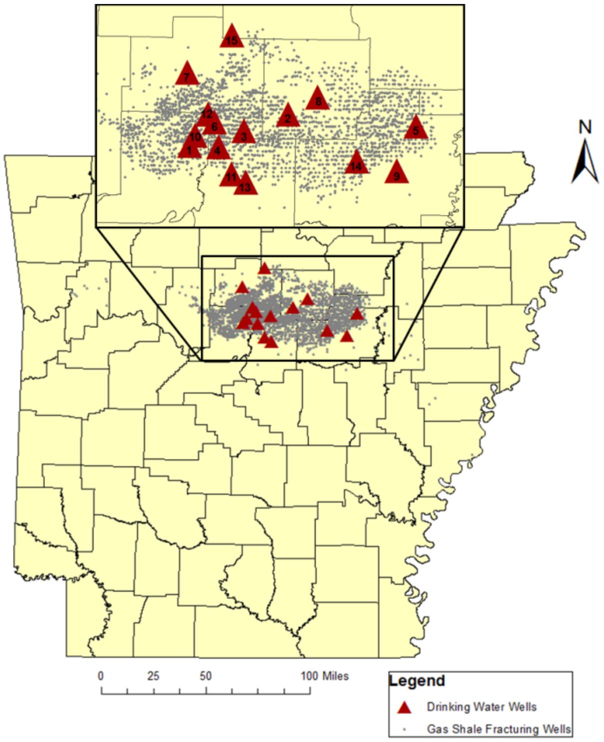


Figure 11: Arkansas groundwater sampling wells.

Each well was selected after homeowners made complaints that the quality of their groundwater had been impacted since horizontal fracturing practices began in their area. All samples from Arkansas were collected by the University of Arkansas Medical for Sciences (UAMS). Numerical site identification was given to homeowner wells in order to protect their privacy. At each site, two samples were collected with zero headspace in 40mL vials for volatile organic analysis along with a field blank. Two additional samples were then collected in 60mL vials with zero headspace for semi-volatile analysis along with a field blank. Samples were stored at 4^{o}C immediately after collection. Semi-volatile samples were acidified using HCl to a $pH \leq 2$. An additional sample was collected and used for total nitrogen and dissolved organic carbon analysis. Trip blanks were filled with laboratory grade DI water and carried to each sampling location. Trip blanks were used to identify if any contamination occurred during the travel and transport of samples.

Seven sampling sites were chosen in New York State in the Marcellus Shale region (Figure 12). These wells were located in a region that has not experienced horizontal gas shale fracturing.

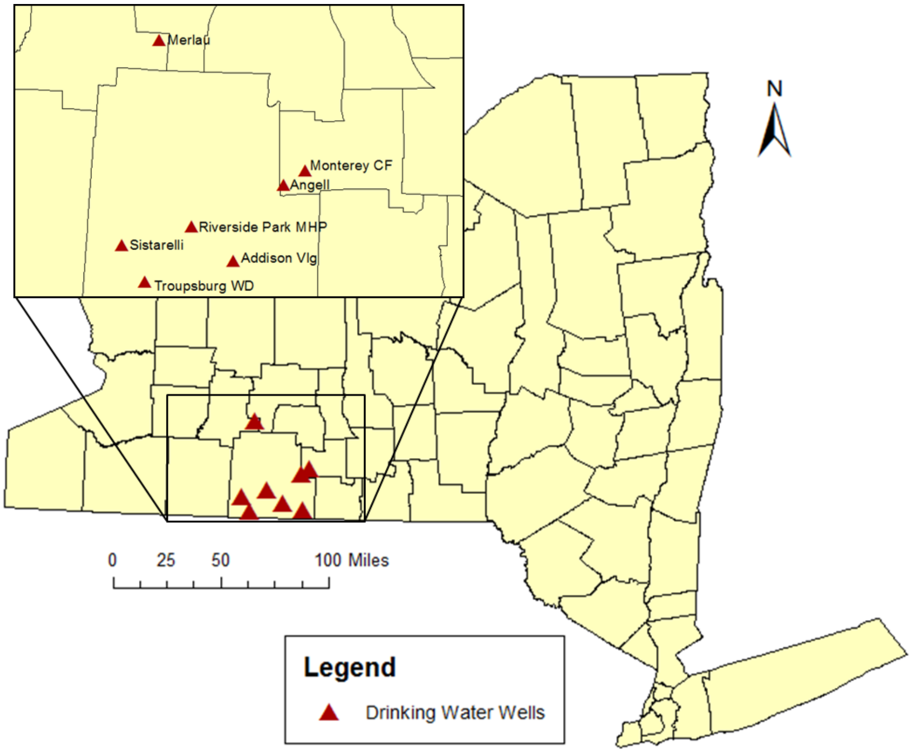


Figure 12: New York groundwater well sampling sites.

All groundwater samples from New York State were collected by the United States Geological Survey (USGS). At each site two samples were collected with zero headspace in 40mL vials for volatile organic analysis along with a field blank. Two additional samples were collected in 60mL vials with zero headspace for semi-volatile analysis along with a field blank. Samples were stored at $4^{o}C$ immediately after collection. An additional sample was collected and used for total nitrogen and dissolved organic carbon analysis. Trip blanks were filled with laboratory grade deionized water and carried to each sampling location.

3.2.2 VOC and SVOC Extraction Methods

- *VOC*

A dead space extraction technique was utilized to remove the groundwater from the 40mL collection vials and transfer it to 20mL headspace vials for VOC analysis. An empty 10mL gas tight syringe equipped with a stop cock with the plunger fully depressed was inserted through the polytetrafluoroethylene (PTFE) septa on the 40mL vial. A 10mL gas tight syringe equipped with a stop cock filled with 10mL of helium gas was also inserted through the septa. The stop cock valves were opened, and the plunger of the syringe filled with helium was slowly depressed while simultaneously extracting sample into the empty syringe at the same rate. Once 10mL of sample was extracted, the stop cock valves were closed and the syringes were removed. The sample was then transferred to a 20mL headspace vial. Headspace vials were first placed under vacuum for 3 minutes and before being filled with 5psi of helium. Afterwards, the 10mL of sample was injected into the headspace vial. The trip blank was extracted for each location. A method blank filled with laboratory quality DI water was extracted every for every ten samples. The method blank was used to identify any contamination that occurred during the extraction phase. Additional quality control and quality assurance procedures can be found in Appendix C.

- *Semi-VOC*

SVOC samples were extracted using a modified EPA method 625. The samples were acidified using HCl. Once the sample reached a $pH \leq 2$, 2mL of methylene chloride was added to the groundwater samples. The samples were then sonicated under heat for 15 minutes until the methylene chloride had settled to the bottom of the vial in a clear solution. The methylene chloride was extracted from the sample using a long tip pasteur pipette. The methylene chloride was then run through a pasteur pipette containing Na_2SO_4 and glass wool filter into a 2mL crimptop vial. At that point, the sample was blown down until all liquid had evaporated using nitrogen gas and reconstituted to 150µL with methylene chloride. The 150µL sample was transferred to a low volume spring insert, which was placed inside a 2mL crimptop vial. Once the acid extraction was completed, a base extraction was performed. KOH was added to the 60mL vial and the pH was brought up to ≥ 13 and the extraction process was repeated. A trip blank was also extracted along with a method blank filled with laboratory quality de-ionized water. Additional quality control and quality assurance procedures can be found in Appendix C.

3.2.3 VOC and SVOC Analytical methods

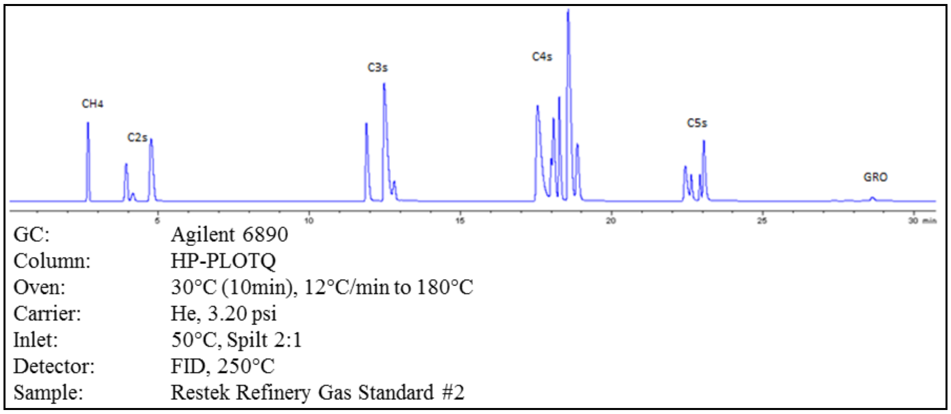
- *VOC*

Concentrations of VOCs in groundwater samples were analyzed using a static headspace method. VOCs from methane to GRO (Table 5) were quantified using a gas chromatograph (Agilent G6890N) equipped with a flame ionization detector (FID).

Table 5: Volatile organic compounds of interest

Analytes of Interest	
Methane	Isobutylene
Ethane	1,3 Butadiene
Ethylene	Trans-2-Butadiene
Acetylene	Butene-1
Propane	IsoPentane
Propylene	N-Pentane
Propadiene	Trans-2-Pentane
Isobutane	1-Pentene
N-butane	GRO

The samples were introduced to the gas chromatograph via a headspace autosampler (Agilent G1888). The samples were separated using a HP-PlotQ column, which was fed into a nickel catalyst methanizer and then quantified using a FID. Concentrations of VOCs were recorded in mg/L except for GROs, which were recorded in µg/L. The conditions of the GC along with a sample chromatograph are shown in Figure 13.



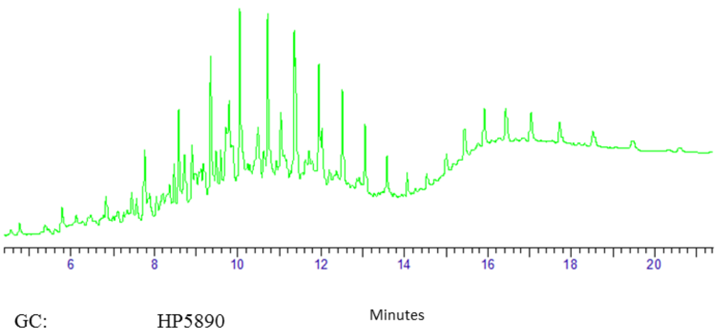
GC:	Agilent 6890
Column:	HP-PLOTQ
Oven:	30°C (10min), 12°C/min to 180°C
Carrier:	He, 3.20 psi
Inlet:	50°C, Spilt 2:1
Detector:	FID, 250°C
Sample:	Restek Refinery Gas Standard #2

Figure 13. GC conditions and sample chromatograph for VOCs.

Duplicates of each sample location were analyzed when possible. The averages were calculated and the variability between samples was represented by the standard deviation. Samples that fell below of the limit of quantification (LOQ) were recorded as zero. Samples below the LOQ were used in the calculation of averages. The LOQ for methane and ethane was 1 µg/L and 10 µg/L for GROs. Samples were analyzed for statistical significance by the Mann-Whitney Rank Sum Test using SigmaPlot 12.5 statistical software. A continuous calibration verification (CCV) and continuous calibration blank (CCB) were run every ten samples, along with a method blank and trip blank. Additional quality control and quality assurance procedures can be found in appendix C.

- *Semi-VOC*

The concentration of SVOCs in groundwater samples was analyzed using direct aqueous injection autosampler (HP6890) combined with a gas chromatograph (HP5890). SVOCs detectable were in the DRO range from C_{10}-C_{32}. The sample was separated using DB-5 column and quantified using a FID detector. Concentrations of DROs from both extractions were added together and recorded in mg/L as total DROs. Conditions for the GC along with a sample chromatogram are shown in Figure 14.



GC:	HP5890
Column:	DB-5, 0.53mm x30m
Oven:	45°C (2min), 20°C.min to 310°C
Carrier:	He, 7.5psi
Inlet:	250°C, Spiltless
Detector:	FID, 330°C
Sample:	2uL of 25ppm 10W30 Motor oil: diesel fuel #2 (1:1 blend)

Figure 14. GC conditions and sample chromatogram for SVOCs

Duplicates of each sample location were analyzed when possible. The averages were calculated and the variability between samples was represented by the standard deviation. Samples that fell below of the limit of quantification (LOQ) were recorded as zero. Samples below the LOQ were used in the calculation of averages. DRO samples that fell below of the LOQ of 0.1 mg/L were recorded as zero. Samples were analyzed for statistical significance by the Mann-Whitney Rank Sum Test using SigmaPlot 12.5 statistical software. A CCV and CCB were run every ten samples, along with a method blank and trip blank. Additional quality control and quality assurance procedures can be found in Appendix C.

3.2.4 Total Nitrogen Analytical Method

Total nitrogen (TN) was analyzed with Teledyne Tekmar Apollo 9000 Total Organic Carbon (TOC) analyzer. A catalytic combustion column converted nitrogen to $NO_{(g)}$. This $NO_{(g)}$ was combined with ozone to induce an excited state. The energy from this reaction was given off from reaction in the form of light (hv) and was measured using a chemiluminescence photodiode detector. The amount of light given off was directly related to the amount of $NO_{(g),}$ which was related to the amount of total nitrogen in the sample. Concentrations of TN were recorded in mg/L. The averages were calculated and the variability between samples was represented by the standard deviation. The minimum detection limit (MDL) was approximately 0.02 mg/L. Samples that fell below of the MDL were recorded as zero. Samples below the MDL were used in the calculation of averages. A CCV and CCB were run every ten samples in order to ensure accuracy of the analyzer.

3.2.5 Dissolved Organic Carbon Analytical Method

Dissolved Organic Carbon (DOC) was analyzed using a persulfate-ultraviolet oxidation method using a Teledyne Tekmar Phoenix 8000 UV-Persulfate TOC analyzer. In this method, the organic carbon was oxidized into carbon dioxide (CO_2) by sodium persulfate activated by ultraviolet irradiation. The CO_2 was then quantified using a nondispersive infrared (NDIR) analyzer. Concentrations of DOC were recorded in mg/L. The averages were calculated and the variability between samples was represented by the standard deviation. The minimum detection limit (MDL) was approximately 0.03 mg/L. Samples that fell below of the MDL were recorded as zero. Samples below the MDL were used in the calculation of averages. A CCV and CCB were run every ten samples in order to ensure accuracy of the analyzer.

4. Results

4.1 Flowback Data

4.1.1 Flowback Volume

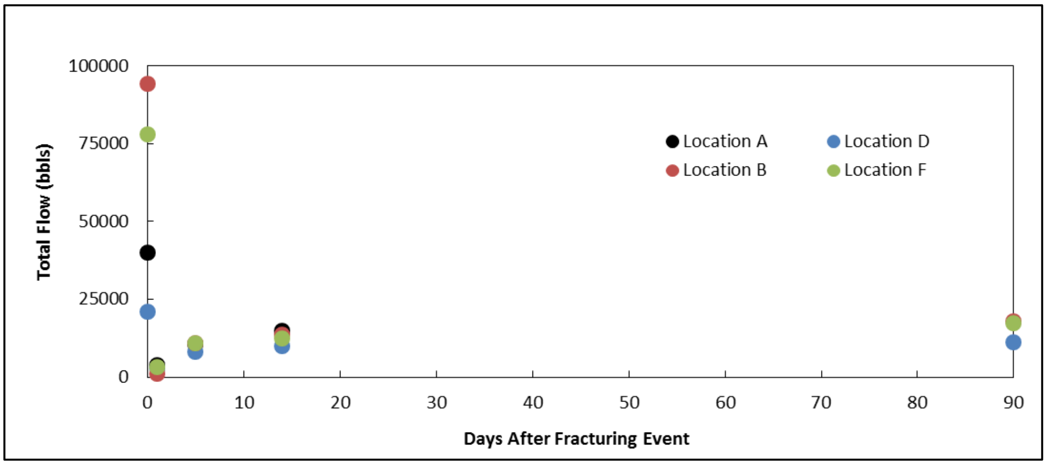


Figure 15: Total volume of flowback water by location (bbls).

The total flow for each well location in bbls is shown in Figure 15. Location B had the largest injection volume at 94,216 bbls and the largest flow on day 90 at 17,890 bbls. All locations saw the highest flow of water during the injection phase. The flow of flowback water decreased at least an order of magnitude for all locations on day 1 and then increased slightly from day 1 until day 90.

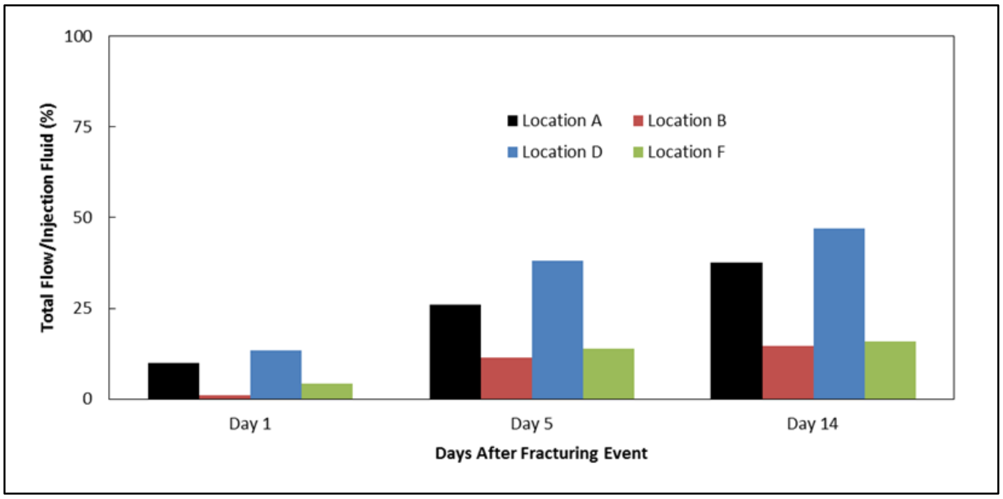


Figure 16: Percentage of injection fluid returning to the surface during the flowback period

The total flow recorded for each day during the flowback period divided by the injection volume used on day 0, is shown in Figure 16. The flowback period begins after the initial fracturing event and ends on day 14. At this time the composition of the water returning up hole changes to produced water. The lowest percentage of injection fluid returning to the surface occurred on day 1 and the largest occurred on day 14 for all locations. The largest percentage was recorded at location B on day 14 at a value of 47.0%.

4.1.2 BTEX

- *Benzene*

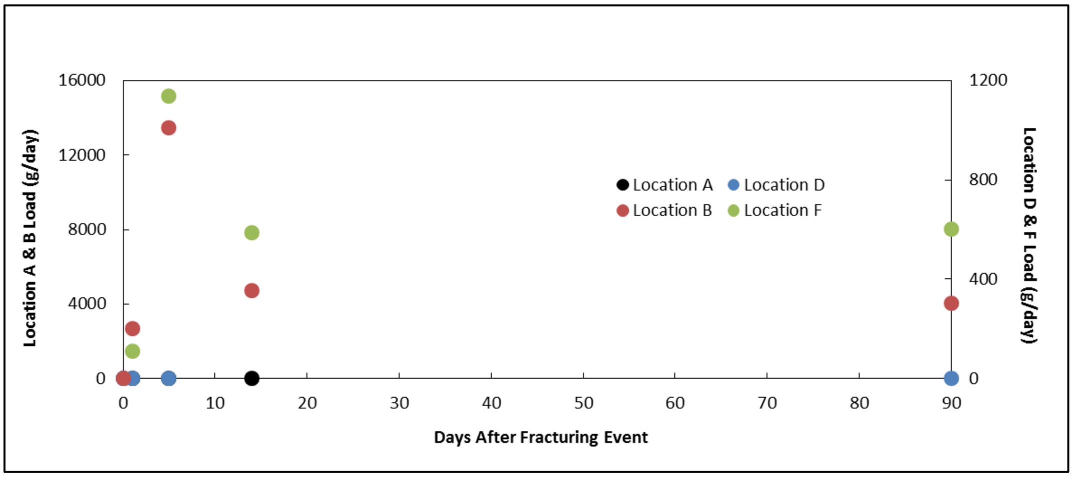


Figure 17: Loading of benzene throughout fracturing process.

Location A showed a low overall load of benzene with loadings above the detection limit for day 1 and 5, reaching a maximum on day 14 at 10.0 g/day (Figure 17). Data for day 90 were not available. Location B and Location F demonstrated load trends in which lowest loading occurred at day 0 and peak loading occurred on day 5. Location B had a peak value of 13481.2 g/day while Location F had a peak value of 1136.4 g/day. Benzene was not detected at Location D.

- *Ethylbenzene*

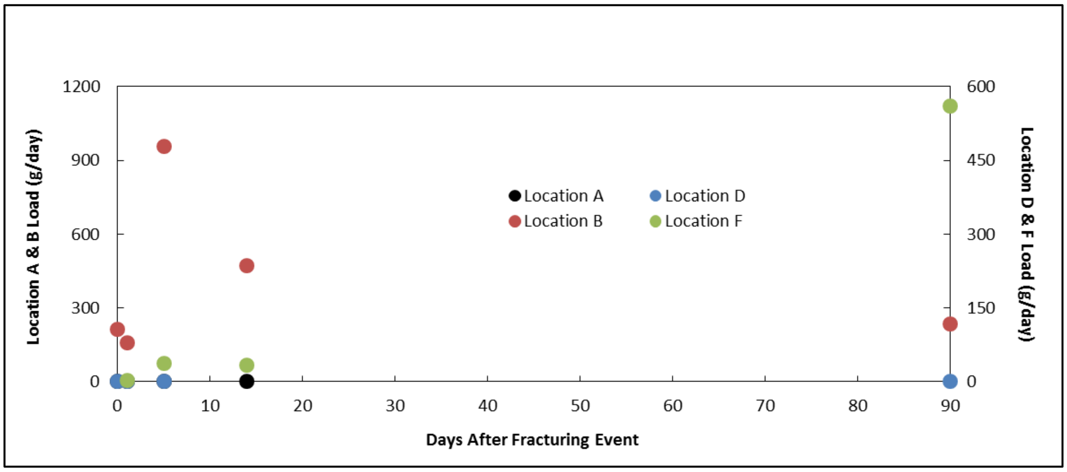


Figure 18: Loading of ethylbenzene throughout fracturing process.

Locations A and D had no detectable levels of ethylbenzene throughout the fracturing process (Figure 18). Location B had an initial load of 213.5 g/day which decreased to 157.3 g/day by day 1. The loading then showed a large increase on day 5 and reached a value of 954.9 g/day before decreasing to 235.9 g/day on day 90. Location F had an initial loading of 3.0 g/day that increased to 33.8 g/day on day 14 and to 560.6 g/day on day 90.

- *Toluene*

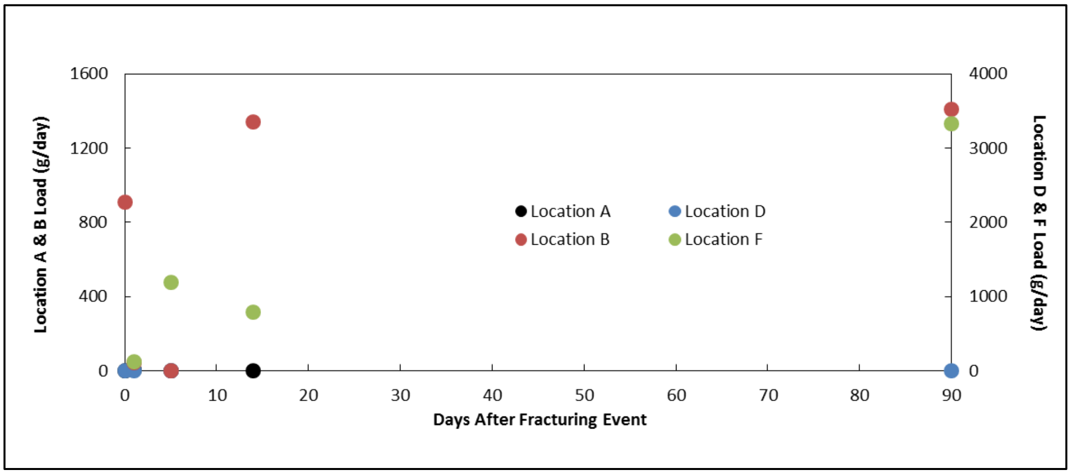


Figure 19: Loading of toluene throughout fracturing process.

On day 1 toluene loading for Location A was 2.4 g/day (Figure 19). After this time concentrations decreased to non-detectable levels. Location D had no detectable loading of toluene throughout the fracturing process. Location B had an initial toluene loading of 910.0 g/day, which decreased to the detection limit on day 5. The loading value then increased dramatically to 1341.3 g/day on day 14 and from increased slightly to 1407.9 g/day on day 90. Location F had a loading of 117.0 g/day on day 1. This value increased to 1188.1 g/day on day 5. The final loading recorded on day 90 was 3322.1 g/day.

- *Xylenes (Total)*

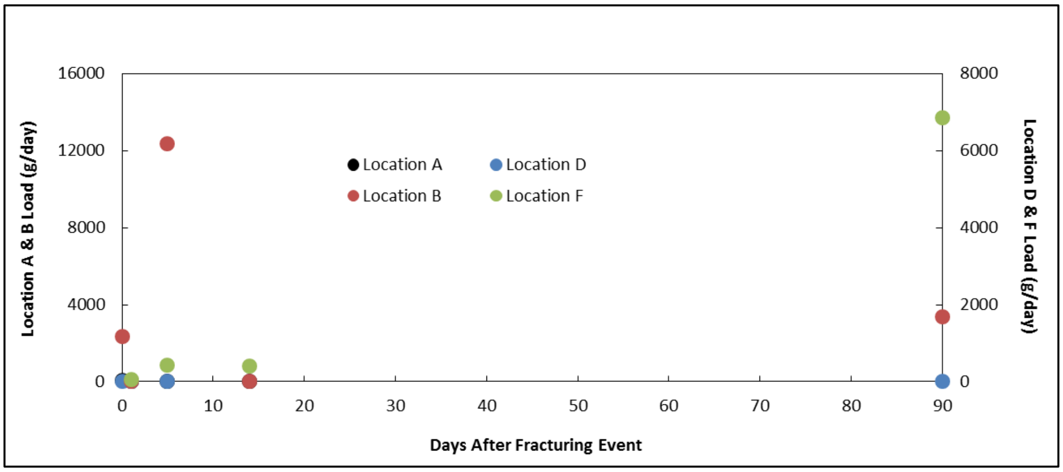


Figure 20: Loading of xylenes throughout fracturing process.

Location A had an initial xylene loading of 86 g/day (Figure 20). One day following the fracturing event, the xylene loading was below the detection limit. Location B had an initial loading of 2359.2 g/day, which decreased to the detection limit by day 1. On day 5, the loading for Location B increased to 12357.8 g/day, and on day 14 it dropped to a value of 0.0 g/day. On day 90, the loading was 3370.3 g/day. Xylene was below the detection limit at Location D over the fracturing process. Location F followed a unique trend where the loading on day 1 was 46.8 g/day, this loading increased to a value of 439.1 g/day on day 5 and slightly lower on day 14. On day 90, the loading increased dramatically to value of 6851.9 g/day.

4.1.3 GROs

- *Vertically fractured wells*

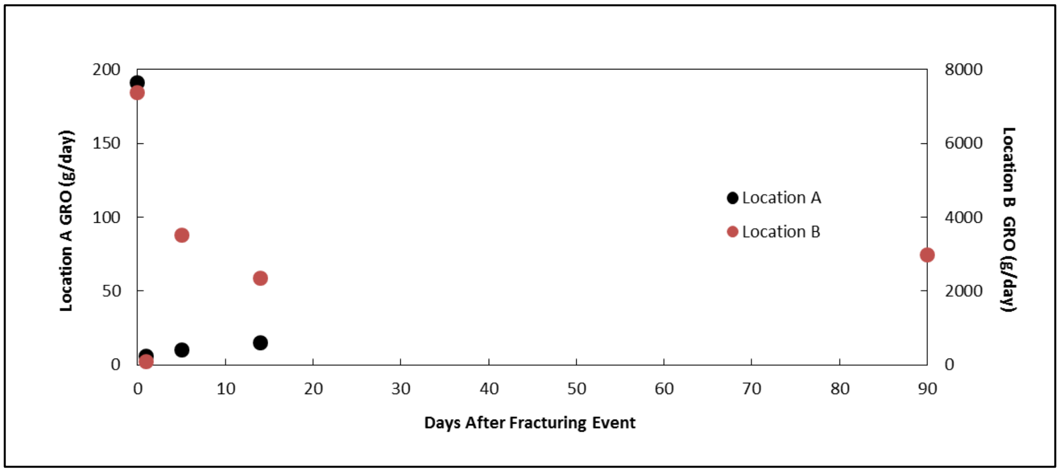


Figure 21: Loading of GRO compounds throughout vertical fracturing process.

The loading of GRO compounds for the vertically fractured sites Location A and Location B are shown in Figure 21. Location A had an injection loading of 191.0 g/day, but then the load decreased considerably to 6.0 g/day. The loading reached 15.2 g/day by day 14. There was no recorded value for day 90. Location B shows an initial decrease from day 0. Injection fluid used for this fracture had a loading of 7392.2 g/day. The GRO loading for Location B decreased to 94.9 g/day on day 1, it then increased to 3518.8 g/day on day 5. The loading then decreased on day 14 and showed a slight increase on day 90.

- *Horizontally fractured wells*

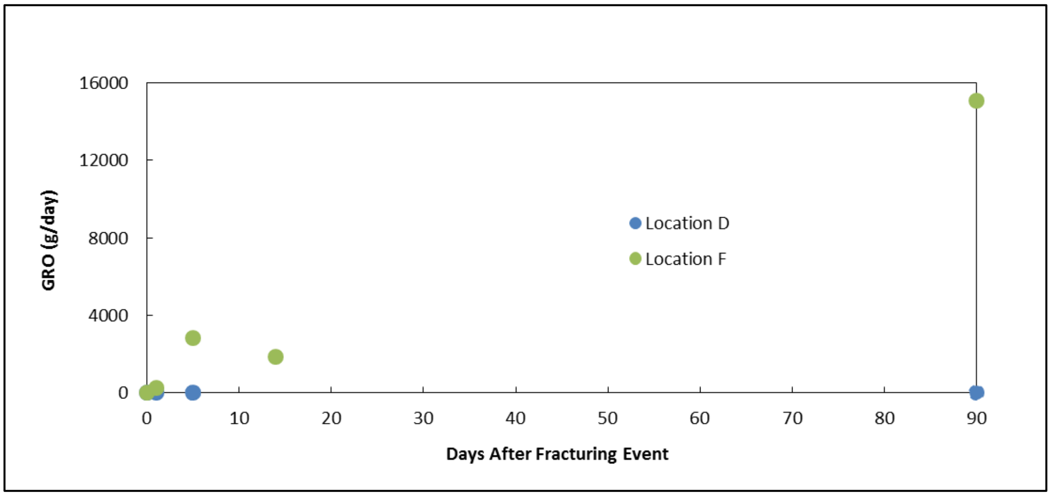


Figure 22: Loading of GRO compounds throughout horizontal fracturing process.

The loading of GROs for Locations D and F, both of which were horizontally fractured are shown in Figure 22. No GROs were detected at Location D. Location F had an initial GRO load below the detection limit; this increased to 2910.8 g/day day 5 and, then decreased to 1907.0 g/day on day 14. The final loading on day 90 was 15834.1 g/day. The final loading concentration was 544.0% larger than the largest previously recorded value at Location F on day 5.

4.1.4 DROs

- *Vertically fractured wells*

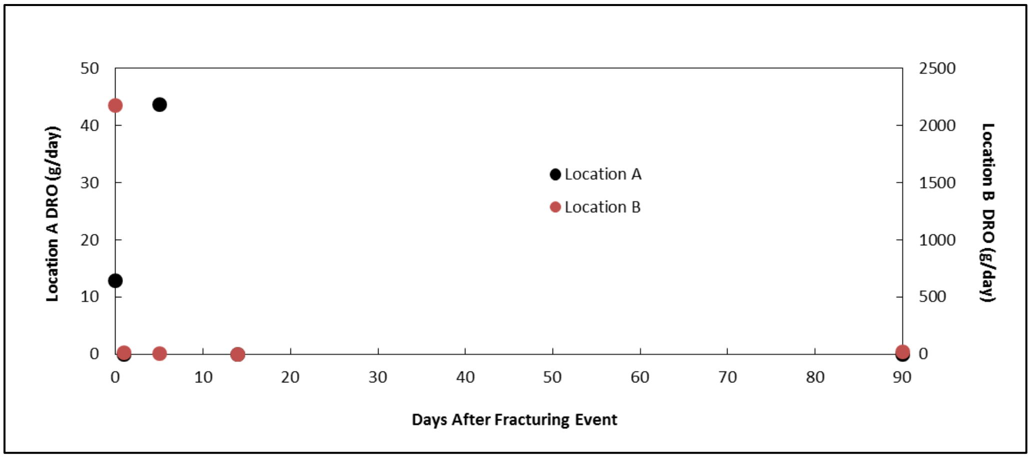


Figure 23: Loading of DRO compounds throughout vertical fracturing process.

Location A had a DRO initial loading of 12.9 g/day while Location B had an initial loading of 2179.5 g/day (Figure 23). The loading for Location A then decreased to below the detection limit. On day 5 there was a spike in the loading, reaching a value of 43.6 g/day. The loading then returned to below the detection limit for both day 14 and day 90. Location B declined to below the detection limit at day 14, which increased to 20.9 g/day on day 90.

- *Horizontally fractured wells*

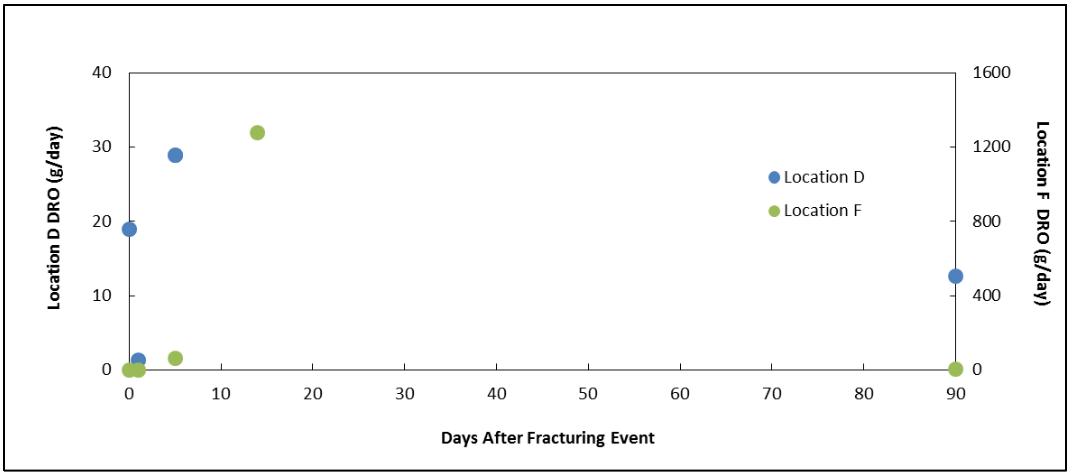


Figure 24: Loading of DRO compounds throughout horizontal fracturing process.

Location D had an initial loading of DRO of 18.9 g/day. This loading decreased to 1.3 g/day on day 1 (Figure 24). The loading then increased on day 5 to its maximum recorded value of 28.9 g/day; data on day 14 were unavailable and is represented by a dashed line. The load on day 90 was 12.7 g/day, slightly below the injection load. Location F demonstrated a similar trend. The initial and day 1 load were below the detection limit. Loading then increased to a maximum value of 1279.2 g/day on day 14. Loading returned to below the detection limit on day 90.

4.2 <u>Groundwater Samples</u>

4.2.1 DOC

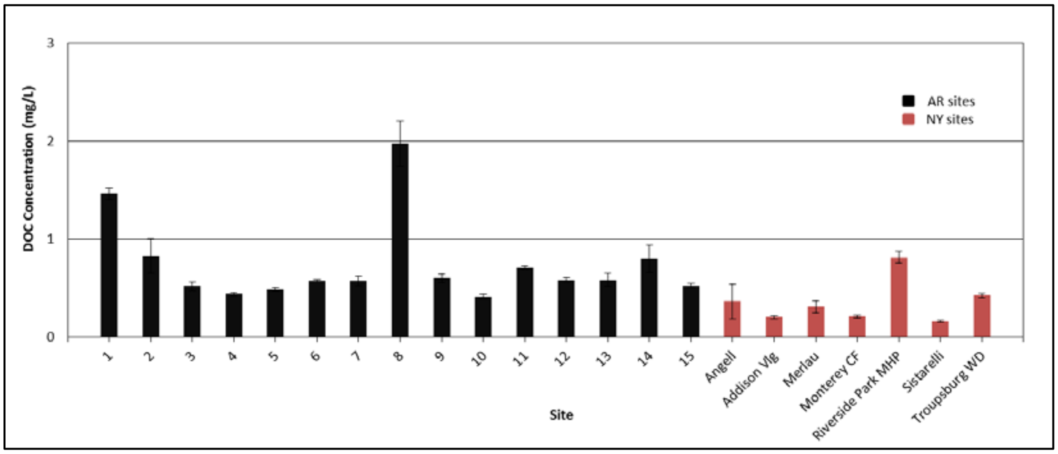


Figure 25: DOC concentration for groundwater samples.

DOC concentrations from groundwater samples ranged from 0.16±0.01 mg/L at the Sistarelli site to 1.98±0.23mg/L at site 8 (Figure 25). Arkansas samples ranged from 0.42±0.02 mg/L at site 10 to 1.98±0.23mg/L at site 8 with an average concentration of 0.74±0.43 mg/L. New York samples ranged from 0.16±0.01 mg/L at the Sistarelli site to 0.43±0.02 mg/L at the Troupsburg WD site, with an average concentration of 0.36±0.22mg/L. Arkansas and New York groundwater samples were found to be statistically different (P = 0.006 Mann-Whitney Rank Sum Test).

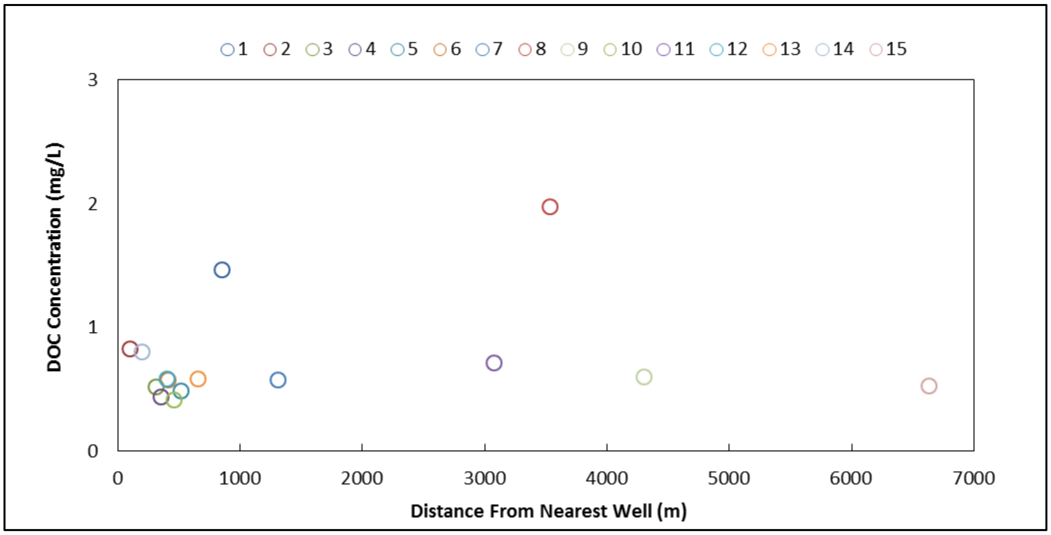


Figure 26: DOC vs. the distance to the nearest gas shale fracturing well for the Arkansas groundwater samples.

Site 8 had the highest concentration of DOC and is located 3537.0m away from a fracturing site (Figure 26). Concentrations of Arkansas sites within 1000m of a gas shale fracturing well were found to not be statistically different than sites further than 1000m (P = 0.256 Mann-Whitney Rank Sum Test).

4.2.2 TN

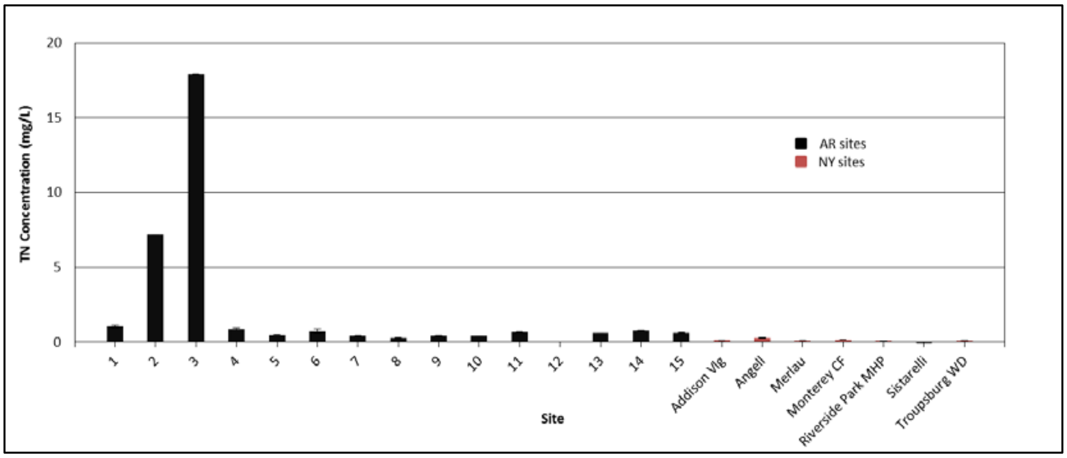


Figure 27: TN concentration for groundwater samples.

Concentrations of TN in groundwater samples ranged from 0.03± 0.00 mg/L to 17.92mg/L. Sites 2 and 3 had the largest concentrations, at 7.19 mg/L and 17.92 mg/L respectively (Figure 27). The average for the Arkansas sites was 2.18 ± 4.68mg/L. New York site concentrations ranged from 0.07 ± 0.00 mg/L to 0.29±0.01mg/L. The average for the New York locations was 0.12±0.09mg/L. Arkansas and New York groundwater samples were found to be statistically different (P = 0.001 Mann-Whitney Rank Sum Test).

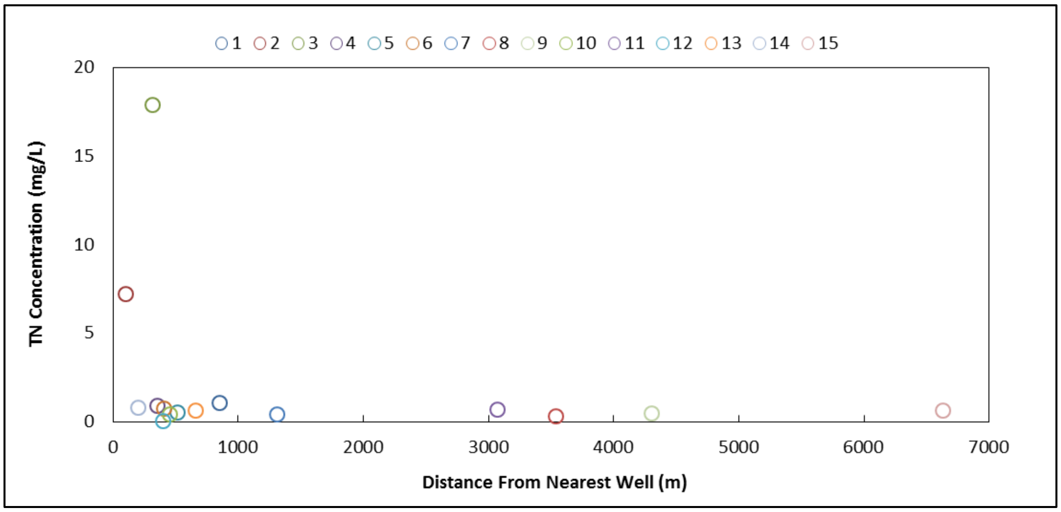


Figure 28: TN vs. the distance to the nearest gas shale fracturing well for the Arkansas groundwater samples.

Site 2 and 3 had the largest concentrations of TN and were located within 1000m of a gas shale fracturing well (Figure 28). There was not a statistical difference between sites 1000m away from a gas shale fracturing well and sites further than 1000m (P = 0.159 Mann-Whitney Rank Sum Test)

4.2.3 VOCs

Only compounds that were detected in groundwater samples are represented graphically.

a. Methane & Ethane

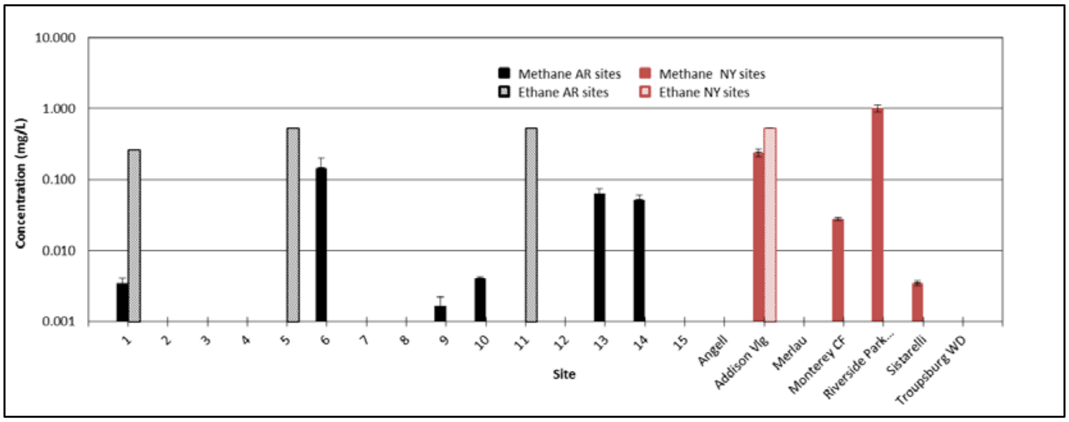


Figure 29: Methane and ethane concentrations for groundwater samples.

Figure 29, shows that six out of fifteen Arkansas groundwater samples contained detectable levels of methane. These concentrations range from non-detectable levels to 0.146 ± 0.055 mg/L, with an average concentration of 0.018 ± 0.041 mg/L. Four out of five of the New York groundwater samples contained detectable levels of methane. Concentrations ranged from non-detect to 1.023 ± 0.112 mg/L. The average concentration for groundwater samples in New York was 0.185 ± 0.380 mg/L. Arkansas and New York groundwater samples were found to be not statistically different (P = 0.299 Mann-Whitney Rank Sum Test).

Ethane was detected in three of fifteen Arkansas and one of three New York groundwater samples (Figure 29). The concentration in Arkansas samples ranged from non-detect 0.528 ± 0.00 mg/L. The value for the New York site was 0.531 mg/L. Arkansas and New York ethane concentrations were found to not be statistically different (P = 0.917 Mann-Whitney Rank Sum Test).

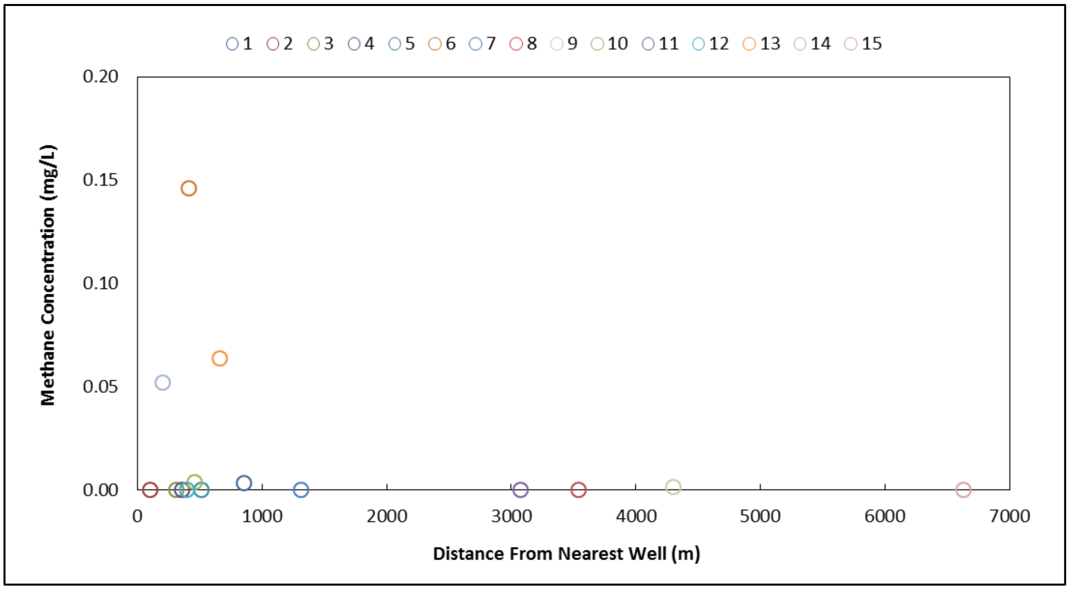


Figure 30: Methane concentrations vs. the distance to the nearest gas shale fracturing well for the Arkansas groundwater samples.

The three highest concentrations of methane in groundwater wells are located at sites 3, 13, and 14 (Figure 30). All sites were within 1000m of a gas shale fracturing well. Concentrations of Arkansas sites within 1000m of a gas shale fracturing well were found to not be statistically different than sites further than 1000m (P = 0.189 Mann-Whitney Rank Sum Test).

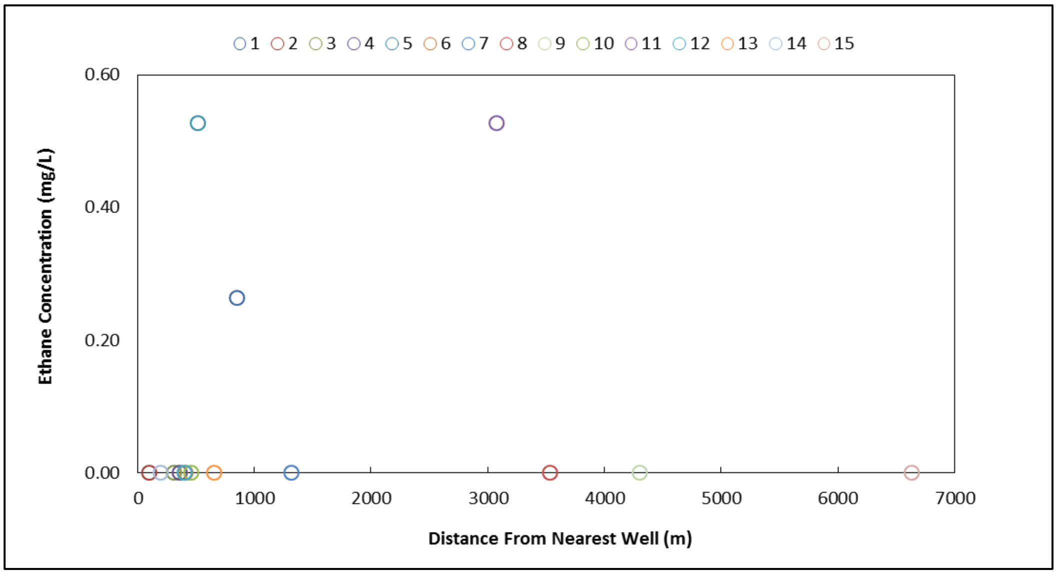


Figure 31: Ethane concentrations vs. the distance to the nearest gas shale fracturing well for the Arkansas groundwater samples.

Two of the three locations with detectable concentrations of ethane were located within 1000m of a gas shale fracturing well (Figure 31). Concentrations at sites 1 and 5 were 0.264±0.00 mg/L and 0.528±0.00mg/L, respectively. The third location with a detectable ethane concentration was site 11, with a concentration of 0.531µg/L and was located 3072.0m away from the nearest gas shale fracturing well. Ethane concentrations for Arkansas sites within 1000m of a gas shale fracturing well were found to not be statistically different than sites further than 1000m (P = 0.479 Mann-Whitney Rank Sum Test).

b. GROs

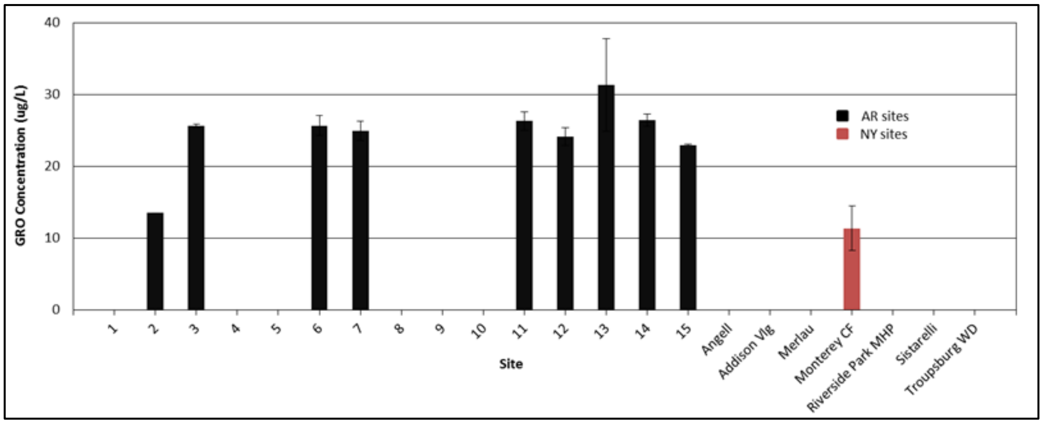


Figure 32: GRO concentration for groundwater samples

Nine of fifteen groundwater samples in Arkansas contained GROs. Concentrations of GROs in samples collected from Arkansas ranged from non-detect to 31.4 ± 6.4 µg/L; with an average concentration of 14.73 ± 12.95 µg/L (Figure 32). One New York site out of five, Monterey CF, contained GROs with a detectable concentration of 11.4 ± 3.1 µg/L. Concentrations of GROs in Arkansas were compared to sites in New York and found to be statistically different (P = 0.042 Mann-Whitney Rank Sum Test).

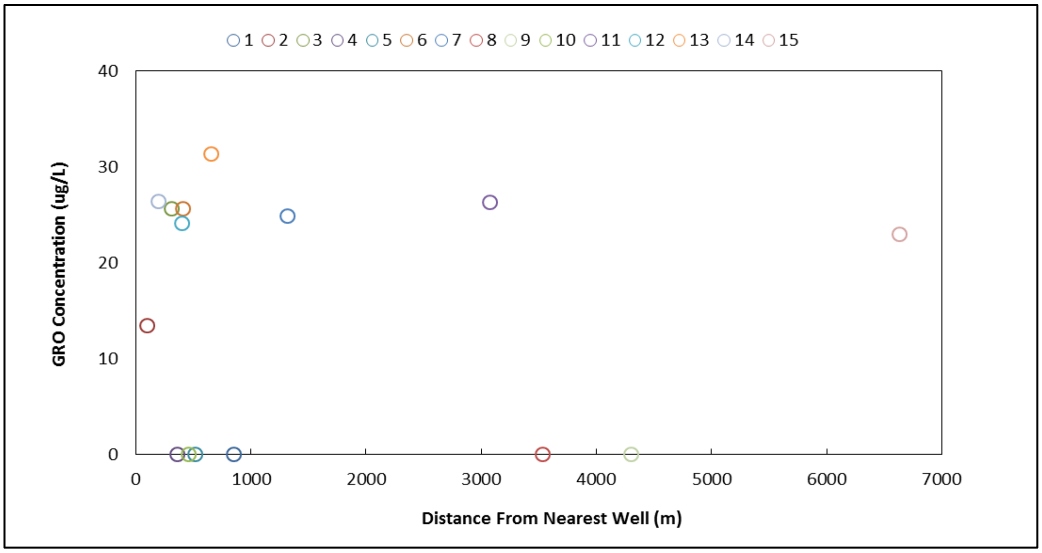


Figure 33: GRO concentrations vs. the distance to the nearest gas shale fracturing well for the Arkansas groundwater samples.

Six groundwater wells within 1000m of gas shale fracturing well contained measurable levels of GROs. The detectable concentrations within 1000m ranged from 13.5 µg/L to 31.4±6.4 µg/L (Figure 33). Two of the four groundwater wells (sites 11 and 15) at distance further than 1000m contained detectable GROs, ranging from 23.0±0.1 µg/L to 26.3±1.3 µg/L. Concentrations of GRO at Arkansas sites within 1000m of a gas shale fracturing well were found to not be statistically different than sites further than 1000m (P = 0.610 Mann-Whitney Rank Sum Test).

4.2.4 SVOCs

a. DROs

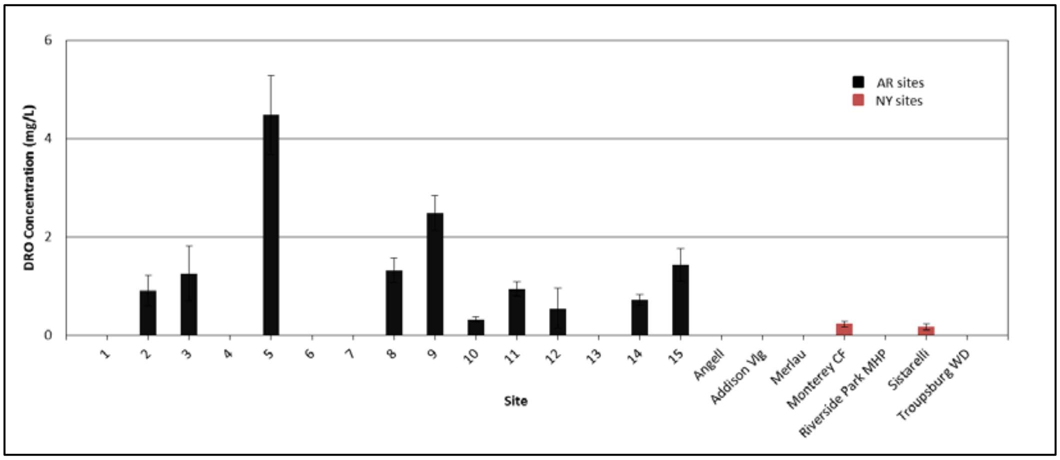


Figure 34: DRO concentration for groundwater samples.

Ten of fifteen groundwater sites in Arkansas contained detectable levels of DROs (Figure 34). DRO concentrations in Arkansas ranged from non-detect to 4.48±0.81 mg/L, with an average concentration of 0.96 ± 1.21 mg/L. Two of five sites in New York contained detectable levels of DROs; concentrations ranged from non-detect to 0.23±0.06 mg/L. Concentrations of DROs in Arkansas samples were found to be statistically different than New York sites (P = 0.029 Mann-Whitney Rank Sum Test).

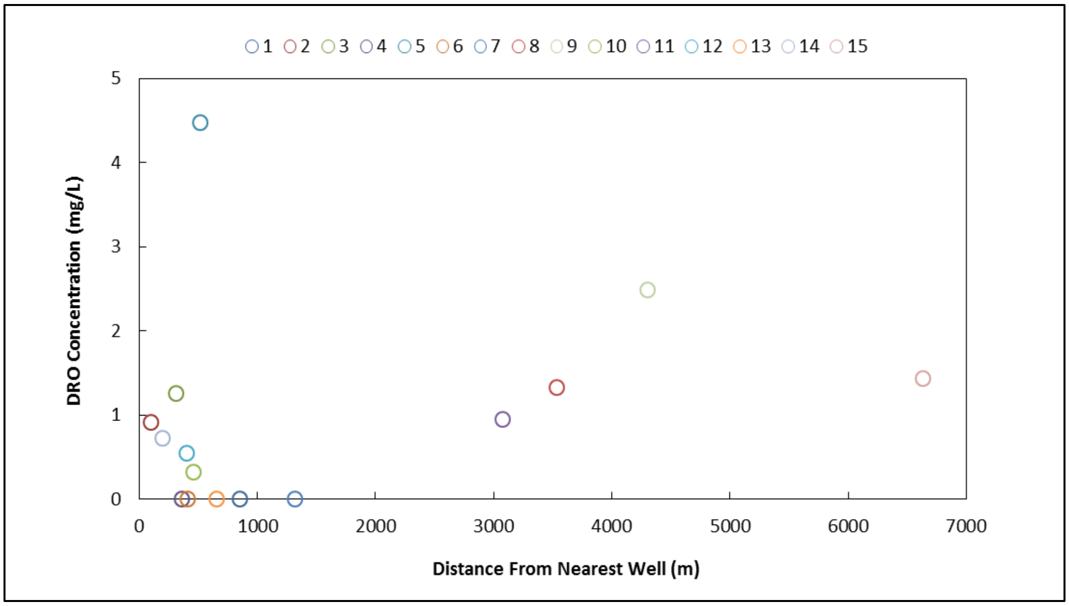


Figure 35: DRO concentrations vs. the distance to the nearest gas shale fracturing well for the Arkansas groundwater samples.

Six groundwater sites in Arkansas within 1000m of a gas shale fracturing well contained DROs (Figure 35). Concentrations within 1000m ranged from non-detect to 4.48 ± 0.81 mg/L. Four sites at a distance greater than 1000m were found to contain DROs. Concentrations at distances greater than 1000m ranged from non-detect to 2.49±0.36 mg/L. Concentrations of DRO at Arkansas sites within 1000m of a gas shale fracturing well were found to not be statistically different than sites further than 1000m (P = 0.151 Mann-Whitney Rank Sum Test).

5. Discussion

5.1 Flowback Data

5.1.1 GRO and BTEX

Patterns for GROs were present in the collected flowback data. The largest loading occurred at Location F, which is a horizontally fractured well. The initial load for Location F was below detection limit, while the final loading was 15834.1 g/day. However, GROs were not detected at Location D which was also a horizontally fractured well. GROs were detected in both vertically fracture wells. The initial loading was the largest recorded loading for both wells. The final loadings for Location A and B amounted to 8% and 40% of the initial load, respectively. This suggests that the type of fracture, or method of completion, does have an influence on when the peak loading occurs. When locations experienced a vertical fracture, the largest loading was at the time of injection. For Location F the largest loading was on day 90. Since day 14 indicates the change of flowback waters to produced waters (Hayes, 2009), the final loading is influenced by the geological formation.

Note that Location B and F are within 10 miles of each other. Location B and F both showed an increase in loading on day 5 which subsided on day 14. On day 90, both locations showed an increase in loading from values recorded on day 14. This pattern suggests that the geographic location is an important factor that influences loading trends. Results from other studies suggest that BTEX compounds exist at concentrations below maximum contaminant levels (MCLs), and therefore do not pose an imminent risk (Hayes, 2009). This conclusion can have a large effect on control factors (Hayes, 2009). However, data from this study suggest that the long-term monitoring of plugged well locations is necessary, as the loadings of GROs remains high after fracturing is complete.

In order to further examine influence of GROs, BTEX compounds were analyzed. Location A had a small loading of benzene that reached a peak of 15.2 g/day, while Location D contained no benzene. However, Location B and F showed similar trends. Both locations experience a spike in benzene on day 4 which lessened by day 14 and day 90 to a value still greater than the loading recorded on day 1. This similar trend again suggests that the geographic location of these fractures has an influence and that fracture type is not the sole governing factor. It should be noted that the vertically fractured well (Location B) had a benzene loading that was an order of magnitude greater than the horizontally fractured well (Location F). While the overall GRO loading was much lower for Location B when compared to Location F.

Ethylbenzene was not detected at either Location A or D. Location B and F both experienced a peak on day 5 followed by a decrease on day 14. Location B then saw a 50% decrease in the ethylbenzene loading on day 90, whereas Location F saw an 1178.5% increase from day 14 in loading. This pattern suggests that the type of fracture did have an effect on the loading of ethylbenzene and more importantly that the fracture facies has an effect on final loading values. However, loading values for ethylbenzene were slightly lower compared to other BTEX components.

Toluene was not detected at Location A or D. At Location F, the pattern was similar to the other BTEX component's with a spike occurring on day 5 that decreased when produced water was initially introduced. On day 90, Location F saw an increase in toluene loading. Location B showed a unique trend. The initial concentration decreased to below the detection limit on day 5. The loading increased to 1341.3 g/day where it remained near this level on day 90. This pattern was much different compared to the other BTEX compounds. It suggests that the majority of toluene from the flowback water was recovered. While the produced water contained a larger loading compared to the injection waters.

Xylenes (total) made up a large percentage of the GROs when compared to other BTEX components for Locations B and F. Xylene loading at Location A began with a concentration of 86.0 g/day before reaching a value below the detection limit. Location D had a loading below the detection limit throughout the entire fracturing process. Location B and Location F had similar patterns with very different loading values. Location B had a spike in loading on day 5 similar to Location F. Location F had a much less dramatic peak compared to Location B and saw a final loading that was nearly 1560.6% greater than the spike on day 5. While the final loading on day 90 for Location B was 369.6% lower than the spike on day 5. The similar patterns in these compounds may again be related to the geographic location of these sites. While the large difference in the final loading values may due to the difference in rock facies. It would be expected that the shale facies would have a larger concentration and loading since it contains a great deal of trapped oil and gas.

5.1.2 DROs

DRO loadings showed a unique pattern when compared to GRO patternd. Unlike GROs, DROs were detected at all locations. In the vertically fractured wells, both locations had a detectable initial concentration of DROs. The loading at Location A decreased to below the detection limit after injection. The loading at Location B on day 90 was 20.9 g/day which represents a 10898% decrease from the initial value. Location A did experience a spike in loading on day five that returned to below the detection limit by day 14. Horizontally fractured wells demonstrated an increase that peaked on or near the 14th day. Loading decreased in both locations after day 14. These data suggest that DRO loadings for vertically fractured wells are governed more by the injection fluid itself. During the flowback period, the concentrations will be at their highest. Once the fracture is completed and the flowback period ends produced water reaches the surface, loadings will reach near zero detection limit vaules. Therefore, making DROs less of a concern compared to GROs for vertically fractured well. This agrees with Hayes (2009) who found that DROs exist at low or trace levels. However, DRO loading for horizontally fractured wells appear to be influenced by geology. The Marcellus shale facies contains naturally occurring higher chain hydrocarbons causing the produced water load to be greater than the flowback waters load. Due to this characteristic, DROs are an important issue to consider for the rest of the producing well's life including during the plugging phase.

5.2 Groundwater Data

5.2.1 DOC and TN

DOC makes up a large fraction of dissolved organic matter (DOM), and can be used to help describe the overall DOM biogeochemistry (Kang and Mitchell, 2013). The subsurface transport of organic contaminants has been shown to be related to the amount of DOC located throughout the subsurface (Jardine, 1989). A number of soil chemical and hydrological characteristics control the mobility and bioavailability of DOC. These factors may in turn affect the transport of organic contaminants (Jardine, 1989). DOC data from groundwater wells near horizontally fractured sites ranged from 0.42 ± 0.02 to 1.98 ± 0.23 mg/L and were found to be statistically different compared to groundwater samples in New York which ranged from 0.16 ± 0.01 to 0.43 ± 0.02 mg/L (P = 0.006). This difference may affect the way organic contaminants move through the environment. DOC concentrations were similar to concentrations collected in 1997 by the United States Geologic Survey during National Water Quality Assessment project (USGS, 1997). DOC concentrations ranged from 0.2-1 mg/L for sites near New York locations and from 0.1-1mg/L for sites in the proximity of Arkansas locations. There was no correlation to the distance of the nearest fracturing site (P = 0.256). Thus, suggesting that DOC levels were statistically similar throughout the sampled shale play. Therefore the differences in DOC levels between the New York and Arkansas sites are most likely due to a variety of environmental factors, such as local geology. Variations of DOC may be due to differences in organic matter absorbed to clay particles that were deposited with the marine sediments during sedimentation (Grøn, et al., 1992).

Nitrogen is required for microbial growth; however, petroleum products contain only trace amounts. Therefore, the required nitrogen must come from other bioavailable sources. This makes TN a limiting factor in the biodegradation of petroleum hydrocarbons (Koren et al., 2003). Arkansas and New York groundwater TN values were found to be statistically different (P = 0.001). Arkansas sites had a larger average TN concentration with concentrations ranging from 0.03± 0.00 mg/L to 17.92mg/L compared to New York sites which ranged from 0.07 ± 0.00 mg/L to 0.29±0.01mg/L. However, a statistical relationship between site distance and the nearest hydraulic fracturing well was not found (P = 0.159). The two largest concentrations were within 1000m of a gas shale fracturing site. Identifying the source of the elevated TN concentration at site 2 and 3 elevated is difficult. It is possible these sites may have been influenced by nearby agricultural activity. Examining land cover may be an effective method in eliminating agricultural activity as a potential source.

5.2.2 VOCs

Methane levels in New York were found not to be statistically different than methane levels in Arkansas samples (P = 0.299). Concentrations of methane in New York groundwater samples ranged from non-detect to 1.023 ± 0.112 mg/L, while Arkansas samples ranged from non-detect to 0.146±0.055 mg/L. Methane concentrations in New York were similar to concentrations for non-active wells within Marcellus region collected in 2011, which averaged 1.9±6.3 mg/L of methane (Osborn et al., 2011). Concentrations also agreed with dissolved methane concentrations in New York groundwater within the southern tier region from 1999–2011 which ranged from 0.001-1mg/L of methane (Kappel and Nystrom, 2012). Arkansas methane concentrations fell within the range of concentrations found in 2011 by the USGS (Kresse et al., 2012). This report concluded that the methane concentrations were not associated with gas shale fracturing. Results from this study add support to this report, as there was no statistical difference between methane concentrations in areas with active gas shale drilling and non-active areas ($P = 0.189$). It is interesting to note that the largest concentrations of methane from Arkansas were within 1000m of the nearest gas shale fracturing well. However, since no isotopic work was performed the source of the methane is unknown.

Ethane concentrations in groundwater ranged from non-detect to 0.528mg/L for sites in Arkansas. Only one groundwater sample from New York contained detectable levels of ethane at 0.531 mg/L. The average ethane concentration found by Osborn et al. (2011) in areas near hydraulically fractured wells was 0.18 mg/L. Ethane levels in groundwater samples from Arkansas sites were also found to be not statistically different compared to New York sites ($P = 0.917$). This result further supports the 2011 USGS report, as studies have shown that the detection of ethane in groundwater is common when sites are located near active drilling sites (Osborn et al., 2011). It has been suggested that the relationship between ethane and methane concentrations can be used to identify areas where gas shale fracturing has affected water quality (Osborn et al., 2011). However, my study did not see any relationship between ethane and methane. Sites 5 and 11 had no detectable methane but, did have detectable ethane concentrations. Methane and ethane were also detected in groundwater samples located in areas where no gas shale fracturing practices are occurring. Studies have also shown that propane can be associated with areas of active drilling but not in non-active areas (Osborn et al., 2011). None of the collected samples for this study contained propane.

GRO concentrations in Arkansas were found to be statistically different than GRO concentrations in New York (P = 0.042). Only one site in New York contained GROs with a concentration of 11.4 ±3.1 µg/L, while 9 of 15 sites in Arkansas contained GROs. Concentrations of GROs found in groundwater samples from Arkansas ranged from non-detect to 31.4 ± 6.4 µg/L. Concentrations of GROs at sites within 1000m of a gas shale fracturing site were not statistically different from sites further than 1000m (P = 0.610). However, 6 of the 10 wells within 1000m of gas shale fracturing well did have a detectable level of GROs. Since there was no relationship between well distance and GRO levels it is difficult to draw conclusions on the source of these contaminants. Limited background data were available concerning GROs, since the commonly employed analytical methods look at BTEX compounds exclusively. There is no federal regulations passed addressing MCLs for the GRO group as a whole. However, there are strict guidelines on BTEX compounds. The lowest MCL for any contaminant within this group is benzene, at 5 parts per billion (ppb). Although GRO concentrations were above this level, further testing for BTEX compounds would be needed to determine if remediation is required.

5.2.3 DROs

DRO concentrations in Arkansas were found to be statistically different compared to concentrations in New York (P = 0.029). In Arkansas 10 out of 15 locations contained DROs, compared to only 2 of 5 locations in New York. DRO concentrations in groundwater samples from Arkansas ranged from non-detect to 4.48 ± 0.81 mg/L. While DRO concentrations from the two locations in New York were 0.23±0.06 mg/L and 0.17±0.06 mg/L. There was no statistical significance between the sampling location and the nearest gas shale fracturing site (P = 0.151). However, the largest concentration of DROs was found within 1000m of a gas shale fracturing site. Based on these data it is difficult to identify the source of these contaminants. Preliminary data from an EPA report monitoring two deep well groundwater sites in Pavilion, Wyoming found an increase in DROs as gas shale fracturing continued in the nearby area (EPA, 2011). The final concentration found in the EPA study were 1.440 mg/L for the first monitoring well and 4.050mg/L for the second monitoring well (EPA, 2011). These concentrations are similar to concentrations I measured in Arkansas wells. However, based on the data found in my study it is not possible to identify the source of these contaminants. Currently, there are no federal guidelines for DROs in water sources. New York and Arkansas do not have a regulatory standard for DROs specifically, however, many states have begun to develop MCLs on DROs (EPA, 1993). The state of Oklahoma requires remediation to occur when residential groundwater contains a DRO concentration of 1 mg/L or greater (Oklahoma Department of Environmental Quality, 2012). Washington State requires cleanup to occur when concentrations of DROs reach or exceed 0.5 mg/L (Washington State Department of Ecology, 2014).

6. Conclusions

As advancements in technology allow previously unattainable shale gas reserves to be exploited, there has been an increase in concern involving the potential for groundwater contamination. Due to this, improvement in technology is crucial to improve the understanding of key concepts regarding to the fate and transport of organic compounds associated with gas shale fracturing. Distinct patterns in VOCs and SVOCs were found in flowback water in the Marcellus Shale region. Unique comparisons of VOCs and SVOCs were also found in groundwater samples from Arkansas, in areas that has been exposed to horizontal fracturing, and New York in an area that has undergone no horizontal fracturing.

6.1 Flowback water

Visible trends for GROs were present in flowback data. Vertically fractured wells, Location A and Location B, saw their largest loading during the injection phase. GROs were not detected in one of the horizontally fractured wells, Location D. However, Location F showed similarities to Location B and was located within 16 kilometers of the drill site. These data suggest that the method of completion, which as mentioned earlier refers to the type of fracture, is not the sole driving factor in GRO patterns. Instead, other key factors, such as geographic location may play an important role in the loading values for these VOCs. BTEX constituents, which are components concern within the GRO range, showed similar results. Benzene loadings were very similar for Location B and Location F. Other BTEX components varied slightly but, demonstrated a constant overall pattern.

Noticeable patterns were present for DRO flowback data. Vertically fractured wells saw a high initial loading that decreased to zero or near zero values by day 90. Horizontally fractured wells saw a peak in loading on or near day 14, when flowback water shifts to produced water.

Thus, a peak at this point is indicative of the influence that the fracturing facies have on DRO mobilization. These data suggest that the method of completion does affect DRO loadings and is a key factor to consider.

6.2 Groundwater

DOC values for Arkansas and New York sites were found to be statistically different. The transport of organic contaminants has been shown to be linked to the mobility of DOC. However, the values for the two locations fell within the ranges found by the 1997 USGS National Water Quality Assessment. The differences in concentrations between these locations may have an effect on how these organic contaminants behave in groundwater systems. TN which can affect the breakdown of these organic components was also shown to be statistically different between Arkansas and New York.

Measured VOCs and SVOCs showed important differences and similarities in groundwater samples collected from Arkansas and New York. Methane is an important compound, which is frequently studied by researchers attempting to show potential pathways between fracturing fluids and groundwater systems. There was no statistical difference in methane concentrations between areas of primarily horizontal fracturing and areas of vertical fracturing. There was also no statistical difference between ethane concentrations for New York and Arkansas sites. This result supports EPA findings that hydraulic fracturing has not caused water contamination in Arkansas. GRO concentrations in Arkansas groundwater samples were found to be statistically different from those collected in New York. Six of the ten sites within 1000m of a gas shale fracturing site contained detectable levels of GROs. However, no correlation between the well location and the closest drill site could be found.

In Arkansas, 10 out of 15 locations contained detectable DROs. There was a statistical difference found between sites from Arkansas and site from New York. The highest DRO concentration was found within 1000m of a gas shale fracturing site. No statistically significant difference was found between groundwater wells within 1000m of a fracturing site and, those further than 1000m.

7. Suggestions for Future Research:

7.1 <u>Flowback</u>

1. An effort to identify the controlling factors that influence the fate and transport of organic compounds in hydraulic fracturing, focusing on key aspects of such as geographic area, depth of well, etc. is needed.

2. Long-term monitoring of drill sites is needed to fully understand if there is any potential for the migration of flowback/produced water into nearby drinking water supplies.

7.2 <u>Groundwater</u>

1. New methods for estimating aquifer properties are needed to improve the understanding of the factors that influence the fate and transport of organic contaminants in groundwater systems. These data will allow for improvements in the design of remediation systems for groundwater systems.

2. Temporal monitoring of groundwater wells along with an increase in the collection and availability of background data from wells in areas where hydraulic fracturing practices will be implemented. Data before and after hydraulic fracturing processes is needed to evaluate the potential for the migration of organic compounds from the fracturing process.

3. Studies focused on possible relationships between trace organic and inorganic compounds involved in gas shale fracturing that could be used as a tracer for groundwater wells.

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8. Appendix A. Chemical Additives

I. Water – 98% to 99% of total volume of fracturing fluid is water; depending on site location and company procedure a great volume of this water may be recycled produced water (King, 2008).

II. Proppant- 1 to 1.9% of the total volume of fracturing fluid is composed of some type of small particle (King, 2008). Most commonly well sorted fine grained sand is used; however, ceramic beads may also be used. The purpose of the proppant is to keep fractures open after the pressure is reduced (King, 2008). By using well sorted rounded particles such as ceramic beads the productivity of the well is increased.

III. Friction Reducer – approximately 0.025% of the total volume of fracturing waters is composed of a friction reducer (King, 2008). The most common friction reducer is polyacrylamide. The purpose of this is to reduce the friction pressure as the water flows through the pipe during periods of high pumping rates (King, 2008). It is important to note that this compound has the potential to decompose in toxic monomers, such as acrylamide when exposed to high temperatures and/or ultraviolet radiation (Ishizuka et al., 2008). Acrylamide is considered to be a probable human carcinogen, a neurotoxicant, and a genotoxicant according to the World Health Organization (Ishizuka et al., 2008). During the hydraulic fracturing phase injection waters are exposed to temperatures ranging from 65°C to 121°C (King, 2008). Studies have shown that when polyacrylamide is exposed to temperatures of 70°C it may begin to breakdown into acrylamide (Ishizuka et al., 2008). A carrier fluid is used to transport the friction reducing additive; two common carrier fluids are petroleum distillate and hydrotreated light petroleum distillate

(FracFocus, 2014). Winterizing and product stabilizing agents are also often added which may consist of methanol and ethylene glycol (FracFocus, 2014).

IV. Biocide – approximately 0.005% to 0.05% of the total volume of injection water is composed of a disinfectant (King, 2008). The purpose of the disinfectant is to limit the growth of microbes that interfere with the fracturing process often destroying the gelled fracturing fluids. In some cases producing hydrogen sulfide within the reservoir (King, 2008). These microbes are introduced from varying sources such as the injection water, proppant, and polymers. Common chemicals include glutaraldehyde used in the treatment of industrial wastewaters and quaternary amine which is used as an over the counter antiseptic (King, 2008). Hydroxymethyl-phosphonium sulfate is another common biocide used in injection fluids (FracFocus, 2014).

V. Surfactant/Non-Emulsifiers – 0.002% or less of the total volume of fracturing fluid is composed of some type of surfactant mixture (King, 2008). The purpose of this is to lower the surface tension between liquids that reside in the fracturing fluid in order to prevent emulsions (King, 2008). Lauryl sulfate is commonly used to increase the viscosity of the fracture fluid and acts as a non-emulsifier (FracFocus, 2014). Naphthalene is a common carrier fluid that is used to transport the surfactant (FracFocus, 2014). Ethanol, methanol, isopropyl alcohol and 2-Butoxythanol may be used as product stabilizer and/or winterizing agents (FracFocus, 2014).

VI. Gelling agent – Thickeners or gelling agents are common practice in slick water fracturing; however they may be used in hybrid fracturing fluid (King, 2008). These gelling agents help initiate the fracture and act to carry the proppant (King, 2008).. Common gelling agent mixtures consist of guar gum and cellulose polymers such as a polysaccharide blend (FracFocus, 2014). These agents are carried in many cases by petroleum distillate and hydrotreated light petroleum distillate (FracFocus, 2014). Menthol and ethylene glycol are commonly used in the gelling agent mixtures for product stabilization and/or winterization (FracFocus, 2014).

VII. Breaker – Breaker mixtures are often used to create a delay in the breakdown of gelling agents. Ammonium persulfate, Magnesium peroxide and, magnesium oxide are commonly used to delay this process (FracFocus, 2014). Sodium chloride and calcium chloride are also commonly added to the mixture and used as product stabilizers (FracFocus, 2014).

VIII. Scale inhibitors – Scale inhibitor mixtures prevent scale deposits in the well by preventing mineral scale precipices and reducing the possibility of the blockage of piping and tubing (King, 2008). Common compounds in the mixture copolymers of acrylamide and sodium acrylate, sodium polycarboxylate and, phosphonic acid salt (FracFocus, 2014).

IX. Hydrochloric acid (HCl) – 500 to 2000 gallons of used during the initial phase of the hydraulic fracturing phase (King, 2008). The added HCl dissolves minerals which helps initiate creating fissures in the rock. It does this by reducing the pressure need to create the initial fissure (King, 2008). Most of the acid is converted in calcium chloride, water, and carbon dioxide after creating of these fissures (King, 2008).

X. Corrosion Inhibitor – 0.2% - 0.5% of the fracture fluid volume consists of a corrosion inhibitor mixture if acid is being used (King, 2008). This mixture prevents the corrosion of pipes during the fracturing process (King, 2008). Formic acid and acetaldehyde are common corrosion inhibitors. Isopropanol and methanol are used as product stabilizers and/or winterizing agents (FracFocus, 2014).

XI. Iron Control – due to the geology of many well iron controls are need to prevent the precipitation of metal oxides. Common compounds used include citric acid, acetic acid, thioglyoclic acid and, sodium erythorbate (FracFocus, 2014).

XII. Crosslinker – since fracture injection fluids are exposed to high temperatures crosslinker mixtures are added to ensure that fluid viscosity remains the same as temperature increases (FracFocus, 2014). A variety of compounds made be used as cross linkers depending on the injection fluid mixture being used including potassium metaborate, triethanolamine, zirconate sodium tetraborate, boric acid, zirconium complex and, borate salts. Petroleum distillate and hydrotreated light petroleum distillate are used as carrier fluids if borate salt and zirconate crosslinker compounds are in use (FracFocus, 2014). Ethylene glycol and methanol may be added as product stabilizers and/or winterizes (FracFocus, 2014).

XIII. pH Adjuster – pH adjusting agents are often added to maintain the effectiveness of many chemical components, such as crosslinkers, during the fracturing phase (FracFocus, 2014). Sodium hydroxide, potassium hydroxide, acetic acid, sodium carbonate and, potassium carbonate are commonly used as adjusting agents (FracFocus, 2014).

9. Appendix B. QA/QC Information for Flowback Locations

Sites:

- Location A
- Location B
- Location D
- Location F
-

Source:

Hayes, Thomas. "Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas." Gas Technology Institute, 31 Dec. 2009.

Sampling:

Five grab samples from each location (19 total locations) were taken. Because the number of constituents tested for was very large only one sample was be completed to test for all constituents (Table 2). Others were only tested for major elements (Table 1).

The following grab samples were collected:

- A supply water sample (before additives were blended)
- One influent water sample following the blending with fracturing additives (excluding sand)
- Flowback water samples collected on 1, 5, and 14 days after hydraulic fracturing
- Water from the producing well at 90 days after completion

The volatile Organics were analyzed following analytical method: SW846 8260B and prepared using method: SW846 5030B.

Field methods:

The samples were collected from frac tank. To minimize volatilization a representative composite sample of the flow back water samples was collected from the top of a frac tank or flow back impoundment. In scenarios where an impoundment stores flow back water on site in an impoundment a sample were be taken following day 1, 5 and 14.

Field/ Trip Blank:

The trip blank was prepared by filling a batch of pre-cleaned 40-mL vials with laboratory-grade water. A trip blank was taken only when measuring VOC. The sample was taken onsite then returned to the laboratory. To check the quality of data from field sampling efforts, field blanks and the field duplicates were taken. These samples were treated as separate samples for identification, logging and shipping.

Equipment Blank/Calibration:

One equipment blank was collected during the characterization study. The equipment blank was collected under worst case scenario. The field equipment used was calibrated once a day at a minimum, while the lab equipment was calibrated as required.

Internal Laboratory QC Checks:

The laboratory followed the internal QC checks specified in its QAM for each data analysis, at a minimum:

- Initial and continuing calibration
- Preparation/method blanks
- Matrix spike and matrix spike duplicate or matrix spike and laboratory duplicate analysis
- Surrogate spike standard performance; and
- Calibration check compounds and reagent blanks

Preparation/method blanks were prepared at 1 for every 20 samples or one a day, whichever was greater. For all analysis where matrix spiking was possible, 1 in 20 samples is analyzed as matrix spikes and matrix duplicates. Surrogate standard determinations were performed on all samples and blanks for organic analysis. All samples were fortified with surrogate spiking compounds before purging or extraction to monitor the preparation and analysis of samples.

10. Appendix C. QA/QC Information for Groundwater Samples

Sites:

- 1
- 2
- 3
- 4
- 5
- 6
- 7
- 8
- 9
- 10
- 11
- 12
- 13
- 14
- 15
- Merlou, NY
- Riverside Park, NY
- Sisterelli, NY
- Troupsburg, NY
- Addision Vlg, NY
- Angell, NY

Source:

University of Arkansas for Medical Sciences – AR Samples

USGS- NY Samples

Sampling:

Four grab samples from each location (21 total locations) were taken.

The following grab samples were collected:

- 2- 40mL VOC samples
- 2- 60mL VOC samples

Organics were analyzed following analytical method: EPA 8015C

Field/ Trip Blank:

The trip blank was prepared by filling a batch of pre-cleaned 40-mL and 60mL vials with laboratory-grade water. A trip blank was taken when measuring VOCs/Semi-VOCs. The sample was taken onsite then returned to the laboratory. To check the quality of data from field sampling efforts field blanks were taken. These samples were treated as site samples exposed to the same identification, logging and shipping process.

Calibration:

Lab equipment was calibrated as needed.

Internal Laboratory QC Checks:

The laboratory followed the internal QAQC, at a minimum:

- Initial and continuing calibration
- Preparation/method blanks
- Matrix spike and matrix spike duplicate or matrix spike and laboratory duplicate analysis
- Calibration check compounds (CCV) and reagent blanks (CCB)

Preparation/method blanks were prepared at 1 for every 10 samples. For all analysis where matrix spiking was possible, 1 in 10 samples is analyzed as matrix spikes and matrix duplicates. Two CCV samples and two CCB samples were prepared every 10 samples.

11. Appendix D. Flowback Data

Total Volume (bbls)	Vertically Fractured		Horizontally Fractured	
	Location A	Location B	Location D	Location F
Day 0	40046	94216	21144	77995
Day 1	3950	1095	2854	3272
Day 5	10456	10782	8077	10830
Day 14	15023	13718	9938	12331
Day 90	-	17890	11185	17413
Total Frac Fluid Used, bbls	40,046	94216	21,144	77995

Total volume of fluid used/returned during the fracturing process (bbls). These values were provided by Hayes (2009). In some case, there are significant figures that are not justified.

DRO (µg/L)	Vertically Fractured		Horizontally Fractured	
	Location A	Location B	Location D	Location F
Day 0	2.7	194.0	7.5	0.0
Day 1	0.0	118.4	3.7	0.0
Day 5	35.0	6.3	30.0	47.0
Day 14	0.0	0.0	-	870.0
Day 90	0.0	9.8	9.5	3.0

Concentration of DROs (µg/L) throughout the fracturing process for vertically and horizontally fractured wells. These values were provided by Hayes (2009). In some case, there are significant figures that are not justified.

DRO (g/day)	Vertically Fractured		Horizontally Fractured	
	Location A	Location B	Location D	Location F
Day 0	12.9	2179.5	18.9	0.0
Day 1	0.0	15.5	1.3	0.0
Day 5	43.6	8.1	28.9	60.7
Day 14	0.0	0.0	-	1279.2
Day 90	0.0	20.9	12.7	6.2

Amount of DROs (g/day) throughout the fracturing process for vertically and horizontally fractured wells. These values were provided by Hayes (2009). In some case, there are significant figures that are not justified.

GRO (µg/L)	Vertically Fractured		Horizontally Fractured	
	Location A	Location B	Location D	Location F
Day 0	40.0	658.0	0.0	0.0
Day 1	12.8	727.0	0.0	723.8
Day 5	8.0	2737.0	0.0	2254.0
Day 14	8.5	1443.0	-	1297.0
Day 90	-	1399.0	0.0	7626.0

Concentration of GRO (µg/L) throughout the fracturing process for vertically and horizontally fractured wells. These values were provided by Hayes (2009). In some case, there are significant figures that are not justified.

GRO (g/day)	Vertically Fractured		Horizontally Fractured	
	Location A	Location B	Location D	Location F
Day 0	191.0	7392.2	0.0	0.0
Day 1	6.0	94.9	0.0	282.4
Day 5	10.0	3518.8	0.0	2910.8
Day 14	15.2	2360.4	-	1907.0
Day 90	-	2984.4	0.0	15834.1

Amount of GROs (g/day) throughout the fracturing process for vertically and horizontally fractured wells. These values were provided by Hayes (2009). In some case, there are significant figures that are not justified.

Benzene (g/day)	Vertically Fractured		Horizontally Fractured	
	Location A	Location B	Location D	Location F
Day 0	0.0	0.0	0	-
Day 1	3.6	2696.2	0	109.2
Day 5	10.0	13481.2	0	1136.4
Day 14	15.2	4718.4	0	588.1
Day 90	-	4044.4	0	602.1

Amount of benzene (g/day) throughout the fracturing process for vertically and horizontally fractured wells. These values were provided by Hayes (2009). In some case, there are significant figures that are not justified.

Ethylbenzene (g/day)	Vertically Fractured		Horizontally Fractured	
	Location A	Location B	Location D	Location F
Day 0	0.0	213.5	0	-
Day 1	0.0	157.3	0	3.0
Day 5	0.0	954.9	0	37.4
Day 14	0.0	471.8	0	33.8
Day 90	-	235.9	0	560.6

Amount of ethylbenzene (g/day) throughout the fracturing process for vertically and horizontally fractured wells. These values were provided by Hayes (2009). In some case, there are significant figures that are not justified.

Toluene (g/day)	Vertically Fractured		Horizontally Fractured	
	Location A	Location B	Location D	Location F
Day 0	0.0	910.0	0	-
Day 1	2.4	44.4	0	117.0
Day 5	0.0	0.0	0	1188.1
Day 14	0.0	1341.3	0	794.0
Day 90	-	1407.9	0	3322.1

Amount of toluene (g/day) throughout the fracturing process for vertically and horizontally fractured wells. These values were provided by Hayes (2009). In some case, there are significant figures that are not justified.

Xylene Total (g)	Vertically Fractured		Horizontally Fractured	
	Location A	Location B	Location D	Location F
Day 0	86.0	2359.2	0	-
Day 1	0.0	0.0	0	46.8
Day 5	0.0	12357.8	0	439.1
Day 14	0.0	0.0	0	411.7
Day 90	-	3370.3	0	6851.9

Amount of Xylene (g/day) throughout the fracturing process for vertically and horizontally fractured wells. These values were provided by Hayes (2009). In some case, there are significant figures that are not justified.

12. Appendix E. Groundwater Data

Sample	Average Site Concentration (mg/L)					
	1	2	3	4	5	6
Methane	0.003	0.000	0.000	0.000	0.000	0.146
Ethane	0.264	0.000	0.000	0.000	0.528	0.000
Ethylene	0.00	0.00	0.00	0.00	0.00	0.00
Acetylene	0.00	0.00	0.00	0.00	0.00	0.00
Propane	0.00	0.00	0.00	0.00	0.00	0.00
Propylene	0.00	0.00	0.00	0.00	0.00	0.00
Propadiene	0.00	0.00	0.00	0.00	0.00	0.00
Isobutane	0.00	0.00	0.00	0.00	0.00	0.00
N-butane	0.00	0.00	0.00	0.00	0.00	0.00
Isobutylene	0.00	0.00	0.00	0.00	0.00	0.00
1,3 Butadiene	0.00	0.00	0.00	0.00	0.00	0.00
Trans-2-Butadiene	0.00	0.00	0.00	0.00	0.00	0.00
Butene-1	0.00	0.00	0.00	0.00	0.00	0.00
IsoPentane	0.00	0.00	0.00	0.00	0.00	0.00
N-Pentane	0.00	0.00	0.00	0.00	0.00	0.00
Trans-2-Pentane	0.00	0.00	0.00	0.00	0.00	0.00
1-Pentene	0.00	0.00	0.00	0.00	0.00	0.00
GRO	0.0070	0.0080	0.0090	0.0100	0.0110	0.0120
DRO	0.00	0.91	1.26	0.00	4.48	0.00

Concentration of organic constituents in groundwater samples from Arkansas and New York. Samples below limit of quantification were reported as zero.

Sample	Average Site Concentration (mg/L)					
	7	8	9	10	11	12
Methane	0.000	0.000	0.002	0.004	0.000	0.000
Ethane	0.000	0.000	0.000	0.000	0.528	0.000
Ethylene	0.00	0.00	0.00	0.00	0.00	0.00
Acetylene	0.00	0.00	0.00	0.00	0.00	0.00
Propane	0.00	0.00	0.00	0.00	0.00	0.00
Propylene	0.00	0.00	0.00	0.00	0.00	0.00
Propadiene	0.00	0.00	0.00	0.00	0.00	0.00
Isobutane	0.00	0.00	0.00	0.00	0.00	0.00
N-butane	0.00	0.00	0.00	0.00	0.00	0.00
Isobutylene	0.00	0.00	0.00	0.00	0.00	0.00
1,3 Butadiene	0.00	0.00	0.00	0.00	0.00	0.00
Trans-2-Butadiene	0.00	0.00	0.00	0.00	0.00	0.00
Butene-1	0.00	0.00	0.00	0.00	0.00	0.00
IsoPentane	0.00	0.00	0.00	0.00	0.00	0.00
N-Pentane	0.00	0.00	0.00	0.00	0.00	0.00
Trans-2-Pentane	0.00	0.00	0.00	0.00	0.00	0.00
1-Pentene	0.00	0.00	0.00	0.00	0.00	0.00
GRO	0.0249	0.0000	0.0000	0.0000	0.0263	0.0241
DRO	0.00	1.32	2.49	0.32	0.94	0.55

Concentration of organic constituents in groundwater samples from Arkansas and New York. Samples below limit of quantification were reported as zero.

Sample	Average Site Concentration (mg/L)					
	13	14	15	Angell	Addison Vlg	Merlau
Methane	0.064	0.052	0.000	0.000	0.240	0.000
Ethane	0.000	0.000	0.000	0.000	0.531	0.000
Ethylene	0.00	0.00	0.00	0.00	0.00	0.00
Acetylene	0.00	0.00	0.00	0.00	0.00	0.00
Propane	0.00	0.00	0.00	0.00	0.00	0.00
Propylene	0.00	0.00	0.00	0.00	0.00	0.00
Propadiene	0.00	0.00	0.00	0.00	0.00	0.00
Isobutane	0.00	0.00	0.00	0.00	0.00	0.00
N-butane	0.00	0.00	0.00	0.00	0.00	0.00
Isobutylene	0.00	0.00	0.00	0.00	0.00	0.00
1,3 Butadiene	0.00	0.00	0.00	0.00	0.00	0.00
Trans-2-Butadiene	0.00	0.00	0.00	0.00	0.00	0.00
Butene-1	0.00	0.00	0.00	0.00	0.00	0.00
IsoPentane	0.00	0.00	0.00	0.00	0.00	0.00
N-Pentane	0.00	0.00	0.00	0.00	0.00	0.00
Trans-2-Pentane	0.00	0.00	0.00	0.00	0.00	0.00
1-Pentene	0.00	0.00	0.00	0.00	0.00	0.00
GRO	0.0314	0.0264	0.0230	0.0000	0.0000	0.0000
DRO	0.00	0.72	1.43	0.00	0.00	0.00

Concentration of organic constituents in groundwater samples from Arkansas and New York. Samples below limit of quantification were reported as zero.

Sample	Average Site Concentration (mg/L)			
	Monterey CF	Riverside Park MHP	Sistarelli	Troupsburg WD
Methane	0.028	1.023	0.003	0.000
Ethane	0.000	0.000	0.000	0.000
Ethylene	0.00	0.00	0.00	0.00
Acetylene	0.00	0.00	0.00	0.00
Propane	0.00	0.00	0.00	0.00
Propylene	0.00	0.00	0.00	0.00
Propadiene	0.00	0.00	0.00	0.00
Isobutane	0.00	0.00	0.00	0.00
N-butane	0.00	0.00	0.00	0.00
Isobutylene	0.00	0.00	0.00	0.00
1,3 Butadiene	0.00	0.00	0.00	0.00
Trans-2-Butadiene	0.00	0.00	0.00	0.00
Butene-1	0.00	0.00	0.00	0.00
IsoPentane	0.00	0.00	0.00	0.00
N-Pentane	0.00	0.00	0.00	0.00
Trans-2-Pentane	0.00	0.00	0.00	0.00
1-Pentene	0.00	0.00	0.00	0.00
GRO	0.0114	0.0000	0.0000	0.0000
DRO	0.23	0.00	0.17	0.00

Concentration of organic constituents in groundwater samples from Arkansas and New York. Samples below limit of quantification were reported as zero.

13. Bibliography

American Petroulem Institute. "Hydraulic Fracturing Operations— Well Construction and Integrity Guidelines." *Guidance Document HF1* 1 (2009).

Aruthur, Daniel, Brain Bohm, Bobbi Coughlin, and Mark Layne. *Hydraulic Fracturing Considerations for Natural Gas Wells of the Fayetteville Shale*. Tech. ALL Consulting, 2008.

Boyer, Elizabeth W., Bryan R. Swistock, James Clark, Mark Madden, and Dana E. Rizzo. *The Impact of Marcellus Gas Drilling on Rural Drinking Water Supplies*. Pennsylvania: Pennsylvania General Assembly, 2011.

Chen, Yudao, Yaping Jiang, Yinian Zhu, Yuan Xia, Yaping Cheng, Yuequn Huang, and Hanle Liu. "Fate and Transport of Ethanol-blended Dissolved BTEX Hydrocarbons: A Quantitative Tracing Study of a Sand Tank Experiment." *Environmental Earth Sciences* 70.1 (2013): 49-56.

Colborn, Theo, Carol Kwiatkowski, Kim Schultz, and Mary Bachran. "Natural Gas Operations from a Public Health Perspective." *Human and Ecological Risk Assessment: An International Journal* 17.5 (2011): 1039-056.

Davies, Richard, Gillian Foulger, Annette Bindley, and Peter Styles. "Induced Seismicity and Hydraulic Fracturing for the Recovery of Hydrocarbons." *Marine and Petroleum Geology* 45 (2013): 171-85.

Fontaine, J., N. Johnson, and D. Schoen. *Design, Execution, and Evaluation of a "Typical" Marcellus Shale Slickwater Stimulation: A Case History*. Proc. of 2008 SPE Eastern Regional/AAPG Eastern Section Joint Meeting, Pittsburgh. Society of Petroleum Engineers, 2008.

Gross, Sherilyn A., Heather J. Avens, Amber M. Banducci, Jennifer Sahmel, Julie M. Panko, and Brooke E. Tvermoes. "Analysis of BTEX Groundwater Concentrations from Surface Spills Associated with Hydraulic Fracturing Operations." *Journal of the Air & Waste Management Association* 63.4 (2013): 424-32.

Haluszczak, Lara O., Arthur W. Rose, and Lee R. Kump. "Geochemical Evaluation of Flowback Brine from Marcellus Gas Wells in Pennsylvania, USA." *Applied Geochemistry* 28 (2013): 55-61.

Harper, J. A. "Chapter 7: Devonian." *The Geology of Pennsylvania*. By Charles H. Shultz. Harrisburg, PA: Pennsylvania Geological Survey, 1999.

Hayes, Thomas. *Sampling and Analysis of Water Streams Associated with the Delevopment of Marcellus Shale Gas*. Rep. Des Plaines, IL: Marcellus Shale Coalition, 2009. Final Report.

Ishizuka, Mayumi, Kazutoshi Fujioka, and Takayuki Shibamoto. "Analysis of Acrylamide in a Complex Matrix of Polyacrylamide Solutions Treated by Heat and Ultraviolet Light." *Journal of Agricultural and Food Chemistry* 56.15 (2008): 6093-096.

Jackson, R. B., A. Vengosh, T. H. Darrah, N. R. Warner, A. Down, R. J. Poreda, S. G. Osborn, K. Zhao, and J. D. Karr. "Increased Stray Gas Abundance in a Subset of Drinking Water Wells near Marcellus Shale Gas Extraction." *Proceedings of the National Academy of Sciences* 110.28 (2013): 11250-1255.

Jardine, P. M., J. F. Mccarthy, and N. L. Weber. "Mechanisms of Dissolved Organic Carbon Adsorption on Soil." *Soil Science Society of America Journal* 53.5 (1989): 1378.

Kang, Phil-Goo, and Myron J. Mitchell. "Bioavailability and Size-fraction of Dissolved Organic Carbon, Nitrogen, and Sulfur at the Arbutus Lake Watershed, Adirondack Mountains, NY." *Biogeochemistry* 115.1-3 (2013): 213-34.

Kao, C.m., C.y. Chen, S.c. Chen, H.y. Chien, and Y.l. Chen. "Application of in Situ Biosparging to Remediate a Petroleum-hydrocarbon Spill Site: Field and Microbial Evaluation." *Chemosphere* 70.8 (2008): 1492-499.

Kappel, W. M., and E. A. Nystrom. *Dissolved Methane in New York Groundwater, 1999—2011*. Working paper no. 2012-1162. U.S. Geological Survey Open-File Report, 2012.

Kell, Scott. "State Oil and Gas Agency Groundwater Investigations And Their Role in Advancing Regulatory Reforms, A Two-State Review: Ohio and Texas." *Ground Water Protection Council* (2011).

King, George. *SPE Hydraulic Fr Acturing Technology Conference*. Proc. of Hydraulic Fracturing 101: What Every Representative, Environmentalist, Regulator, Reporter, Investor, University Researcher, Neighbor and Engineer Should Know About Esti Mating Frac Risk and Improving Frac Performance in Unconventional Gas and Oil Wells, The Woodlands, Texas. Society of Petroleum Engineers, 2012. SPE 152596.

Koren, O., V. Knezevic, E. Z. Ron, and E. Rosenberg. "Petroleum Pollution Bioremediation Using Water-Insoluble Uric Acid as the Nitrogen Source." *Applied and Environmental Microbiology* 69.10 (2003): 6337-339.

Kresse, T. M., N. R. Warner, P. D. Down, A. Vengosh, and R. B. Jackson. *Shallow Groundwater Quality and Geochemistry in the Fayetteville Shale Gas-production Area, North-central Arkansas, 2011*. Rep. no. 2012–5273. U.S. Geological Survey Scientific Investigations Report, 2012.

McFarland, John David. *Stratigraphic Summary of Arkansas*. Little Rock, AR: Arkansas Geological Commission, 1998.

Milici, Robert, and Christopher Swezey. *Assessment of Appalachian Basin Oil and Gas Resources: Devonian Shale–Middle and Upper Paleozoic Total Petroleum System*. Rep. United State Gological Survery, 2006. File Report Ser. 2006-1237.

Myers, Tom. "Potential Contaminant Pathways from Hydraulically Fractured Shale to Aquifers." *Ground Water* 50.6 (2012): 872-82.

Oklahoma Department of Environmental Quality. "Risk-Based Levels for Total Petroleum Hydrocarbons (TPH)." *Department of Environmental Quality's Resources*. Oklahoma Department of Environmental Quality, 2012.

Osborn, S. G., A. Vengosh, N. R. Warner, and R. B. Jackson. "Methane Contamination of Drinking Water Accompanying Gas-well Drilling and Hydraulic Fracturing." *Proceedings of the National Academy of Sciences* 108.20 (2011): 8172-176.

Powers, Susan E., Craig S. Hunt, Stephen E. Heermann, Henry X. Corseuil, David Rice, and Pedro J. J. Alvarez. "The Transport and Fate of Ethanol and BTEX in Groundwater Contaminated by Gasohol." *Critical Reviews in Environmental Science and Technology* 31.1 (2001): 79-123.

Soeder, D. J., and William M. Kappel. *Water Resources and Natural Gas Production from the Marcellus Shale*. Reston, VA: U.S. Dept. of the Interior, U.S. Geological Survey, 2009.

Soeder, D. J., and William M. Kappel. *Water Resources and Natural Gas Production from the Marcellus Shale*. Reston, VA: U.S. Dept. of the Interior, U.S. Geological Survey, 2009. USGS Fact Sheet 2009-3032.

United States. Energy Information Adminstration (EIA). Office of Integrated and International Energy Analysis. *Annual Energy Outlook 2013 with Projections to 2040*. Annual Energy Outlook 2013 With Projections to 2040 April 2013 U.S. Energy Information Administration, Apr. 2013.

United States. Environmental Protection Agency. Office for Underground Storage Tanks. *State Summar of Soil and Groundwater Cleanup Standards for Hydrocarbons*. By Tamlyn Oliver, Paul Kstecki, and Edward Calavbrese. Amgerst, 1993.

United States. Environmental Protection Agency. Office of Research and Development. *Investigation of Ground Contamination near Pavillion, Wyoming*. By D. DiGiulio, R. Wilkin, C. Miller, and G. Oberley. 2011. Draft.

United States Geological Survey. National Water Quality Assessment Data Warehouse. 1997. Raw data. Virginia, Reston.

US Environmental Protection Agency. "Proceedings of the Technical Workshops for the Hydraulic Fracturing Study : Well Construction & Operations." *Office of Research and Development* (2011).

Ver Straeten, C. A., and C. E. Brett. *Lower and Middle Devonian Foreland Basin Fill in the Catskill Front: Stratigraphic Synthesis, Sequence Stratigraphy, and the Acadian Orogeny*. Proc. of New York State Geological Association. 1995. 313-56. 67th Annual Meeting Field Trip Guidebook.

Washington State Department of Ecology. "Table 720-1 Method A Cleanup Levels for Groundwater." *Access Washington*. Washington State Department of Ecology, 2014.

"What Chemicals Are Used." *FracFocus Chemical Disclosure Registry*. Groundwater Protection Council and Interstate Oil and Gas Compact Commission, 2014.

Youngster, Laura K. G., Piyapawn Somsamak, and Max M. Häggblom. "Effects of Co-substrates and Inhibitors on the Anaerobic O-demethylation of Methyl Tert-butyl Ether (MTBE)." *Applied Microbiology and Biotechnology* 80.6 (2008): 1113-120.

VITA

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