TAILORED ANALYTICAL METHODS
FOR SURVEYING GROUNDWATER
QUALITY IN AREAS OF
UNCONVENTIONAL DRILLING

by

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Dedication

To the ones I love:

With God as your guide, may you seek opportunities and develop them beyond your wildest dreams.

Acknowledgements

I would like to open with acknowledging my research mentor, Dr. Kevin A. Schug, who saw potential in me early on and challenged me to achieve every bit of it. His tenacity for advancing the analytical research field has allowed opportunities and developed me beyond what I could have imagined just a few years ago. I would also like to express appreciation to my committee members, Dr. Brad Pierce, Dr. Roshan Perera, and Dr. Subhrangsu Mandal, for broadening my understanding of research topics and offering professional advice along the way.

I also must recognize the research fervor of co-workers Dr. Brian Fontenot, Dr. Zacariah Hildenbrand, and Dr. Laura Hunt. Their passions for research led them to seek out analytical expertise for surveying groundwater in areas of hydraulic fracturing in May 2011. Without their ideas and expertise, this resulting dissertation topic would not have existed.

I cannot express enough appreciation to my loving wife Leah who thought the most of me and reminded me of this whenever I felt inadequate for the challenges ahead. My daughter Atlie Belle could always lightened the atmosphere after a long day as I watched her playing with her Giant Microbe collection. And finally, to my parents, thank you for giving me every opportunity to make the most of myself, whatever it would be.

April 21, 2014

Abstract

TAILORED ANALYTICAL METHODS FOR SURVEYING GROUNDWATER QUALITY IN AREAS OF UNCONVENTIONAL DRILLING

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The University of Texas at Arlington, 2014

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Many questions have been raised over the environmental impact of unconventional drilling techniques, especially on the groundwater of the extraction area. Analytical approaches and methods specific to hydraulic fracturing had to be developed due to the lack of available research at the time. The analytical approaches chosen for the extensive survey of groundwater quality included general groundwater measurements, bulk water characterization, and organic, inorganic, and ionic speciation. Some of the chosen targets included volatile and semivolatile ingredients in hydraulic fracturing fluid, metals associated with drilling fluids or formation waters, and total carbon and nitrogen measurements. These methods were developed and then implemented in studies to understand the effect unconventional drilling techniques have on the groundwater in the Barnett Shale region of north Texas and the Cline Shale formation of west Texas. Measured constituents were correlated to distance to the nearest gas well, databased information before unconventional drilling occurrences, and changes over time in the Cline Shale. Groundwater for the regions was collected through private residential water wells.

Interpretations of the findings herein have resulted in a few conclusions regarding unconventional drilling in two regions of Texas. First, it was concluded that the Barnett Shale seems to be victim to subsurface perturbations giving rise to sporadic elevated arsenic, strontium, selenium, and total dissolved solids as compared to the decade of the 1990s, a time before widespread unconventional drilling in the area. Second of all, heavy metal concentrations were highest in areas closest to natural gas wells and in more shallow wells. The third conclusion, resulting from a time-lapse study located within the Cline Shale, was variable lifetimes are present for fluctuating groundwater parameters, bulk water measurements, and endogenous organic compounds.

Also found within these pages is a fundamental study quantifying the amount of matrix effect present in elemental analysis of 19 metals for selected groundwater samples across the Barnett Shale region. Reversed phase – solid phase extraction was used to separate hydrophobic constituents from the samples to assess the influence toward observed matrix effects of the ionic and hydrophobic portions of the water. General water quality parameters like total dissolved solids and salinity were also considered. Discussion is presented toward suggested sample preparation depending on the analyte of interest.

Lastly, presented is a biological assay, QwikLite™ 200, which would be suitable for rapid response field analysis of chemical spills related to unconventional drilling. The assay was capable of accurately responding to glutaraldehyde and hydrochloric acid, two common constituents in fluid mixtures of unconventional drilling, in as little as 4 hours. The assay demonstrates similar or greater sensitivity than other bioassays for these two compounds and a quicker response time.

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Chapter 1

Introduction

The newest form of fossil fuel energy in the United States, culminating from technological advances, is natural gas from non-porous shale or tight-sand formations[1]. This type of natural gas is referred to as unconventional natural gas (UNG) since it requires unconventional drilling techniques like horizontal drilling, hydraulic fracturing, or shale acidization for extraction to be economically attractive. These techniques have allowed for tremendous growth in UNG production over the past 10 years and more to come[2]. While this newly-available resource has been a notably positive impact on local and national economies[2,3], the concerned uncertainty of the environmental impacts, primarily for water resources, has been nearly on the same magnitude[1,4,5].

The rapid development of unconventional drilling affecting millions of Americans across the country has outran the pace of tailored analytical methods specific to drilling and hydraulic fracturing to develop objective professional conclusions of the efficacy of UNG. Previous works have investigated dissolved gases in groundwater[6,7] and ions in groundwater and surface water[8,9]. These studies have shown evidence of elevated gases and ions present in groundwater and surface water, but have had difficulties in making definitive conclusions because of multiple sources for the analytes and lack of baseline values before the expansion of unconventional drilling.

The first requirement of this work was to understand and develop analytical methods that would be specific to drilling and hydraulic fracturing activity. Within the Barnett Shale region of north Texas[10], 91 private water wells within 3 km of a natural gas well were sampled, along with 9 reference private water wells removed from natural gas drilling. Water analysis included general water quality measurements onsite, a biological assay for bulk water measurements, gas chromatography – mass spectrometry (GC-MS) for ingredients in hydraulic fracturing fluids, headspace – GC (HS-GC) for light alcohols, and inductively coupled plasma – MS (ICP-MS) for arsenic, barium, selenium, and strontium quantification. Detected analytes were compared to a regional dataset[11] of information of well water quality in the sampled counties from 1989-1999. Comparisons of the current measurements with the historical dataset, sample distance from natural gas wells, and water well depth where then made in order to assess the impact of unconventional drilling in north Texas.

Once the efficacy of the methods had been tested and proven, a time-lapse study of four data sets over 15 months was conducted in Nolan County of the Cline Shale formation of west Texas. Well water samples from a concentrated area in the county before and after hydraulic fracturing in the area. General water quality measurements and HS-GC for alcohols were kept the same as in the Barnett Shale study. Other methods progressed with new information and analytical capabilities. The target list of hydraulic fracturing ingredients was expanded for GC-MS, ICP – optical emission spectroscopy (ICP-OES) was incorporated to quantify additional metals, total carbon and total nitrogen measurements replaced the biological assay for bulk water measurements, and ICP-MS still quantified As and Se. Absolute concentrations of constituents in the well water, along with changes over time and with baseline information, are key discussion points of the resulting UNG impact when bringing into account distance to the nearest gas well and the dates of drilling activity.

A fundamental study[12] was conducted to investigate the different matrices present in 20 samples from the Barnett Shale survey[10] and their affect toward the accuracy of quantification with ICP-OES. These samples were subject to different sample preparation strategies to isolate ionic and organic constituents from the bulk solution. Each system was assessed for matrix effects present for 19 different metals through standard addition. Preparation strategies for quantification were then discussed for each metal with respect to its water quality measurements and identified matrix effects.

The biological assay QwikLite™ 200[13] was studied[14] along the way to determine the sensitivity and the practicality for utilizing this tool for rapid response to groundwater contamination events related to the unconventional drilling techniques of hydraulic fracturing and shale acidization. The light output of bioluminescent *Pyrocystis lunula* was tested against the endogenous metals arsenic, barium, selenium, and strontium and the exogenous compounds glutaraldehyde and hydrochloric acid. The experimentally determined IC_{50} value for each analyte was then monitored over a time period of 4 to 96 hours to determine how quickly an accurate determination could be made in an instance warranting rapid response.

These methods and techniques discussed herein are in effort to establish the new analytical frontier in understanding the implications of UNG on the surrounding groundwater. Applying these methods to studies such as in the Barnett Shale and Cline Shale allow for sound conclusions to be made about the livelihood of private well water quality and the life cycle of compounds that may be introduced into the groundwater system during UNG processes. Over time, proven methodologies will allow research to flourish and come to accepted conclusions on the value of UNG.

Chapter 2

Possible Analytical Targets for Studying Potential Groundwater Contamination by Unconventional Drilling

2.1 Introduction into Shale Gas and Extraction

The proliferation of natural gas wells in the United States of America over the past 10 years (Figure 2-1) has been made possible through unconventional drilling techniques like horizontal drilling and hydraulic fracturing. Gas found in low-permeability reservoirs which was previously uneconomic to extract and required additional extraction techniques, i.e., unconventional natural gas (UNG)[15], is now the target of many energy providers and quickly changing American living across the nation[3]. Shale gas rose from being a negligible gas source in 1990 to contributing 30% of all gas production today. As of 2012, UNG from shale and tight sand represented 34% and 24%, respectively, of total natural gas production in the U.S.[2]. Estimates project[16] that by 2040, natural gas will overtake coal as the greatest generator of electricity for the country, while others[17] identify the 50-year future of natural gas to be “not sustainable”. Figure 2-2 shows shale gas production in the United States through 2012, which was dominated by three shale formations: The Marcellus Shale (29%); the Haynesville Shale (23%); and the Barnett Shale (17%)[2]. There are currently 7234 shale gas wells in Pennsylvania of the Marcellus Shale[18], 3253 wells producing in the Haynesville Shale of Texas and Louisiana[19,20], and 17,494 wells in the Barnett Shale[21].

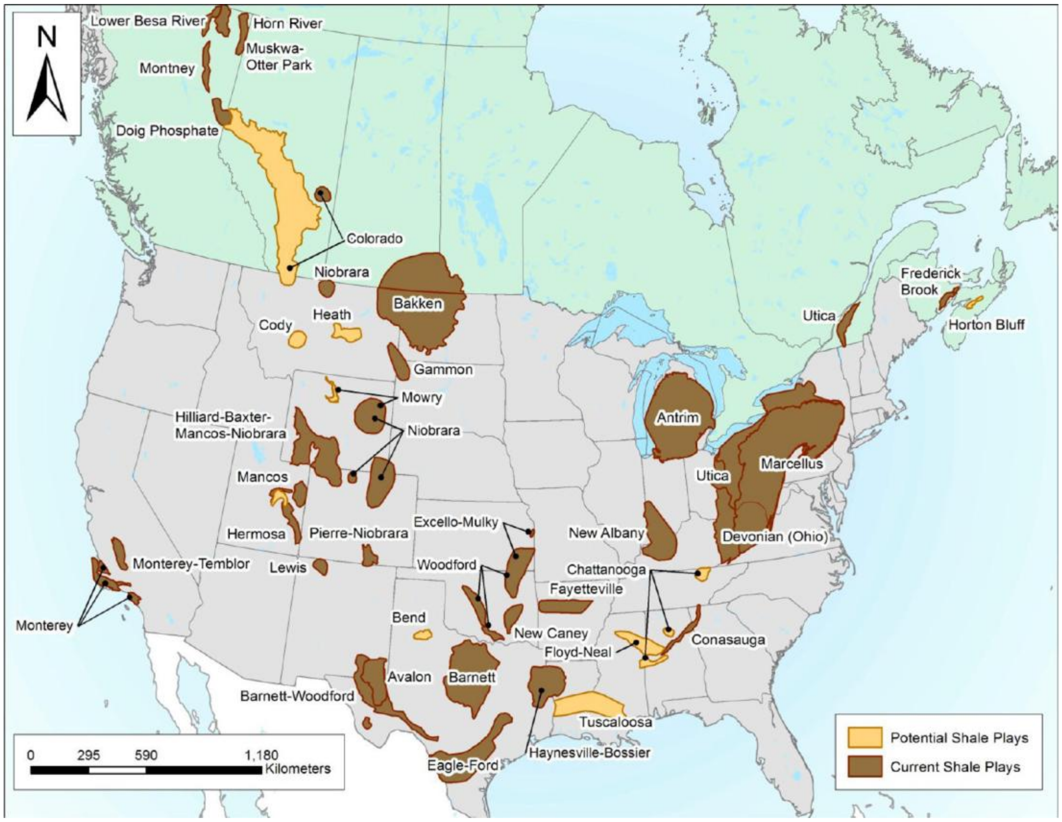

Figure 2-1: Gas shale formations across the lower 48 and Canada

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A brief sequence for accessing UNG includes vertical and horizontal borehole drilling, casing, hydraulic fracturing, gas collection, and completion. Each of these processes for UNG come with unique occupational, environmental, and public health risks[22]. Concern about groundwater safety stem from: (i) The high pressures of the fracturing fluids allowing flow and discharge of fluid and gas to shallow aquifers; (ii) the discharge of produced waters (a mixture of fracturing fluids and saline formation water) with unknown toxicity and radioactivity into the environment; (iii) the potential explosion and asphyxiation hazard of natural gas that has seeped into groundwater; and (iv) the necessity of shallow groundwater for household and agricultural use in rural communities which are typically unregulated and untreated[7]. These concerns, each with varying probability, have caused organizations to propose monitoring legislation and invest in risk assessment and modeling[23].

The variation and uncertainty of hydraulic fracturing fluid blends between operators has hampered targeted contaminant monitoring. Research teams have begun developing methods for organic and inorganic species cited to be possibly present, but fracturing fluid recipes can vary from operator to operator, and from shale to shale. Regulatory methods have failed to be developed because the 2005 Energy Policy Act exempts hydraulic fracturing operations from the U.S. Environmental Protection Agency's Safe Drinking Water Act (SDWA). The only exception to this granted exemption is the regulating of the injection of diesel fuel. Also, most oil and gas regulatory monitoring is conducted by state agencies rather than federal agencies, meaning suggested techniques, target compounds, and regulatory limits are variable throughout the country.

This chapter will discuss the analytes and techniques chosen by various academic, industrial, and government agencies, which are attempting to identify possible groundwater alterations as a result of UNG extraction techniques. Targeted analytes include gaseous analytes, organic constituents, and ions and isotopes, which includes naturally occurring radioactive material (NORM). The chapter is concluded with discussions of the methods that have been developed and implemented for the Texas Well Study (TWS) conducted by the University of Texas at Arlington. Insight and explanations are given for analyte selection and method parameter choices.

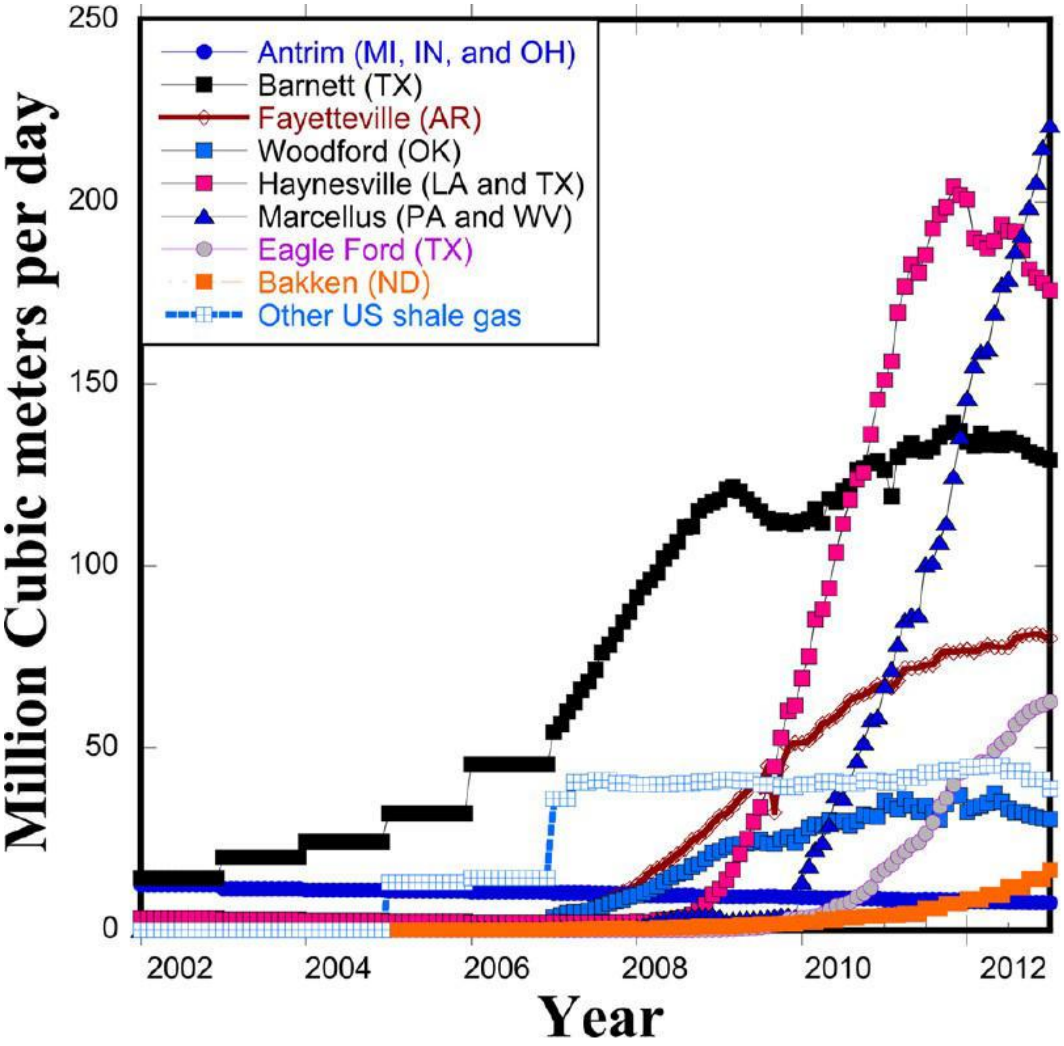

Figure 2-2: Progression of natural gas produced from various shale plays in the U.S.

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2.2 Targeted Analytes

2.2.1 Gaseous Analytes

To date, the majority of analytical research efforts have been in the quantification of light hydrocarbons (methane, ethane, and propane) in the groundwater of areas in proximity to UNG extraction. The majority of natural gas is methane with lesser amounts of ethane and propane. If borehole casings failed or hydraulic fractures intersected abandoned oil wells or faults, there is the possibility of stray gas coming in contact with the overlying aquifers[24]. Analysis is performed using gas chromatography (GC), typically outfitted with a flame ionization detector (FID). Some reports have used a mass spectrometer (MS) or thermal conductivity detector (TCD) to also be able to quantitate N_2, O_2, CO_2, H_2S, and H_2O[6,25]. The dissolved gases are typically liberated from the groundwater sample by either purging with an inert gas and trapped on a sorbent, i.e. purge and trap[26], or by creating a headspace in the vial, agitating, and/or heating and withdrawing the vapor phase, i.e. headspace analysis[27]. Separation of the gaseous species can be achieved with a capillary PLOT Q-phase (bonded polystyrene-divinylbenzene) column[26,28]. Separation of the light hydrocarbon gases can be achieve with packed columns[29], but require different fitting and pressure controllers as compared to the typical capillary column GC. Sub-optimized methods can also use packings with very high affinity for the saturated hydrocarbons[30], significantly increasing analysis time.

Surveying of dissolved gases present in groundwater has taken place in northeastern Pennsylvania and upstate New York[7]. In this region, it was found that methane concentrations in the drinking well water was greatest in areas nearest UNG wells, specifically within 1 km. The origin of the methane was determined to be from thermogenic (geologic) sources. A recent report[31] states that thermogenic methane in shallow groundwater of the Marcellus Shale is quite prevalent due to the presence of the hydrocarbon-rich Catskill and Lock Haven Formations and coal stringers throughout the aquifers. Methane has also been detected in a majority of sampled water from the Watenberg Field in northeastern Colorado. 95% of the detected methane had microbial origins which reduces UNG extraction contributions. The St. Lawrence platform of the

Utica Shale in Canada is reported to have nearly 600 occurrences dating back to the 1950s of dissolved gases in water wells, but the origin was not investigated[23]. In the same region, recent investigations[32] concluded that the majority of the methane found had biogenic origins and was of low concentrations.

With each study of methane, the origins must also be identified. Methane in groundwater can either be result of microbial processes or of thermogenic origins. Origin can be identified through ratios of methane to ethane plus propane or through isotopic abundances of ^{13}C and deuterium. Thermogenic gas has a greater proportion of C_2-C_5 hydrocarbons (ethane, propane, butane, and pentane) relative to methane as compared to microbial gas which dominantly containing methane and CO_2 [33]. The isotopic and hydrocarbon signatures can be unique for each formation, even within a given vertical space[6]. This can further delineate whether the source of the gas is from the target shale formation or from intermediate formations, which can then in turn indicate possible operational causes[7,34]. In summary, it is suggested that stray gas from shallow formations are able to leak up through the well annulus and gas from deep shale target formations can be introduced through poorly constructed or failing well casings[35]. A quantitative measurement of the severity of well casing failure is through sustained casing pressure (SCP) which indicates inadequate isolation of the annulus and can allow stray gas to surface. Statistics by the United States Minerals Management Service[36] show that 34% of wells in the outer continental shelf of the Gulf of Mexico have reported SCP at one time within the first 5 years of installation. After 15 years of installation, 1 of every 2 wells will have measureable SCP in one or more casing annuli.

Other gases present in the groundwater can be used as environmental tracers to age the water or identify a source[37-41]. The United States Geological Survey (USGS) used the dissolved gases of various chlorofluorocarbons, sulfur hexafluoride, tritium, helium, neon, argon, krypton, and xenon to identify any degree of subsurface water mixing of target groundwater[42].

2.2.2 Organic Constituents

The source for anthropogenic organic constituents investigated in groundwater of UNG would be presumed to originate from hydraulic fracturing fluids. While stray gas can migrate to the shallow aquifers via incipient faults and fractures[24], hydraulic fracturing fluids would have a much more difficult route to travel. Some notions hypothesize induced fractures reaching the overlying aquifer[43], but others believe subsurface pressure of the aquifers and varying layers of geology between the shale and aquifer retard the propagation of induced fractures from the borehole[44,45]. The possibility of fluid introduction to the aquifer via casing failures or nearby poorly constructed or improperly plugged wellbores is still possible[46]. The higher density of drilling fluids compared to that of stray gas would greatly limit upward migration of leaking fluid in the subsurface[47,48]. On the contrary, one model indicates that because of the physical strain on the geologic formations, upward migration of fracturing and shale liquids could be as soon as six years[43].

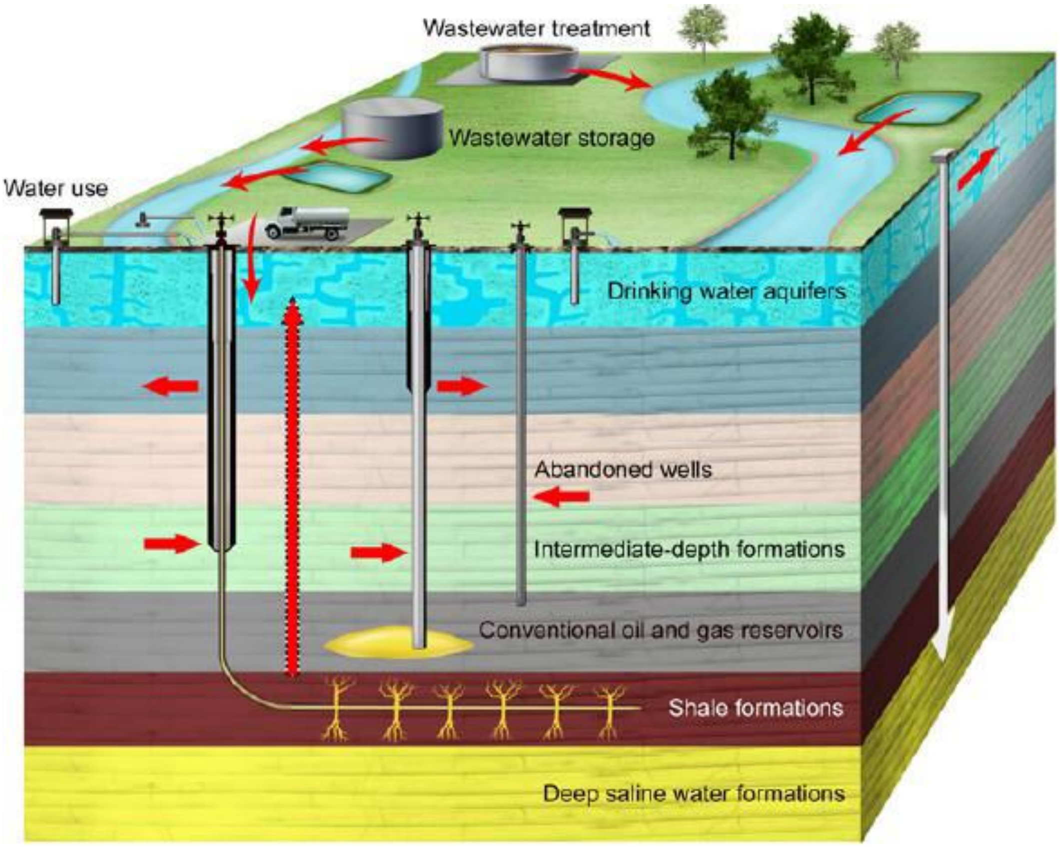

Figure 2-3: Proposed pathways for possible groundwater contamination from hydraulic fracturing

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Hydraulic fracturing fluids are generally 95-99% water, a solid proppant, and a mixture of chemicals acting as lubricants, biocides, scale inhibitors, cross linkers, surfactants, and corrosion inhibitors. As of 2011, the U.S. Congress[49] compiled a list of over 750 different ingredients documented to be found in hydraulic fracturing fluid products. The popularity and proportions of these compounds vary extensively between shale formation and drilling operator, making universal methods for monitoring almost impossible.

An area outside Pavillion, Wyoming became a site of great scrutiny and investigation of possible contamination events in 2008. The US EPA reported their findings in 2011[50], which were then followed up by the USGS in 2012[42]. Volatile organic carbons were analyzed using EPA Method 8260B, semivolatile organic carbons used EPA Method 8270D, and gasoline and diesel range organics used EPA Method 8015D, all of which were analyzed by GC. Certain EPA methodologies would manifest compounds associated with petroleum-based additives including gasoline range organics, diesel range organics, BTEX (benzene, toluene, ethyl benzene, and o-, m-, and p-xylene), naphthalenes, and trimethylbenzenes. The initial EPA report detected these compounds, along with many other semivolatile compounds corresponding with ingredients listed in MSDSs of products used for fracturing or well completion. Glycols were detected by EPA Method 8015 utilizing a GC-FID, but could not be replicated with a LC-MS/MS method, concluding inadequacies of Method 8015 due to false positives.

Follow up work in Pavillion by the USGS was quite thorough and exhaustive. Glycols and alcohols were analyzed using EPA Method 8015B. Gasoline range organics, BTEX, and MTBE were analyzed using EPA Methods 8015B and modified 8021. Methylene blue active substances, e.g. anionic surfactants, were investigated by EPA Method 425.1. Numerous volatile and semivolatile compounds were identified that were not the initial targets of the regulatory methods. The USGS report could not confirm any of the semivolatile compounds identified in the initial EPA report in 2011.

There is a hypothesized mode of how stray methane gas could propagate into other organic species in the shallow aquifers[4]. Organic matter in the presence of halogenated solutions can generate trihalomethanes (THMs), compounds with halogen atoms substituted for hydrogens in the methane molecule. Even so, no data has been reported for a correlation between the presence of THMs and stray gas contamination.

The presence of endocrine disrupting chemicals has also been associated with groundwater in proximity to UNG. Water samples from Garfield, CO, a region identified to have stray gas and salinization present in the drinking aquifer[51], have been reported to exhibit estrogenic activity in 89% of water samples, according to reporter gene assays[52]. No further efforts were made to identify the endocrine disrupting chemicals.

2.2.3 Ions and Isotopes

2.2.3.1 Groundwater Ions and Metals

In efforts to achieve maximum recovery of UNG, many saline as ionic solutions are encountered. Drilling muds use large proportions of barite, a mineral of barium sulfate, as a weighting agent. Hydraulic fracturing and well completion fluids contain various acidic and basic solutions. The flowback water, or water that resurfaces during hydraulic fracturing, is a mix of the shale formation brine and fracturing fluid, which in turn is vary saline. Produced water, water surfacing concurrently with natural gas, is brine from the shale formation. Multiple options are available for the identification and quantification of ionic constituents in these solutions and mixtures. Elemental analysis is popular for measurements of cations such as Na, Mg, and Ba. Multi-element measurements are typically made for these complex mixtures, so simultaneous measurement techniques such as inductively coupled plasma – optical emission spectroscopy (ICP-OES) or mass spectrometry (ICP-MS) are typically used to increase throughput[53]. The ICP source is subject to many types of matrix effects which will affect quantification accuracy[12,54]. Conductivity detection with ion chromatography circumvents some of the matrix issues and offers the benefit of speciating ionic forms such a bromide and bromate[55]. Organic anions such as acetate and formate can also be quantified using IC which would be undetected with ICP techniques.

Groundwater in Pavillion, WY measured by the US EPA was found to be enriched with K and Cl, as well as exhibit an alkaline pH[42,50]. Well Completion Reports and MSDSs of products used indicate KOH was present in a crosslinker and as a solvent, along with 6% KCl solutions for foam jobs and potassium metaborate used in crosslinkers at 5-10% and 30-60%. Chloride is believed to be a sufficient indicating parameter of possible groundwater contamination due to gas extraction activities because of its conservative solution transport characteristics and elevated concentrations in produced waters[56]. A survey[51] of databased data for water wells in Garfield County, CO identified increased Cl concentrations with an increase in thermogenic methane over time as the number of UNG activity increased in the area. The portion of drinking water wells having chloride concentrations >250 mg/L, the EPA threshold for drinking water, doubled between 2002 (4%) and 2005 (8%). While this relationship may be true in Colorado, groundwater affected by stray gas in northeastern Pennsylvania has not shown signs of salinization resulting from leaking natural gas wells to date[4].

2.2.3.2 Isotopic Abundance and Ratios

Ions are also excellent tracers to identify subsurface water mixing, primarily deep saline groundwater with the overlying shallow aquifers used for drinking wells or flowback contamination from casing failures or surface spills. Flowback water resembles deep brines from the target formation which are high in chloride, bromide, sodium, and sulfate[7-9]. Increases of these ions in the groundwater over time indicate anthropogenic sources, one of which can be UNG extraction processes. The ratio of the concentrations of Br and Cl in solution, Br/Cl, can be indicative of the formation origin of the water, with shale water having a high (>0.001) Br/Cl ratio. The ratio of $^{87}Sr/^{86}Sr$ is also specific to a geologic formation, with different formations able to be differentiated by ratios that vary only by a few ten thousandths[8]. These precise measurements of isotope ratios and percentages with certainty up to the sixth decimal place must be performed on dedicated isotope ratio mass spectrometers and not typical MS systems used for the other applications discussed.

Isotopic abundance of ^{13}C is a function of the carbon source. The isotopes of ^{18}O and ^{2}H can be used collectively for water origination or individually, primarily ^{2}H values for methane origin investigations. A single source of these elements will have a characteristic isotopic abundance range, generally different for each geologic formation. Once the given isotopic range for an elemental tracer has been identified for possible sources, e.g., 3 aquifers and 6 geologic formations in the Western and Eastern Pennsylvania Plateau[8], outliers can then be rationalized based on dilution factors of foreign species.

While these isotopic and ion ratio tracers can identify source water mixing, they are not specific to mixing induced by UNG techniques. Reports across North America have identified mixing of subsurface waters, independent of oil and gas operations[8,57-59].

2.2.3.3 Naturally Occurring Radioactive Material (NORM)

Quantification of naturally occurring radioactive material (NORM) like ^{226}Ra, ^{228}Ra, and ^{222}Rn in groundwater have become indicators of deep geological water mixing with the shallow groundwater[7,42]. Even without speciating NORMs, bulk radioactivity of the groundwater will be higher if there is brine mixing[8].

2.3 Texas Well Studies Methodologies

2.3.1 State of the Field in 2011

In 2011, our research team initiated the Texas Well Studies (TWS) with the intent of surveying 100 privately-owned water wells in the Barnett Shale region of North Texas. An early decision made was to identify which data we felt was most valuable to measure and how feasible the measurements would be. The feasibility of the measurements encompassed considerations into instrument availability and robustness of a resulting value, either because of instrumental or sampling factors. Many targeted analytes can only be measured by a select few techniques and contracting a lab to analyze a large number of samples can become quite expensive if you are not able to conduct measurements internally. If instrumentation is not an issue, then sample collection, preservation, and holding time can be a limiting factor. For example, collection for dissolved gases, e.g. methane, can be quite burdensome in the field. Water must be collected from a purged well with a low flow and constant pressure to reduce degassing of the water. Isotech Laboratories suggests using a dual-valved system to reduce degassing of the water, atmospheric compounds, and achieve zero headspace in the sampling bag. The sampling bag must be evacuated prior to use and also contains a capsule of bactericide to reduce bacterial gas degradation or generation[60]. Analysis then must be performed within 14 days.

In the inception of the TWS, few reports had been published regarding the potential for environmental contamination in conjunction with UNG mining. The highlight publication and information resource relevant to our project were a) Jackson and coworkers'[7] methane contamination analysis in PA and b) a US Congressional report[49] on ingredients in hydraulic fracturing fluids. The University of Texas at Arlington had an expansive suite of analytical instrumentation available to perform measurements “in house” to reduce costs and hone expertise. An instrument that our team did lack at our immediate disposal was an isotope ratio mass spectrometer which is heavily used in identifying the origins of C, H, and O containing compounds in the subsurface (see Section 3.3). This reality, coupled to the intensive sampling protocol, and debated nature of methane measurements directed us to focus on other analytical measurements.

2.3.2 GC-MS for Ingredients in Hydraulic Fracturing Fluids

Many of the compounds the Congressional report[49] listed as most prevalent, carcinogenic, Safe Drinking Water Act regulated, and Clean Air Act regulated in were either volatile or semivolatile, a key requirement to separation by GC. The use of a MS detector with the common electron ionization (EI) source provided an excellent avenue for compound detection and identification through the characteristic fragments formed during ionization and the thorough EI-MS libraries available. We then selected 31 compounds listed below in Table 2-1, acquired standards of 95% quality or higher, and determined their retention time and the MS base peak which would be used for quantification. The base peak ion was also used for selected ion monitoring (SIM) mode, a MS setting more sensitive than acquiring data over the entire mass spectral range. Within each MS method group, i.e., timed segment of specific MS settings, a scan event was added to assist in identification of unknowns detected and confirmation of targets detected from SIM mode ions.

The variability in GC amenable compounds that could possibly be present in groundwater due to fracturing fluid contamination discourages the use of compound class-specific extraction techniques, e.g., polycyclic aromatic hydrocarbons, total petroleum hydrocarbons, and alcohols and glycols. A solvent extraction using ethyl acetate was chosen to extract a diverse set of compounds. Because disclosures of UNG extraction processes are very limited, it is of importance to try to characterize as many compounds present in groundwater as possible.

2.3.3 Headspace – GC Analysis for Alcohols

The column selected for the GCMS analysis, the Rxi-5ms (30 m X 0.25 mm X 0.25 µm) general-purpose non-polar column, was adequate for small molecules and alcohols listed on the compound list of Table 2-1 but was not sufficient for confident identification and quantification. The ethyl acetate used for analyte extraction also possessed many trace impurities that convoluted the chromatogram and resulting mass spectrum of these early-eluting compounds. An automated static headspace (HS) – GC method was developed and tailored to the separation of light alcohols and solvents. This method consisted of using a mid-polarity column more selective for the light alcohols, the ZB-BAC2 (30 m X 0.32 mm X 1.2 µm), commonly used in conjunction with blood alcohol determinations in forensics laboratories[61]. Method development was mindful to ensure baseline resolution between methanol and ethanol. The resulting separation method resulted in 0.4 minute separation of methanol and ethanol (k' = 0.39 and 0.77, respectively), as opposed to the minimal 0.10 minute separation (k' = 0.06 and 0.12, respectively) observed on the Rxi-5ms column for GC-MS. The increased capacity factor also provides better precision for quantification.

Table 2-1 Selected compounds targeted by the TWS for GCMS analysis

Compound	**CAS Number**	**SIM Ion**	**Compound**	**CAS Number**	**SIM Ion**
Methanol	67-56-1	31.1, 29.1	1,3,5-Trimethyl Benzene	108-67-8	105.15
Ethanol	64-17-5	31.1, 29.1	1,2,4-Trimethyl Benzene	95-63-6	91.1
Isopropanol	67-63-0	45.1, 29.1	Isopropyl Benzene	98-82-8	105.1
n-Propanol	71-23-8	31.1	Benzyl Chloride	100-44-7	91.1
Propargyl Alcohol	107-19-7	55.1	Acetaldehyde	75-07-0	29.1
n-Butanol	71-63-3	56.1	Glutaraldehyde	111-30-8	44.1
Ethylene Glycol	107-21-1	31.1	Dimethyl Formamide	68-12-2	44.1
Propylene Glycol	57-55-6	45.1	Naphthalene	91-20-3	128.1
2-Butoxy Ethanol	111-76-2	57.1	1-Methyl Naphthalene	90-12-0	142.15

Table 2-1 *(Continued)*

2-Ethyl Hexanol	104-76-7	57.1	2-Methyl Naphthalene	91-57-6	142.15
Benzene	71-43-2	78.1	1-Naphthol	90-15-3	144.15
Ethylbenzene	100-41-4	91.1	2-Naphthol	135-19-3	144.15
Toluene	108-88-3	91.1	Bisphenol A	80-05-7	213.1
o-Xylene	95-47-6	91.1	d-Limonene	5989-27-5	68.1
m-Xylene	108-38-3	91.1	Acetophenone	98-86-2	105.1
p-Xylene	106-42-3	91.1			

The HS injection technique was chosen to eliminate signals from solvent and solvent impurities. Static HS sampling involves heating and possibly agitating the sample to liberate volatile and semivolatile compounds from the sample, solid or liquid; the vapor phase of the vial is injected onto the GC column. For our application, the water sample was placed into a 20 ml septum-top vial which had been loaded with a 0.25 M NaCl (aq) solution to reduce the solubility of the alcohols in the water[62,63]. Each sample was heated and agitated by the AOC-5000 plus automated HS autosampler and then injected with a heated syringe onto the GC column. The resulting water vapor present in the injection is not detected by the flame ionization detector (FID) used for the analysis. Analytes such as methanol, ethanol, isopropanol, dichloromethane, and similar can be quantified by this method.

2.3.4 Metals Analysis

In our earliest publication[10], arsenic, barium, selenium, and strontium were detected with inductively coupled plasma – mass spectrometry (ICP-MS). These metals were selected based on their prevalence in aspects of the drilling process. Special attention must be made when analyzing ^{75}As by ICP-MS because of the polyatomic interference of $ArCl^-$. The ICP source is argon plasma and groundwater naturally contains sufficient concentrations of chloride. This interference can either be alleviated by using hydride generation to form the volatile AsH_3 or through the use of a collision cell to dissociate $ArCl^-$ clusters in the gas phase. The Varian 820 ICP-MS with a collision cell used for these measurements was housed at the University of North Texas in Dr. Guido Verbeck's laboratories. Samples were prepared as a 2% nitric acid solution and quantified through a generated calibration curve. The lower limit of linearity for As, Sr, and Ba was 1 µg/L and 10 µg/L for Se when measurements were made in 2012. For the latest measurements made in 2013-2014, only As and Se were measured, each linear down to 1 µg/L. Barium and strontium measurements are discussed in the next section.

2.3.5 Ion Chromatography for Inorganic Ions

Beginning in 2013, analysis of metals besides As and Se are being performed in-house with the Shimadzu ICPE-9000 ICP-OES (optical emission spectrometer). As and Se are still measured with ICP-MS because of the needed sensitivity that cannot be achieved with the ICP-OES. This instrument allows for simultaneous measurements of selected wavelengths for up to 73 different elements. The method currently quantifies 12 metals using a standard addition quantification technique. Standard addition was used to quantify these metals because it is able to account for sample variability and different matrices to help ensure accuracy, even though it is a more laborious sample preparation and data analysis. Even within the same aquifer, element specific variations can occur from location to location[12]. As for the other metals capable of being measured but are not quantified, estimated concentrations are recorded during measurements. The calculation of estimated concentrations is made possible through calibrating an elemental response database to multiple wavelengths of aluminum and barium, which are then used as reference responses for the measured emission intensities of the other metals whose response factors are known. While these values should not be reported as absolute concentrations, they can be used to compare relative concentrations of an element between samples.

2.3.6 TOC/TN Analyzer and QwikLite™ 200 for Bulk Water Measurements

Another analytical technique that began after the initial study in the Barnett Shale[10] was measuring bulk carbon and nitrogen in each sample. Using a TOC (total organic carbon) analyzer is common non-specific water quality assessment used in various industries. Measurements made in-house with Shimadzu's TOC-L/TN include total carbon (TC), inorganic carbon (IC), TOC, purgable organic carbon (POC), nonpurgable organic carbon (NPOC), and total nitrogen (TN). The intended use of this general measurement is to indicate non-specific changes that should further utilized advanced analytical techniques to speciate the change and further propose the source. This could possibly become a minimally invasive screening technique that could be performed by almost any lab for monitoring purposes.

A predecessor to the TOC-L/TN measurements for rapid bulk water quality characterization was a bioassay, the QwikLite™ 200. This assay uses the light output of bioluminescent dinoflagellate *Pyrocystis lunula* to gauge a degree of foreign constituents in the water sample according to ASTM method E1924 and previously published methods[13]. In short, the water sample was adjusted to a salinity of 30 ppth using crystallized ocean salt. A homogenized suspension of *P. lunula* (Assure Controls, Vista CA) were added to each salinity-adjusted sample, gently mixed, and distributed to each of six replicate cuvettes into the measurement cartridge carousel. After the dinoflagellates are allowed to cure in the sample for 24 hours, the resulting bioluminescence is measured using the QwikLite™ 200, a spectrophotometer and microprocessor. The percent decline in bioluminescence is calculated as a function of light output of *P. lunula* in control solutions of salinity adjusted bottled drinking water. The ability to assess water quality in 24 hrs is quite remarkable for a biological assay.

This assay was used applied to the sample set collected for the initial study conducted in the Barnett Shale[10]. Samples that responded to a high stress environment associated with toxicity could not be correlated to other data acquired. Further investigations[14] indicated that the sensitivity of the dinoflagellates is not sufficient enough to be influenced by the detected levels of arsenic, selenium, barium, or strontium. Additional efforts demonstrated that a responses to hydrochloric acid and glutaraldehyde, known ingredients in acidization and hydraulic fracturing, each were sufficient enough to identify contamination events. Because of the variable sensitivity of *P. lunula*, the bioassay was discontinued for groundwater research conducted by the TWS team.

2.4 Conclusion

These methods developed for the TWS are intended to be built upon as research and understanding of best targets for groundwater monitoring in areas of UNG activity improves. We expect great strides in methods and viable targets to be made by academic institutions over the next few years. The accessible expertise for collaboration within a university allows proper multidiscipline understanding to occur. Partnerships with instrument manufacturers will advance analytical methods and technology for this growing market. The public interest and uncertainties of this topic will continue to initiate focused user groups and regulatory meetings for environmental stewardship of UNG, which will in turn drive research.

Chapter 3

An Evaluation of Water Quality in Private Drinking Water Wells near Natural Gas Extraction Sites in the Barnett Shale Formation

3.1 Abstract

Natural gas has become a leading source of alternative energy with the advent of techniques to economically extract gas reserves from deep shale formations. Here, we present an assessment of private well water quality in aquifers overlying the Barnett Shale formation of North Texas. We evaluated samples from 100 private drinking water wells using analytical chemistry techniques. Analyses revealed that arsenic, selenium, strontium and total dissolved solids (TDS) exceeded the Environmental Protection Agency's Drinking Water Maximum Contaminant Limit (MCL) in some samples from private water wells located within 3 km of active natural gas wells. Lower levels of arsenic, selenium, strontium, and barium were detected at reference sites outside the Barnett Shale region as well as sites within the Barnett Shale region located more than 3 km from active natural gas wells. Methanol and ethanol were also detected in 29% of samples. Samples exceeding MCL levels were randomly distributed within areas of active natural gas extraction, and the spatial patterns in our data suggest that elevated constituent levels could be due to a variety of factors including mobilization of natural constituents, hydrogeochemical changes from lowering of the water table, or industrial accidents such as faulty gas well casings.

3.2 Introduction

Recent advances in technology have facilitated a rapid and widespread expansion of natural gas production from hydrocarbon-rich deep shale formations[64-66]. The increase in drilling activity has raised concern over the potential for environmental contamination[7,8,65,67]. Contamination of groundwater aquifers overlying shale formations is particularly problematic because they provide drinking water in rural areas where private wells are unregulated. A study of the Marcellus Shale formation in the northeastern United States reported increased concentrations of methane[7] in private drinking water wells near natural gas extraction sites. While this study does suggest that natural gas extraction could cause systematic groundwater contamination, most confirmed cases of contamination are the result of mechanical failures in which methane, drilling fluids, or waste products leak through faulty gas well casings[66,68]. Despite a number of recent investigations, the impact of natural gas extraction on groundwater quality remains poorly understood. In a review of scientific literature on natural gas extraction, Vidic et al.[1] point out that there is very little information on groundwater quality prior to natural gas extraction activities.

In the past 10 years, the 48,000 km^2 Barnett Shale formation in Texas has become one of the most heavily drilled shale formations in the United States with approximately 16,743 active wells as of May 2013 (http://www.rrc.state.tx.us/data/index.php). The Barnett Shale formation, located 1500−2400 m below the surface of approximately 17 counties in North Texas, is composed of compressed sedimentary rocks that form a shale layer. The shale traps natural gas in interstitial pores, and modern techniques, such as hydraulic fracturing, have allowed access to these gas reserves. Natural gas extraction in the Barnett Shale formation should have little effect on the overlying Trinity and Woodbine aquifers as they are separated from the shale formation by over a thousand meters of impermeable rock. The United States Geological Survey (USGS) sampled arsenic[69] as well as pesticides, nitrates, and volatile organic compounds (VOCs) in drinking water wells, including wells from aquifers overlying the Barnett Shale formation[70]. Using these data and other data from the Texas Water Development Board[11], Reedy et al.[71] characterized groundwater in the Trinity and Woodbine aquifers as generally good quality with very few exceedances for constituents such as arsenic, selenium, strontium, and barium. Slightly elevated levels of total dissolved solids (TDS) in these aquifers could be attributed to evaporate and gypsum beds and potentially to legacy oil and gas activities.

Here, we evaluate water quality in 100 private drinking water wells from the Trinity and Woodbine aquifers overlying the Barnett Shale formation and the Nacatoch aquifer east of the Barnett Shale formation (Figure 3-1). Samples were collected from areas within the Barnett Shale region both with and without active natural gas extraction, and from areas outside the Barnett Shale region unaffected by natural gas extraction. Analytical tests were conducted to detect volatile and semivolatile compounds identified as contaminants of concern in a congressional report on hydraulic fracturing fluid components[49], and to detect arsenic, barium, selenium, and strontium. These constituents are often included on lists of natural gas extraction waste components[49,68,72]. These data were compared to a historical data set from the same aquifers prior to the expansion of natural gas extraction activities[11]. This study provides information about the potential impact of natural gas extraction activities on groundwater quality in aquifers overlying the Barnett Shale formation by (1) determining if constituents thought to be associated with natural gas extraction techniques are present in private well water samples; (2) evaluating the relationship between water quality and geographic proximity to natural gas extraction activities; and (3) discussing scenarios to explain elevated constituent concentrations.

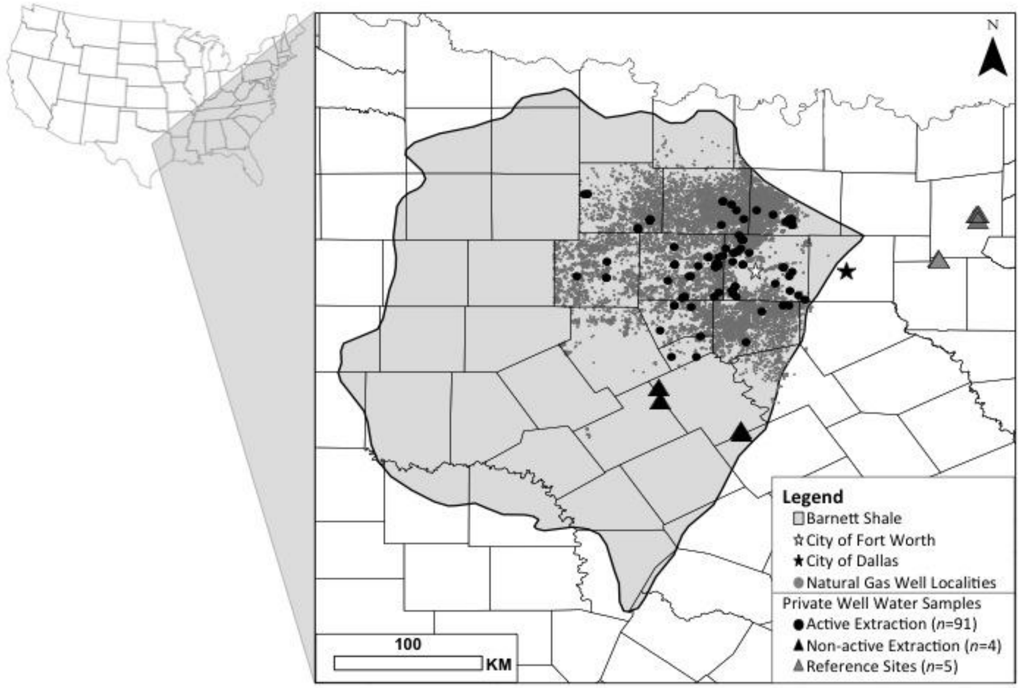

Figure 3-1: Location of private well samples and natural gas wells in the Barnett Shale Formation of Texas

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3.3 Materials and Methods

3.3.1 Sampling

A total of 95 water samples were collected from private drinking water wells that draw from the Trinity and Woodbine aquifers. Five reference wells were sampled from the Nacatoch aquifer (Figure 3-1). We sampled from areas of active natural gas extraction within the Barnett Shale (private wells with one or more gas wells located within a 5 km radius; n= 91), nonactive natural gas extraction areas within the Barnett Shale (private wells with no gas wells located within a 14 km radius; n = 4), and reference sites outside of the Barnett Shale (private wells with no gas wells located within a 60 km radius; n= 5).

Private well samples were obtained from a pool of volunteers who responded to a press release calling for study volunteers from 13 counties located in or near the Barnett Shale region (Bosque, Denton, Hamilton, Hood, Hunt, Jack, Johnson, Kaufman, Palo Pinto, Parker, Somervell, Tarrant, and Wise counties; Figure 3-1). Reference samples from the Nacatoch aquifer were obtained by traveling door-to-door to find volunteers willing to participate, since well owners from this region are not impacted by natural gas extraction and did not respond to our call for volunteers. Sampled water wells drew from the Trinity aquifer (n = 76), the Woodbine aquifer (n = 15), the Nacatoch aquifer (n = 5), and the Palo Pinto and Mineral Wells formations (n = 4) at depths ranging from 9 to 427 m with an average of 105 m. Water wells were overwhelmingly used for drinking water in rural areas without public drinking water systems (n = 82). The remaining wells were used to irrigate private lawns or provide drinking water for livestock (n = 18). To avoid contamination from pesticides, we did not sample water wells that were used for irrigating large agricultural crops.

Water wells were purged for a minimum of 20 min, until measurements of pH, dissolved oxygen (DO), and temperature stabilized, indicating fresh well water was flowing. All samples were collected as close to the outdoor wellhead as possible, bypassing filters or treatment systems. To ensure samples were representative of shallow groundwater quality, wells that could not be purged, could only be accessed through taps, or that could not be sampled before treatment or filtration were excluded. Water quality data collected on site included DO, pH, specific conductance, conductivity, temperature, salinity, TDS, turbidity, and oxidation−reduction potential (ORP). Four duplicate water samples were collected in 40 mL glass vials without headspace and held at 4 °C during transport to The University of Texas at Arlington for chemical analyses. Because the objective of this study was to assess potential exposure risks of drinking water from wells in this region, we chose not to use filtration and acidification techniques. This allowed us to obtain samples representing the quality of water our participants would consume, as well as increased versatility in the number of constituents that could be probed by analytical techniques. We acknowledge that foregoing filtration and acidification can introduce a negative bias into metals analysis; however, this would result in a conservative underestimation of concentrations[73]. Furthermore, the MCL values for drinking water are based on unfiltered samples that have not been acidified[73].

3.3.2 Analysis

Chemical analyses were conducted using gas chromatography−mass spectrometry (GC-MS), headspace-gas chromatography (HS-GC), and inductively coupled plasma – mass spectrometry (ICP-MS). See Appendix A Table A-1 for a list of compounds screened. Arsenic, selenium, strontium, barium, methanol, ethanol, TDS, and volatile organic compounds (VOCs) such as benzene, toluene, ethylbenzene, and xylenes (collectively referred to as BTEX) were the primary targets of chemical analyses. Historical data for the concentrations of target compounds (except alcohols) in private water well samples from this region were obtained to evaluate their occurrence before the expansion of natural gas extraction activities[49]. This historical data set is comprised of 330 private drinking water wells from the Trinity, Woodbine, and Nacatoch aquifers sampled over a ten year period (1989−1999) before natural gas activities began. Wells were located in the same counties that we sampled in this study (Appendix A, Figure A-1). All wells were used for water withdrawal and ranged in depth from 14 to 1090 m with an average depth of 207 m. For more detailed description of methods and analyses, see Appendix A Methods.

3.4 Results and Discussion

3.4.1 Water Quality

We found no evidence of BTEX compounds using both LC-UV-MS and GCMS. Levels of TDS in active extraction areas averaged 585 mg/L and ranged 200−1900 mg/L, while TDS in nonactive/reference areas averaged 500 mg/L and ranged 400−600 mg/L. Exceedances for the Environmental Protection Agency’s (EPA) TDS Drinking Water Maximum Contaminant Limit (MCL) of 500 mg/L were detected in 50 of 91 samples from active extraction areas and 7 of 9 samples from the nonactive/reference areas (Table 3-1). The maximum TDS values detected in the active extraction area were over three times higher than the maximum value from the nonactive/reference areas. These aquifers naturally show somewhat elevated levels of TDS, so these concentrations are not unusual for the area[71], and the mean TDS concentration in active extraction areas is similar to levels seen in historical data for this region (585 mg/L versus 670 mg/L).

Table 3-1: Concentrations of Constituents in Barnett Shale Private Water Well Samples[a]

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	Historical Data (1989 – 99)				Active Extraction Area Wells (*N = 91)*				Nonactive and Reference Area Wells (*N* = 9)			
	N	Range	Mean ± std error	% ≥ MCL	*N*	Range	Mean ± std error	% ≥ MCL	*N*	Range	Mean ± std error	% ≥ MCL
TDS	344	129-3302	6703 ± 21.5	61	91	200-1900	585.1 ± 35.1*	54.9	9	400-600	500 ± 31.6	77.8
Arsenic	241	1-10	2.8 ± 0.1	0	90	2.2-161.2	12.6 ± 2.2*	32.2	9	4.7-9.0	6.9 ± 0.7*	0
Selenium	329	0.1-50	3.9 ± 0.2	0.3	10	10-108.7	33.3 ±10.5*	20				
Strontium	99	20-16700	1028.9 ± 213.7	*N/A*[b]	90	66.2-18195	2319.8 ± 330.1*	*N/A*	9	52.4-76462	1610 ± 787.1	*N/A*
Barium	357	0.1-382	57.2 ± 2.9	0	90	1.8-173.7	32.3 ± 3.3*	0	9	2.9-60	22.4 ± 11.3*	0
Methanol				*N/A*	24	1.3-329	33.6 ± 13.3	*N/A*	5	1.2-62.9	27.4 ± 13.7*	*N/A*
Ethanol				*N/A*	8	1-10.6	4.5 ± 1.2	*N/A*	4	2.3-11.3	6.8 ± 2.4	*N/A*

[a] All values are measured in µg/L except total dissolved solids (TDS), methanol, and ethanol in mg/L. Values denoted by asterisks (*)represent statistically significant differences from historical data values (Mann-Whitney U pair wise analysis; $p < 0.05$). Historical data for the counties sampled in this study were obtained online at www.TWDB.state.TX.us/groundwater/.

[b] EPA recommends stable strontium values in drinking water do not exceed 4000 µg/L.

3.4.2. Levels of Heavy Metals in Private Well Water

Arsenic, selenium, strontium, and barium are known to occur naturally at low levels in aquifers overlying the Barnett Shale formation[71,74]. Chemical analysis using ICP-MS (see Appendix A) detected arsenic in 90 of 91 samples from active extraction areas and 9 of 9 samples from nonactive/reference areas. Concentrations were significantly higher in active extraction areas compared to reference samples and historical samples (Table 3-1). Arsenic concentrations in active extraction areas ranged from 2.2 to 161.2 μg/L, with an average of 12.6 μg/L. The maximum concentration of arsenic detected in a sample from an active extraction area was almost 18 times higher than both the maximum concentration among the nonactive/reference area samples and historical levels from this region. Notably, 29 of 90 water wells in active extraction areas exceeded EPA's arsenic MCL for drinking water of 10 μg/L[75].

Arsenic in this region is derived from Oligocene−Miocene volcanic ash and is adsorbed onto metal oxides and clays[76]. Common forms of arsenic in groundwater are As(V) and As(III), also known as arsenate and arsenite, respectively[77]. Arsenite, a reduced form of arsenate, is more mobile and toxic than arsenate[76,78,79]. Sorption of arsenate is strongest at near-neutral pH, with adsorption rapidly weakening above pH ~8.5[80]; the pH values in our groundwater samples averaged 7.9, with values as high as 9.3. Although we cannot identify the biogeochemical processes that lead to higher pH values and subsequent arsenite mobilization, small perturbations such as lowering of the water table either through groundwater withdrawals or drought conditions could explain these results[76].

Elevated arsenic concentrations can also occur in agricultural areas where pesticide application leads to arsenic introduction[71], or in areas with cultivated cotton as arsenic was used as a defoliant[81]. Reedy et al.[82] showed that applied arsenic is limited to shallow surface soils due to strong interactions between arsenic and iron oxides and clays in soil. Given the low mobility of applied arsenic and the fact that none of our samples were collected from private wells in or adjacent to crop fields, we find agricultural arsenic introduction is unlikely to be the source of elevated arsenic concentrations. Moreover, if agriculture were the cause of elevated arsenic levels, then concentrations in the historical data would likely have been high as well, and we found no evidence of this.

Selenium was less prevalent in the water samples, detected in 10 samples exclusively from active extraction areas. Selenium concentrations averaged 33 μg/L and ranged 10−109 μg/L, a stark contrast to the historical levels, which averaged 4 μg/L and ranged 0−50 μg/L. Two samples exceeded the selenium MCL of 50 μg/L[75], and concentrations in active extraction areas were significantly higher than historical levels although our sample size is too small to make definitive conclusions (Table 3-1).

Strontium was detected in 90 of 91 samples from active extraction areas as well as 9 of 9 samples from the nonactive/reference areas. Strontium concentrations in active extraction areas ranged 66−18 195 μg/L and were significantly higher than historical levels (Table 3-1). There is no established MCL for the stable strontium species analyzed in this study; however, an Agency for Toxic Substances and Disease Registry toxicological profile reports that the EPA currently recommends no more than 4000 μg/L in drinking water[83]. Seventeen samples from the active extraction area and one sample from the nonactive/reference areas exceeded this recommended limit.

Barium was also found in 90 of 91 samples from active extraction areas and 9 of 9 samples from nonactive/reference areas. None of the barium samples exceeded the MCL value of 2000 μg/L[75]; however, the maximum value was much higher in the active extraction area compared to the nonactive/reference areas (174 μg/L and 60 μg/L, respectively). Additionally, the concentrations of arsenic and selenium as well as the concentrations of strontium and barium were positively correlated with one another (Table A-2).

These constituent concentrations could be due to mechanisms other than contamination of aquifers with fluids used in natural gas extraction. For example, lowering of the water table can lead to changes in pH that cause desorption of arsenic and selenium from iron oxide complexes or mobilization of arsenic through pyrite oxidation[80]. The regional water table has slowly risen in recent years as the population has shifted from groundwater to surface water for drinking water[84] (Table A-3). Recent drought conditions have also not had a severe impact on the water table, as levels in the Trinity and Woodbine aquifers are influenced more by the amount of groundwater withdrawal than the lack of recharge from decreased rainfall[85]. While the regional water table has not decreased dramatically in the last 10 years, rural areas with high water withdrawal rates and/or withdrawal of large amounts of groundwater for use in hydraulic fracturing could lead to localized lowering of the water table. Bene et al.[85] project that industrial use of groundwater for hydraulic fracturing will rise from 3% of total groundwater use in 2005 to 7% in 2025, which suggests that current and future industrial water use could cause localized water table reductions. Additionally, pyrite is not found at high levels in these aquifers[86], so it is an unlikely source of arsenic.

Another potential mechanism is detailed in a report[68] suggesting that mechanical disturbances, such as pressure waves from drilling activity, could loosen iron oxide particles from the casings of private water wells, leading to increased turbidity of well water. Arsenic and selenium could be mobilized into groundwater if iron oxide complexes are agitated. Strontium and barium form sulfate or carbonate scales on the interior casings of poorly maintained water wells and mechanical disturbance could also lead to mobilization of these constituents. While arsenic, selenium, strontium, and barium are present at low levels in many private water wells[69,82,87], the levels seen in this study warrant further investigation, as arsenic in groundwater is a health concern[88,89].

3.4.3 Constituents and Distance to Nearest Gas Well

Arsenic, selenium, strontium, barium, and TDS reached their highest concentrations in areas of active extraction in close proximity to natural gas wells (Figure 3-2 and Figure A-2). Samples that exceeded the MCL for TDS, arsenic, and selenium were located an average of 1.1 km from the nearest natural gas well. Similarly, the highest values for both strontium and barium were over twice as high in areas less than 2 km from the nearest natural gas well compared to more distant gas wells. The geographic patterns in our data suggest that lowering of the water table during a drought period cannot fully explain these elevated constituent levels. Concentrations that exceed the MCL occur only in close proximity to natural gas wells (Figure 3-2) suggesting that mechanical disturbances or localized groundwater withdrawals near natural gas wells could play a role in elevated constituent concentrations. If regional drought or widespread public water withdrawals were the cause of elevated constituent levels, then the geographic localities of MCL exceedances would be more evenly distributed throughout the study area, rather than in close proximity to natural gas wells. Additionally, regional lowering of the water table should have resulted in similar constituent concentrations in these aquifers during historical periods when groundwater withdrawal rates were even higher than present levels.

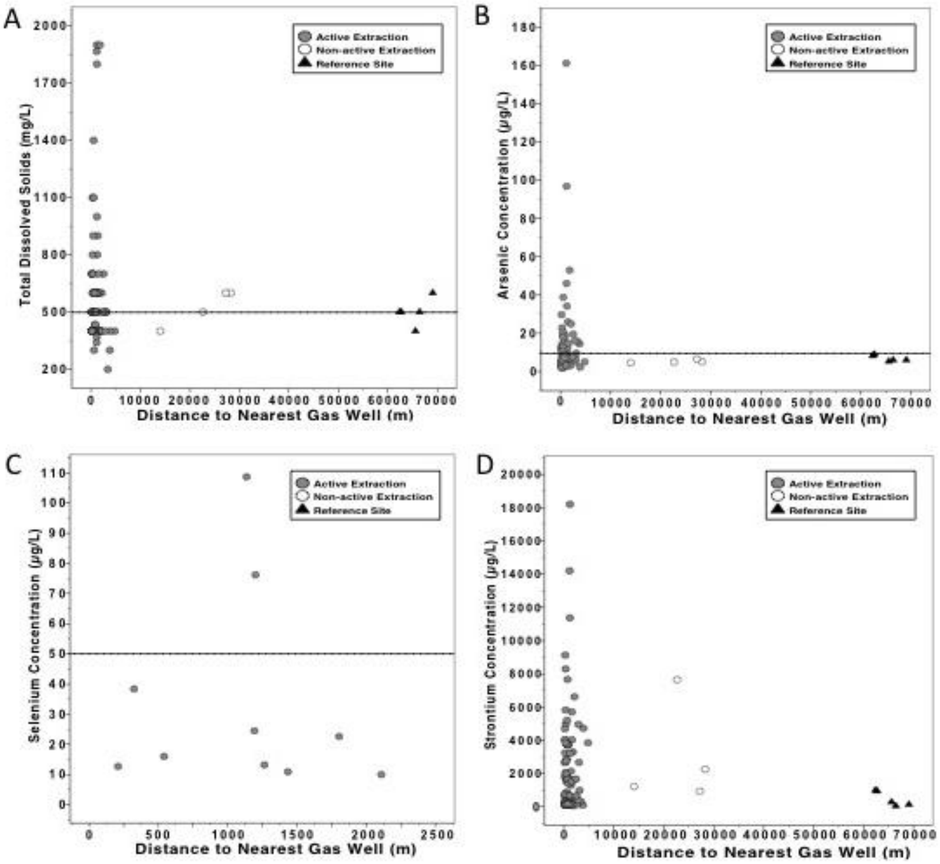

Figure 3-2: Correlation with gas well proximity and TDS, As, Se, and Sr

(A) Total dissolved solids, (B) arsenic concentration, (C) selenium concentration, and (D) strontium concentration versus distance to the nearest natural gas well in Barnett Shale private water well samples. The dashed lines in A-C represent the EPA's Drinking Water Maximum Contaminant Limit for each constituent. Reprinted with permission[10]. Copyright 2013 American Chemical Society

3.4.4 Constituents and Private Water Well Depth

Arsenic, strontium, and barium all showed significant negative correlations with the depth of private water wells (Table A-2). This could be due to contact with surface sources as the highest concentrations of arsenic and other compounds occur at the shallowest depths of private water wells (Figure 3-3). Previous studies also found negative correlations with depth in studies of arsenic and other compounds in the Gulf Coast aquifer of Texas[90] and the Paluxy aquifer[91], which is part of the larger Trinity aquifer. Glenn and Lester[90] attributed their elevated constituent concentrations to a geologic origin, and we cannot rule out that scenario with these data. It is also possible that improper handling of waste materials and faulty gas well casings could result in the introduction of these compounds into shallow groundwater[92]. Healy et al.[93] demonstrated that fluid−matrix interactions in unlined wastewater tanks cause mobilization of naturally occurring salts and other constituents into groundwater, and Vidic et al.[1] indicate that faulty casing seals in natural gas wells can cause groundwater contamination, although these casing failures occur infrequently (1−3% incidence rate in Marcellus Shale operations).

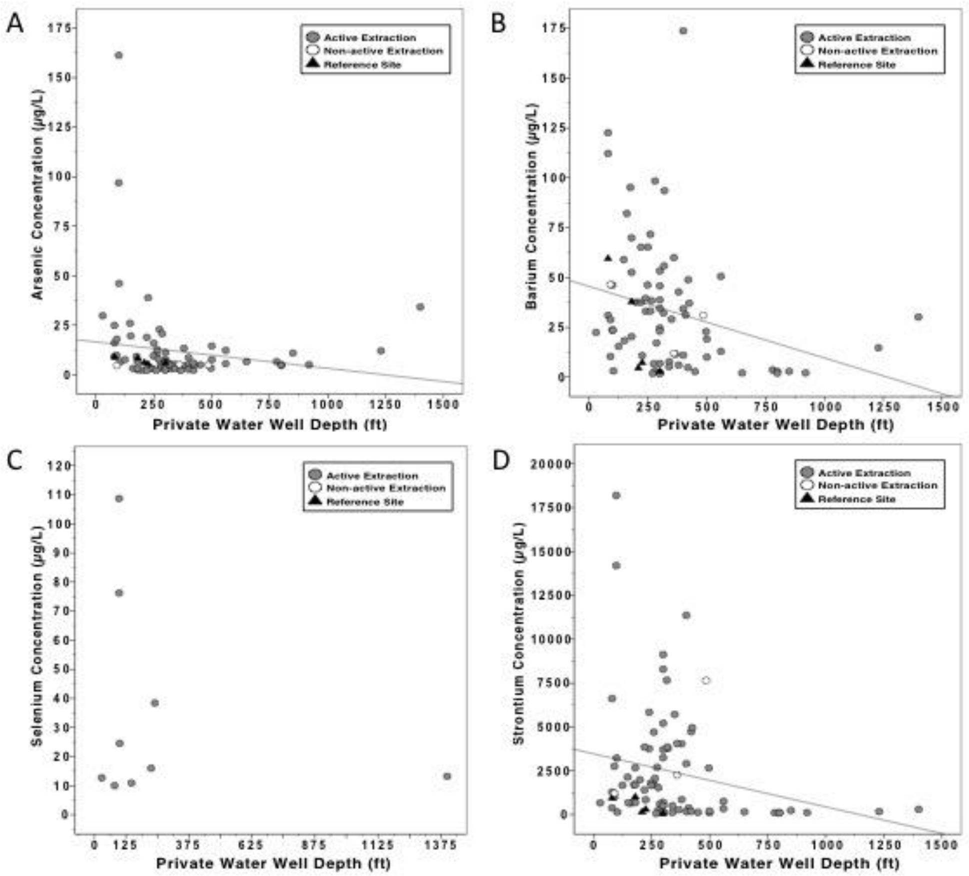

Figure 3-3: Barnett Shale private water well depth versus As, Ba, Se, and Sr concentration

(A) arsenic concentration, (B) barium concentration, (C) selenium concentration, and (D) strontium concentration. Reprinted with permission[10]. Copyright 2013 American Chemical Society

3.4.5 Heavy Metals and Total Dissolved Solids

Selenium was not correlated with TDS (likely due to small sample size), while strontium and barium showed significant negative correlations with TDS (Table A-2). Arsenic showed a significant positive correlation with TDS (Figure A-3 and Table A-2), suggesting that it may be concurrently mobilized into groundwater with TDS during the natural gas extraction process. Again, mechanical disturbances (high pressure fluid injection, mechanical vibration, etc.) associated with natural gas extraction activities could be the cause of elevated levels of TDS and arsenic. Scanlon et al.[81] also found a positive correlation between arsenic and TDS levels from the High Plains aquifer in a semiarid region of western Texas. They attributed this correlation to a counterion effect from an influx of saline water from the underlying Dockum aquifer that triggered a shift from calcium-rich to sodium-rich water, mobilizing arsenic from chemical complexes. Because arsenic levels in this region have historically been low (<10 μg/L) and TDS levels have not changed appreciably compared to historical levels, it seems unlikely that this scenario could explain the correlation between arsenic and TDS seen in this study[71]. Additionally, the clay and nonkarstic carbonate layers separating the Woodbine and Trinity aquifers would not seem to allow a large influx of deep saline water to trigger a similar change in hydrogeochemistry.

3.4.6 Comparison to Historical Data

Concentrations of arsenic, strontium, and selenium were significantly higher in samples from active extraction areas compared to historical data (Table 3-1). Nonactive/reference area samples also showed a significant increase in arsenic compared to historical data (Table 3-1). Both active extraction and nonactive/reference areas showed a significant decrease in barium concentrations from historical levels (Table 3-1). Historical TDS concentrations were not significantly different from nonactive/reference area concentrations but were significantly higher than active extraction area samples (Table 3-1). On average, wells from the historical data set were 102 m deeper than our wells, and this could explain the difference in some constituents. While we cannot draw definitive conclusions due to the fact that the historical data was collected under different sampling conditions, these data do provide a baseline for comparison to preindustrial conditions, which is generally lacking in studies of this nature[1].

3.4.7 Methanol and Ethanol in Private Well Water

Table A-1 lists 29 compounds selected for GCMS analysis based on their inclusion in hydraulic fracturing fluid mixtures[49]. Only methanol and ethanol, often included as anticorrosive agents in natural gas extraction, were detected in this study. Methanol and ethanol concentrations were quantified using HS-GC with flame ionization detection (see the Appendix A Methods). Twenty-nine private water wells contained detectable amounts of methanol ranging 1−329 mg/L, with the highest concentrations from active extraction areas (Table 3-1). All six samples from Wise County contained methanol concentrations ranging 7−54 mg/L, with an average concentration of 28 mg/L. These water wells are located between 215 and 610 m from the nearest natural gas wells and could represent concurrent contamination of multiple private wells, although we cannot identify the contamination source using these data. Ethanol was detected in 12 samples, ranging in concentration from 1 to 11 mg/L. Four out of nine samples from nonactive/reference areas contained both methanol and ethanol, suggesting that these chemicals are already present in groundwater in these areas and could have been introduced through something other than natural gas extraction. Methanol is known to occur naturally in groundwater as a byproduct of microbial metabolism[7,94], but it could also be introduced through contact with industrial wastewater. Similarly, ethanol can occur naturally or be introduced to groundwater through contact with industrial fuels[95]. Naturally occurring ethanol is ephemeral and restricted to deep, anoxic environments different from shallow groundwater[96]. Methanol and ethanol concentrations were not correlated with distance to the nearest gas well.

The historical data did not include methanol and ethanol, so we cannot examine the historical occurrence of these constituents. The samples containing alcohol were collected and analyzed during multiple sampling and analysis events over the entire study, ruling out laboratory contamination as the source. The occurrence of alcohols in our samples is relatively low, but it does warrant further research, as these compounds should have a very short lifespan in the environment and likely require an active source to sustain high concentrations.

3.5 Conclusion

Our results show elevated concentrations of constituents in the Barnett Shale region; however, we are unable to determine the ultimate source of these elevated concentrations directly. Previous studies in the Marcellus Shale used geochemical and isotopic tracers to provide a direct link to the source of industrial or geological contamination (e.g., nonthermogenic methane and deep brine mixing with shallow groundwater[7,8]). Analyses to identify the origin of elevated constituent concentrations are beyond the scope of this study, which was intended simply to examine water quality in areas of natural gas extraction. In lieu of these analyses, we chose to evaluate the geographic occurrence and absolute concentration changes for these constituents over time by comparing this study’s data against previous characterizations of groundwater in this region from the scientific literature and a large historical data set from the same region. This comparison shows a significant increase in the mean concentration, maximum detected concentration, and MCL exceedances for As, Se, and Sr in our study area when compared to historical data and previous characterizations of these aquifers (Table 3-1)[71,86].

While our data indicate elevated levels of potentially harmful compounds in private water wells located near natural gas wells, it is important to recognize that there were also a number of private water wells in close proximity to natural gas wells that showed no elevated constituents. This indicates that natural gas extraction activities do not result in systematic contamination of groundwater. We suggest that episodic contamination of private water wells could be due to a variety of natural and anthropogenic factors such as the mobilization of naturally occurring constituents into private wells through mechanical disturbances caused by intense drilling activity, reduction of the water table from drought or groundwater withdrawals, and faulty drilling equipment and well casings. The geographic locations of elevated constituent levels in our study are consistent with the notion that mechanical disturbance of private water wells and industrial accidents (e.g., equipment failure, faulty well casings, fluid spills, etc.) are more frequent in areas where natural gas extraction is active.

To draw definitive conclusions about the origin of elevated constituent levels in these water wells would require a focused study of groundwater before, during, and after natural gas extraction activities. This was logistically impossible as industrial activities have been ongoing for more than 10 years in this area. Given this limitation, our discussion of the source of elevated constituents is speculative, but we have provided plausible scenarios to explain our data in an effort to increase scientific understanding of this topic and spur future research. At a minimum, these data suggest that private wells located near natural gas wells may be at higher risk for elevated levels of constituents than those located further from natural gas wells. We advocate regular water monitoring utilizing targeted analytical chemistry along with toxicity assays to understand the complex interactions among groundwater constituents and biological organisms[13]. Future research will focus on monitoring private wells in the Cline Shale in the Permian Basin region of Texas before, during, and after natural gas extraction activities, understanding the role of mechanical disturbances, in mobilizing naturally occurring constituents into groundwater, and evaluating the effects of industrial accidents and waste disposal practices. Water quality in the Barnett Shale region is likely to become an even more contentious issue as public concerns and prolonged drought conditions place pressure on water reserves in the region.

Chapter 4

Time-Course Monitoring of Groundwater Quality Relative to Increased Unconventional Drilling in Nolan County, Texas

4.1 Abstract

Proper baseline measurements of regional groundwater can give an accurate depiction of water resources before unconventional drilling activity commences. These measurements can then be the used to provide an accurate setting to measure potential changes in the face of the anthropogenic activity. A study surveying multiple types of groundwater analytes, which includes baseline data, can demonstrate changes and life cycles of the fluctuations with the greatest confidence. Here we present a detailed time-series analysis of groundwater quality in Nolan County, Texas, an area where unconventional drilling activity has recently increased. Four time-point measurements taken over the course of 15 months illustrate changes in pH, sulfate, chloride, and carbon levels when compared to the initial baseline measurements collected prior to hydraulic fracturing in the area. Methylene chloride was detected in a large majority of the groundwater samples during the onset of hydraulic fracturing. Aberrations changed in intensity through the time-course measurement, providing insight into the life cycles of possible contamination event.

4.2 Introduction

The increased use of unconventional drilling to extract oil and natural gas from deep shale formations has kindled notable concern over the anthropogenic effects of this highly articulated process on the surrounding groundwater[43]. The increased use of hydraulic fracturing and underground injection wells during well stimulation and waste storage, respectively, has garnered international interest over groundwater quality[97]. Additionally, the handling, temporary storage and treatment of waste fluid and produced water[98] into open-faced containment units[9] and water remediation facilities[99], has generated interest with regards to the effects on surrounding groundwater and surface water[100]. Previous findings have revealed elevated levels of methane[7], stray thermogenic gas,[34] and evidence of brine contamination[8] in the Marcellus shale, that have been directly linked to hydraulic fracturing and unconventional natural gas extraction. Similar research efforts in the Barnett shale have revealed elevated levels of heavy metals arsenic, barium, selenium and strontium in areas most actively engaged in hydraulic fracturing[10], in which these naturally-occurring groundwater constituents are thought to be liberated into groundwater from highly-concentrated iron oxide rust and scale formations from within the well by mechanical vibrations produced by the unconventional drilling process. Collectively these initial results provide a nascent understanding of the relationship between groundwater quality and unconventional drilling; however, the inability to collect baseline measurements before unconventional drilling activities in these studies has hindered the ability to draw definitive conclusions. This, coupled with the social and political gravity of unconventional drilling debate, has provided an impetus for further investigations to include groundwater quality measurements to be collected before, during, and after surrounding deep shale wells have been stimulated by hydraulic fracturing[1,35].

Here we present a concentrated time-series analysis of groundwater quality in Nolan County, Texas, an area where unconventional drilling activity has recently increased dramatically over the past 2 years. Nolan County amasses 914 square miles on the Eastern side of the Cline Shale formation of West Texas. Nolan County is characterized by a diverse set of energy production modalities, housing historical shallow oil and gas, solar, and wind harvesting activities, in addition to the more recent use of hydraulic fracturing to extract deep shale hydrocarbons. In this study, four sets of measurements were taken over the course of a 15-month period. Parameters monitored were general groundwater parameters, carbon content, nitrogen content, organic constituents found in hydraulic fracturing fluids, and metals associated with the drilling processes. The following will illustrate changes in pH, sulfate, chloride, and carbon levels when compared to the initial baseline measurements collected prior to hydraulic fracturing in the area. Methylene chloride was detected in a large majority of the groundwater samples during the onset of hydraulic fracturing. Additionally, the characterization of production fluids stored in shallow waste pits provides evidence of leaching into surrounding surface water and coincides with the methylene chloride detected in the groundwater. The levels of aberrations changed throughout the time-course and provided insight into the variable life cycle of possible contamination events.

4.3 Materials and Methods

4.3.1 Sampling

A total of 133 data points were collected across the four sampling trips, denoted Rd A, B, C, and D.; in Rd A 38 water wells were sampled. In Rd B 35 water wells, a pond, and 2 storage pits were sampled. In Rd C 20 water wells, a pond, and 1 storage pit were sampled. In Rd D 30 wells, 1 pond, and 1 pit were sampled. The 1 pit sampled in Rd B, C, and D had 2 distinct fluid layers, and each was sampled. A map of the sampled wells and natural gas wells is shown in Figure 4-1. The property is used for ranching and spans approximately 6,000 acres. The private water wells were a mixture of windmill, electric, and solar powered. Well depths were not measured, but information from the landowner is that they should all be near 60 m. The wells draw from the Edwards-Trinity Plateau Aquifer in Nolan County, TX[101]. Sample collection and general groundwater measurements were made as described in Section 3.3.1 and in previous reports[10]. Two deviations from prior procedures were that each sample in this sample were taken in two 125 mL amber HDPE wide-mouth bottles and turbidity was not measured.

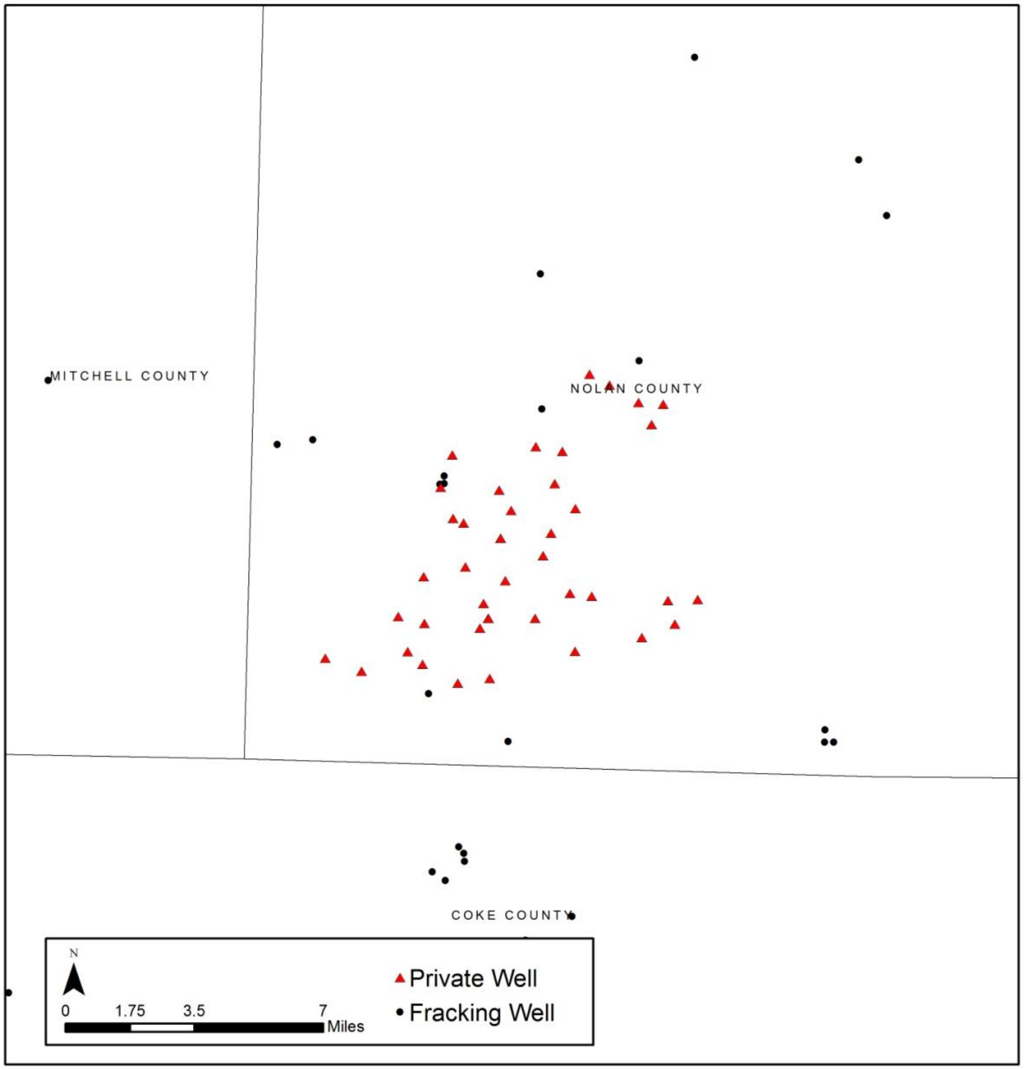

Figure 4-1: Map of the water wells sampled and existing gas well for the study

4.3.2 Analysis

Chemical analyses were conducted using TOC/TN analyzer, gas chromatography – mass spectrometry (GC-MS), headspace – gas chromatography (HS-GC), ion chromatography, inductively coupled plasma – optical emission spectroscopy

(ICP-OES), and ICP-MS. Appendix B gives more insight into the instruments used, method parameters, and analytes screened. In short, the main analytes speciated were As, Ba, Se, Sr, Zr, Cl^-, Br^-, SO_4^{2-}, NO_3^-, BTEX (benzene, toluene, ethyl benzene, and xylenes), methanol, and ethanol.

4.4 Results and Discussion

4.4.1 Water Quality Parameters

Fluctuations in the general groundwater parameters were compared using either the absolute values or the percent increase in measurement relative to Rd A, the pre-drilling baseline measurement. A moderate increase in the mean TDS concentration was observed, peaking in Rd C at 460 ± 140 mg/L vs Rd A at 370 ± 120 mg/L. The median value of Rd C was 100 mg/L higher than initial measurements, 450 vs 350 mg/L. The minimum TDS concentration measured in Rd A was 200 mg/L. Rd C measurements showed a minimum measurement of 293 mg/L. The two wells reporting 200 mg/L TDS in Rd A each had higher TDS concentrations with subsequent sampling dates. Significant correlations could not be drawn between TDS concentration increases and proximity to the nearest gas well, as was shown in our prior publication[10].

Significant changes in the pH of the sampled groundwater over time were detected, as shown in Figure 4-2. The baseline measurements for the 38 water samples yielded an average pH of 7.4 ± 0.2. Water samples collected the subsequent sampling trip, Rd B, six months later had a mean alkaline pH of 8.7 ± 0.5. Rd C and D water samples represent a decline in groundwater pH to the original values measured, 8.0 ± 0.4 and 7.4 ± 0.2, respectively. The deviation of the measurements also increased in a proportional manner with pH. The relative standard deviation is the highest in Rd B, indicating that the source giving rise to the pH increase is affecting water wells in a non-uniform manner.

Cement intrusion into the groundwater while the wellbore is being established typically leads to a pH between 10 and 11 immediately following[102]. Hydroxide compounds, e.g., sodium hydroxide and potassium hydroxide, can be used to adjust the pH[50,103] or as crosslinking agents[50] in some cases.

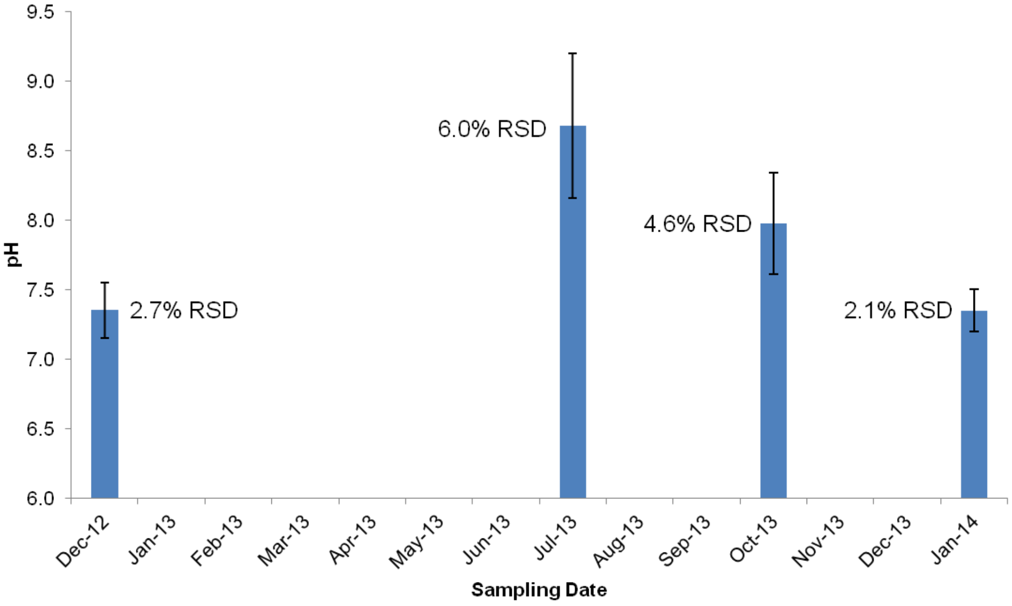

Figure 4-2: Change in mean pH over time. Drilling and hydraulic fracturing began between Dec. 2012 and July 2013

4.4.2 Inorganic Ion Analysis

The changes observed for Inorganic ions in the private well water were evaluated as a function of proximity to the nearest gas well. A negative correlation could be shown between the percent increase in chloride and sulfate concentration and distance to the nearest gas well. Figure 4-3 plots the percent increase in (a) Cl^- and (b) SO_4^{2-} concentrations in Rd B for the 32 samples for which we had both Rd A and B measurements.

Chloride from formation water has been shown[51] to increase in groundwater as the number of gas wells increased. The most affected areas were near structural formations, not gas well locations, where faults and fractures maximize the vertical mobility of the formation water.

Well casing failures could also lead to direct contact of hydraulic fracturing fluids with the drinking water aquifer or deeper formations above the production shale[4,46]. Another possible source of salinization, either from source water or fracturing fluid, is from a breach of waste pits containing flowback water[50] which could possibly leach to the underlying aquifer. There are waste pits within 100 meters of multiple gas wells. These two sources, casing failure and waste pit breaches, could be arguments for concentration gradients with respect to gas well proximity.

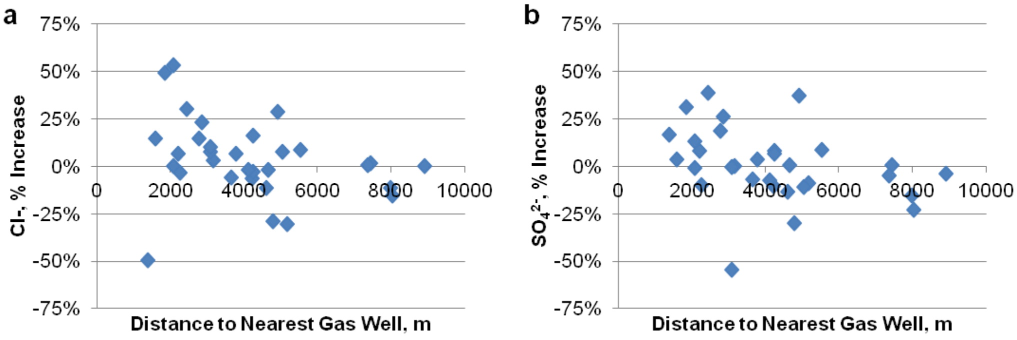

Figure 4-3: Percent increase of (a) chloride and (b) sulfate in Rd B of sampling, compared to Rd A

4.4.3 Fluctuating Carbon Content in Private Well Water

Carbon content of the private well water was measured and assessed as total organic carbon (TOC), inorganic carbon (IC), and total carbon (TC). For the 24 samples with Rd A and Rd B carbon measurements, all increased in TOC, all but 2 in IC, and all but 1 increased in TC content, as shown in Figure 4-3. The 1 well with a measureable decrease in TC, 44.4 mg/L to 34.9 mg/L (-21.4%), was also one of the two wells with a decrease in TC content of 6.9%. This well is also the 3rd furthest well from activity within the set, nearly 8 km away from a natural gas well. Over the sampling time period, TOC had a significant increase in concentration in Rd B, with each sample with a baseline reference point increasing from between 139 and 962%. Rd C and Rd D revealed TOC content similar or below that of Rd A for most samples (Figure 4-3a). A significant correlation between well proximity and TOC values could not be made. IC concentrations of the well water saw a significant increase between Rd A and Rd B, but have remained elevated, unlike TOC (Figure 4-3b). TC content is a function of TOC and IC, therefore, it is still elevated beyond the baseline measurements of Rd A due to the IC contributions (Figure 4-3c)

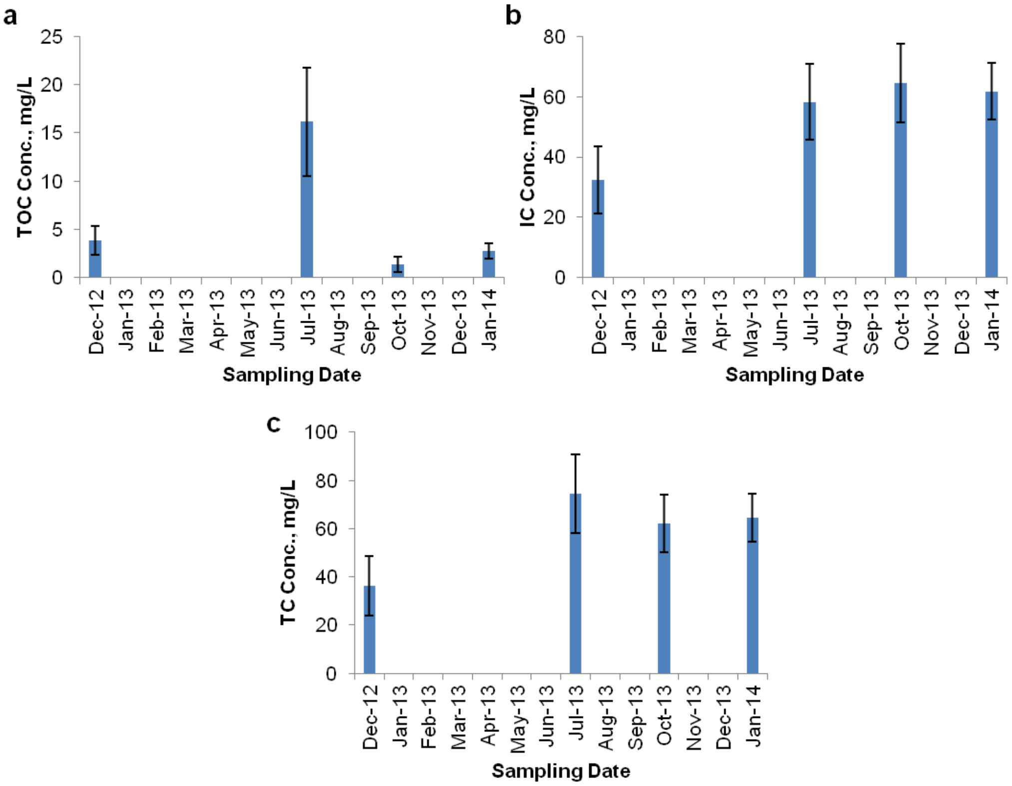

Figure 4-4: Mean carbon concentrations for (a) TOC, (b) IC, and (c) TC over the sampling time period

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4.4.4 Methylene Chloride in Private Well Water

Methylene chloride was detected in 34 of the 35 wells sampled in Rd B at concentrations over 3 mg/L. The maximum concentration measured was 6.54 mg/L in a well within 1 km of a natural gas well. Figure 4-5 displays a negative correlation between concentration and well proximity, as was observed for the increased inorganic ions. Additional confirmation of the presence of methylene chloride in Rd B samples was performed by an independent laboratory. It is believed the spike in TOC concentration only present in Rd B is in part attributed to the methylene chloride content only found in that time set. No methylene chloride was detected in the sampled water in Rd A, C, or D.

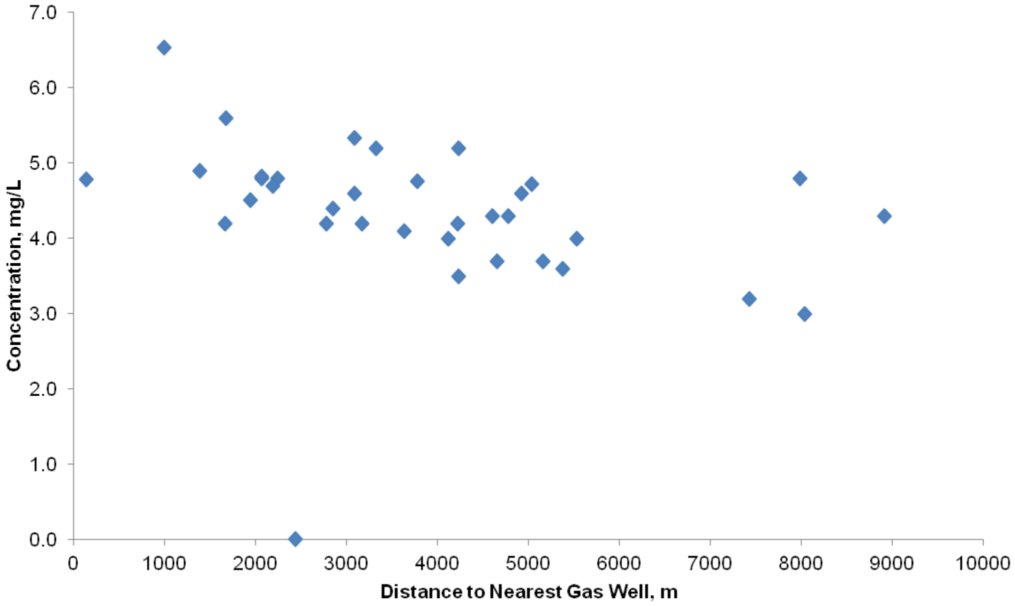

Figure 4-5: Methylene chloride in Rd B water well samples

The solvent methylene chloride is not listed as a drilling or fracturing ingredient in any of the public disclosure databases[49,103] or textbooks[104,105]. A recent report[106] which detected high concentrations of methylene chloride vapors explained the occurrences due to methylene chloride being stored on well pads for cleaning purposes.

Two waste pits were sampled along the property. Comparable amounts to groundwater levels of methylene chloride were detected in these pits. It is expected that the pits contained much higher concentrations, but had lost significant amounts due to the high vapor pressure of the solvent and the arid climate. Methylene chloride that had leached into the soil and eventually groundwater would experience much slower evaporation, if any. Breaches in one of the waste pits are further corroborated by detecting methylene chloride in water from a nearby surface pond. Multiple measured values for this pond, such as TOC and selenium, were more similar to the waste pits than the groundwater.

4.5 Conclusion

The ability to monitor groundwater over a time period before and after unconventional drilling and hydraulic fracturing has proven quite valuable in revealing significant changes occurring in the groundwater[107]. Possessing groundwater measurements before any drilling or fracturing activity allows the data to be interpreted based upon fluctuations and not solely regulatory exceedances or anomalies in absolute concentration. Comparative measurements over time from the same well can account for older or poorly maintained wells that may inherently possess many exceedances for measured constituents. Comparative data of the same well also allows for less emphasis to be given on the aquifer type or well depth which can give rise to differences between wells. Other groundwater studies[6-8,10] have used state agency water quality databases or reports for comparative analysis, but very few, if any, locations of data are the same as the study. Each study also concluded with mention that conclusions could be more definitive with monitoring before drilling with public access to the data. Also, the unique nature of drilling and hydraulic fracturing has given rise to target-specific measurements, e.g. isotopic ratios and BTEX, which cannot be found in databases of general groundwater measurements. The development of standardized specific methods for water monitoring in areas affected by unconventional drilling would help proliferate the generation of data tailored to this process and accelerate research to understand the resulting effects, short or long-term.

The groundwater fluctuations observed along the time period of this study serve as parameters of interest for further studies. Whether the spike in pH, chloride, and sulfate concentrations is a common occurrence to unconventional drilling or from a catastrophic event, it affects the residents all the same and needs to be understood. The lifetime of detectable events gives insight for further recommendations of remediation and concern. The pH of the groundwater did not return to the original reading until Rd D, while methylene chloride was short-lived and only detected during Rd B. Further data sets similar to this study need to be generated across the nation to understand fluctuations inherent to unconventional drilling and also identify possible contamination events more confidently[107]. Hopefully this practice will become more prevalent in the near future through state and local legislation[5].

Chapter 5

Varying Matrix Effects for Elemental Analysis Identified from Groundwater in the Barnett Shale

5.1 Abstract

The quality of analytical measurements can be influenced by the matrix of the sample of interest. Knowledge of the sample matrix allows for appropriate sample preparation, instrumental parameters, and quantification methods in an effort to achieve accurate results. Matrix matching can be difficult when sampling across various water sources with the possible introduction of unknown endogenous contaminants due to various degrees of land use, urbanization, and energy exploration, likely playing a factor. The degree of matrix effects in inductively coupled plasma – optical emission spectroscopy for nineteen metals from twenty groundwater samples across North Texas was assessed using a standard addition method. Matrix effects were characterized in collected groundwater samples with a) no pretreatment, b) after reversed phase solid-phase extraction of possible organic contaminants, and c) for a matrix of organic material retained on the reversed phase sorbent. It was found that without any extraction treatment, only 54% of all measurements experienced no matrix effect. After extracting unknown organic sample constituents, an increase to 74% of measurements showing no matrix effect was recorded. Reconstituting the extracted organic sample matrix found this fraction to be a significant source of the deviated results with only 13% experiencing no matrix effect. Results for the metals investigated are also discussed, along with correlations to water quality parameters such as turbidity, total dissolved solids, and salinity.

5.2 Introduction

Accuracy in the quantification of metals in environmental samples, whether water, soil, or air, is of the upmost importance for the safety of living organisms. The significance of these measurements is made evident by the 200 series of test methods by the United State Environmental Protection Agency (EPA) which is nearly exclusive for elemental analysis and includes extensive sampling, analysis, and verification guidelines for each. Standardization of these methods is important to ensure interlaboratory reproducibility and accuracy for these samples, which will contain varying degrees of complexity in the relative mixtures of compounds and ions. The complex milieu of constituents other than the analyte of interest comprises what is referred to as the sample matrix[108]. The matrix can be highly variable depending on dissolved organic and inorganic matter, pH, turbidity, or even sample source. Depending on the constituents of the sample matrix, a measured analyte signal can be decreased, enhanced, or unaffected relative to how it responds in a pure form and depending on the chosen analyses.

Simultaneous multi-metal analysis for metals in molecular, atomic, or ion form has become dominated by inductively coupled plasma (ICP) techniques[109], coupled with either mass spectrometry (MS) or optical emission spectroscopy (OES). ICP-MS has superior sensitivity over OES measurements, but this sensitivity limits the possible applications. With the proper measurement wavelength selection and viewing mode, ICP-OES has the capability for measuring major, minor, and trace elements in solution and boasts up to ten orders of magnitude in analytical working range[110]. ICP-OES is also unaffected by isobaric ions, a common consideration in ICP-MS. To help ensure the acquisition of accurate data with ICP-OES[111], instrumental parameters such as proper wavelength selection, sample aerosol formation from the nebulizer[112], plasma temperature[113], and emission viewing mode[114] must be carefully optimized. With careful consideration, ICP-OES is an accurate and quite versatile technique for multi-elemental analysis.

Since the sample matrix can affect analyte response[111], the degree of matrix effect should be assessed. Matrix effects can be determined by comparing an analyte's response in the sample of interest to that of an analyte standard in a "matrix-free" environment[115]. Here we define a significant matrix effect as that which elicits a response less than 80% or greater than 120% of a matrix-free calibration standard[116].

Matrix effects in spectroscopy can be classified into three groups: physical, chemical, and spectral[117]. Physical effects include changes due to a sample's viscosity, density, surface tension, and concomitant elements and their concentration. A chemical source for matrix effects result from the analyte forming a new compound with different characteristics. High temperatures of the plasma in ICP-OES typically decompose many compounds into its elemental constituents, which limits this effect. However, precipitation of the analyte before analysis, due to the formation of an insoluble salt in solution, can be problematic in analyte recovery. For example, adding sulfuric acid to a sample solution containing barium will produce barium sulfate, which has a very low solubility in water[118,119]. Spectral effects are caused by the overlap of emission lines of other species at the monitored wavelength. This overlap will enhance the monitored signal, resulting in a positive measurement bias or a false positive in detection[108]. In samples containing high concentrations of copper and minimal amounts of zinc, the copper emission line at 213.853 nm could lead to an overestimation in the response of the Zinc emission line at 213.856[120]. Of the thirty-two elements monitored at trace levels in the US EPA Method 200.7, only ten elements are listed to have no spectral interferants[120,121].

Ensuring the accuracy of elemental measurements in groundwater has been important for researchers and governmental agencies attempting to characterize the quality of aquifers and other water supplies throughout the country. Databases of measurements are often useful as benchmarks in situations where ground contamination events may have occurred. Recently, water in the Barnett Shale formation in North Texas has been of interest, given the expansion of unconventional drilling activities in the region[10]. Throughout the past ten years, the formation, spanning 48,000 km^2, has become one of the most heavily drilled shale formations in the United States for the extraction of natural gas. According to the Texas Rail Road Commission, over 17,000 gas wells are recorded in the area, with the most rapid increase in the number of new wells attributed to advances in horizontal drilling and hydraulic fracturing since 2005 (www.rrc.state.tx.us/data/fielddata/barnettshale/pdf).

Using elemental analysis of groundwater to identify instances of natural gas drilling or hydraulic fracturing contamination has tremendous merit given that many of the metals used in unconventional drilling are well established. Various metals are used in high abundances throughout the drilling, hydraulic fracturing, and extraction process, including barium, boron, molybdenum, and zirconium[104,105]. Even so, inorganic compounds added to drilling and fracturing fluids at the surface are not the only concern. Flowback water that is removed from the ground after hydraulic fracturing has been mixed with the sediments within the shale formation and can be enriched with naturally occurring radioactive heavy metals and brines[7]. A comparison of the aquifer's metal substituents at times prior to drilling and subsequently after would provide a compelling argument regarding the effects of the natural gas extraction process. However, in the Barnett Shale, with the great deal of industrial drilling activity over many years, it is difficult to currently design such a study. Reedy et al.[101] were able to characterize the

Trinity and Woodbine Aquifers (the dominant aquifers in the Barnett Shale region) as generally good quality for organic and inorganic species based upon previous USGS reports[69] and the compiled Texas Water Development Board's (TWDB) database of groundwater measurements[122] across previous decades. A recent publication by Fontenot et al.[10] quantified As, Ba, Sr, and Se in privately-owned water wells from the aquifers coinciding with the Barnett Shale after substantial drilling and hydraulic fracturing had occurred. The team discovered elevated levels of arsenic, selenium, and strontium in the aquifers that were statistically significant when compared to the TWDB dataset of the aquifers from 1989-1999, a time before wide-spread horizontal drilling and hydraulic fracturing. It was also determined that the concentrations of As, Se, and Sr were higher for water wells in closer proximity to unconventional drilling sites than the sampled water wells in lesser productive regions of the shale and outer non-active, reference water well locations. Various possible mechanisms for this finding were posited.

The aim of this work was to identify the similarities and variances in sample matrices which would affect elemental analyses from selected samples from the Fontenot study[10] of the two aquifers overlying North Texas's Barnett Shale region and neighboring aquifer. Many previous studies have investigated the effects of adding easily ionizable elements (EIE)[54,123,124] or varying concentrations of organic acids[125,126] on the response for specific elements, but we are not aware of previous studies that have investigated an unknown matrix and began to explain analyte behavior based on other resulting element concentrations and physical properties of the collected sample. By identifying sample similarity and differences, suggestions are also made for future sample preparation to increase the accuracy of ICP-OES measurements in possibly contaminated groundwater samples collected from a large geographic area.

5.3 Materials and Methods

Twenty samples for this study were collected from fourteen counties across the North Texas region. All the samples were collected from private residential water wells in a manner complying with EPA groundwater well sampling criteria found in SOP #2007[116]. One deviation worth noting is that all water purging and sample collection were performed with the preexisting property owner's pumping system and not separate pumps associated with the research team. Eighteen of the sampled wells were from the two aquifers within the Barnett Shale formation, and the other two well sites were used as a reference outside of the sampling area. Of the eighteen wells within Barnett Shale, sixteen were within 3.5 km of a natural gas well and two were approximately 20 km removed from natural gas extraction sites. A map of the sampling sites is shown in Figure 5-1. While a considerably larger sample set would have been preferred, the detailed and lengthy treatment and analysis of each sample required the study to be limited to twenty samples.

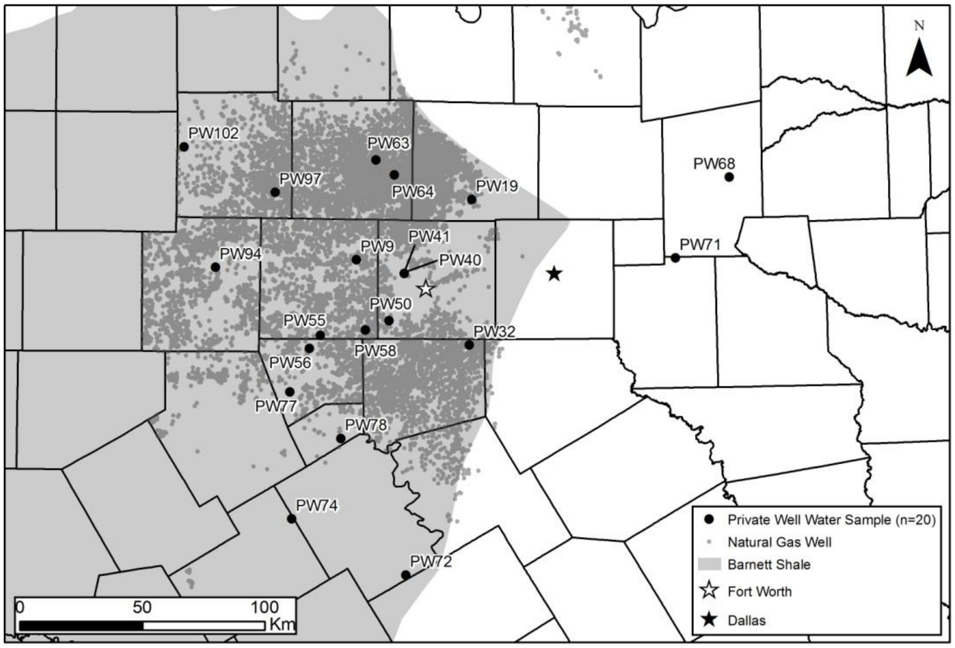

Figure 5-1: Map of the sampling region from North Texas

Measurements were made using a Shimadzu ICPE-9000 optical emission spectrometer (Shimadzu Scientific Instruments, Inc., Columbia, MD). Samples were introduced with a Mini Torch nebulizer, ionized with argon plasma, and introduced into the spectrometer in the axial view. Wavelengths selected for the analysis corresponded to the default wavelength chosen through the *Method Development Wizard* for preliminary sample measurements prior to method optimization. Software features use of elemental response factor information to estimate the concentrations of each element after a calibration with Al and Ba. An average of three measurements per acquisition was selected to calculate estimated concentrations which were used for data analysis of sample response. The nineteen elements chosen for investigation were antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, manganese, molybdenum, nickel, potassium, selenium, thallium, titanium, vanadium, and zinc.

Spectral line intensities for all elements were recorded simultaneously with the large-scale charge-coupled device detector, which is characterized by a resolution of < 5 pm at 200 nm in the ICPE-9000 instrument.

The method of standard addition was used to assess the degree of matrix effect that may be exhibited on the response of each metal from the well water samples. Previous work has shown standard addition to be successful for not only quantifying the influence of matrix effect but also as the most accurate of quantitative methods, when compared to techniques such as internal standardization, matrix matching, and robust plasma operating conditions[127-129]. A response curve for standard in DI water was generated with two additional spiked concentrations of 1 mg/L increments from a multi-metal standard solution obtained from High-Purity Standards (Charleston, SC). The elements present and their concentrations in the standard can be found in Table C-1. The slope of the 3-pt standard addition response curve for each element in DI water was used as our control, the matrix-free response for each metal. A 1-pt standard addition response curve was then created for each water sample before any sample preparation (besides the prescribed acidification to 2% nitric acid by volume for storage). Only one spike analysis was made because of limited sample volume. The response curve for each element in this group with no sample preparation is denoted as “Bulk” for the remainder of this manuscript (Figure 5-2a).

As a means for preparing the samples to reduce matrix components, a 15 mL aliquot of each collected well water sample was loaded onto a Bakerbond C18 solid phase extraction (SPE) cartridge (500 mg, 3 mL; JT Baker; Phillipsburg, NJ). This treatment is expected to remove any hydrophobic organic sample matrix (retained on the SPE cartridge). The unretained portion totaling 15 mL of the groundwater sample, comprised of hydrophilic compounds, metals, and salt ions, was collected. This portion maintained a pH less than 2 and did not need to be re-acidified. This sample lot is called "Fraction 1" (Figure 5-2b). The compounds retained on the reversed-phase SPE cartridge were then collectively eluted with 5 mL of 100% ethanol. The eluent was rotovapped to dryness and reconstituted in acidified DI water to the original loaded sample volume of 15 mL. The aqueous solution of the SPE retained compounds is called "Fraction 2" (Figure 5-2c). A one-point standard addition procedure for Fraction 1 and Fraction 2 were performed in the same manner as the Bulk samples. The response curve for each metal of each fraction was compared to the standard response to assess the degree of matrix effect. Blank solutions and cartridge rinsing with DI water result in metals removed from the SPE silica, none of which are metals of interest in this study that would affect results.

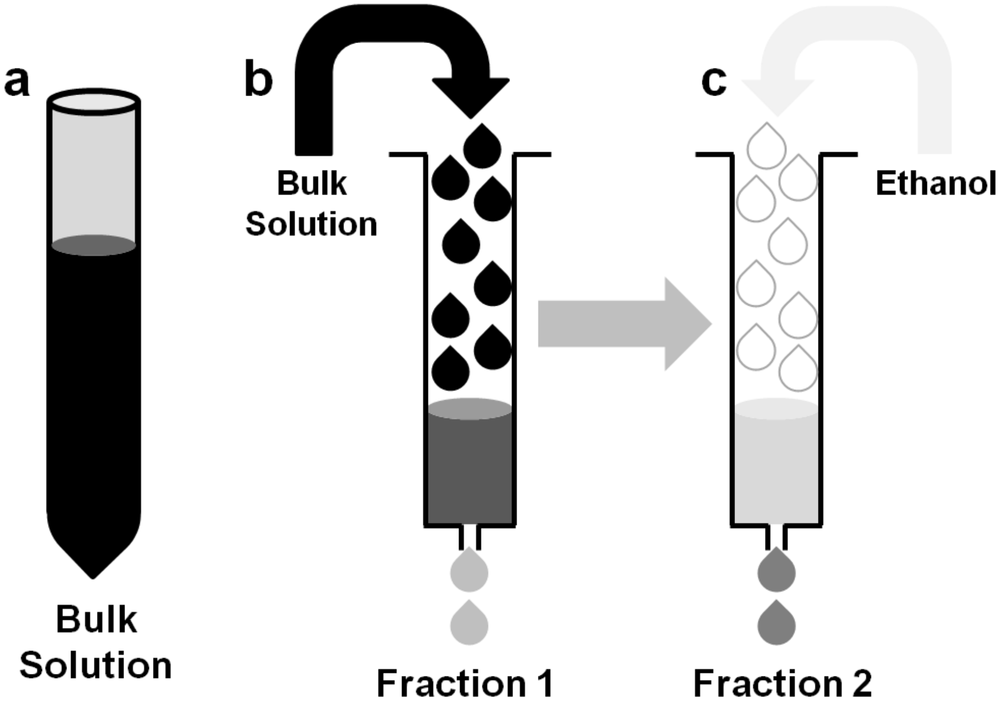

Figure 5-2: Pictorial representation of the three preparation methods used to identify the sources of matrix effects

5.4 Results and Discussion

5.4.1 Performance Summary of Preparations

The unfractionated Bulk groundwater samples contained 204 out of 380 measurements (54%) which showed no noticeable matrix effects for the 19 metals analyzed. The metals barium, beryllium, selenium, and vanadium showed no matrix effect present in the Bulk solution measurements of all 20 measured wells. The metals cobalt and thallium showed negative matrix effects (reduction of analyte signal in the sample versus in DI water) for all wells, while potassium showed positive matrix effects (enhancement of analyte signal in the sample versus in DI water) for every well measured. The survey of resulting matrix effects for Bulk sample solutions are shown in Figure 5-3a.

After passing the water samples through the RP-SPE columns to retain hydrophobic organic compounds that could contribute to a sample matrix, the unretained portion of the sample aliquot, assumed to contain the metal cations, any solvents present, and other ions, was investigated for their degree of matrix present. These samples, Fraction 1, showed fewer metals affected by the groundwater matrix than did the Bulk sample solution metals, with 252 out of 342 measurements (74%) exhibiting no matrix effects through standard addition, as shown in Figure 5-3b. The metals in Fraction 1 that showed no significant matrix effects in all well water samples were beryllium, chromium, copper, iron, manganese, molybdenum, antimony, vanadium, and zinc. Barium, which showed no matrix effects in Bulk solution resulted in two wells having a positive matrix effect of 24% and 26% in Fraction 1.

The last set of examined sample matrix was comprised of the compounds that were retained on the RP-SPE sorbent. This matrix was eluted from the sorbent, dried, and reconstituted in water. This system, identified as Fraction 2, exhibited the least amount of measurements with no matrix effect, 50 out of 380 (13%), as shown in Figure 5-3c. No one metal showed an absence of matrix effect in Fraction 2 across all 20 wells. The displayed effects were quite variable for each metal and within each metal for each well. PW50 consistently returned the highest response for 18 of the 19 metals. Cobalt was the only metal where PW50 was not the most responsive, falling to 2nd by 8% to PW32. The sample where the lowest responses were regularly observed was from PW40, yielding the lowest response in 18 of the 19 metals, and 2nd lowest in titanium response by 1.2% behind PW77.

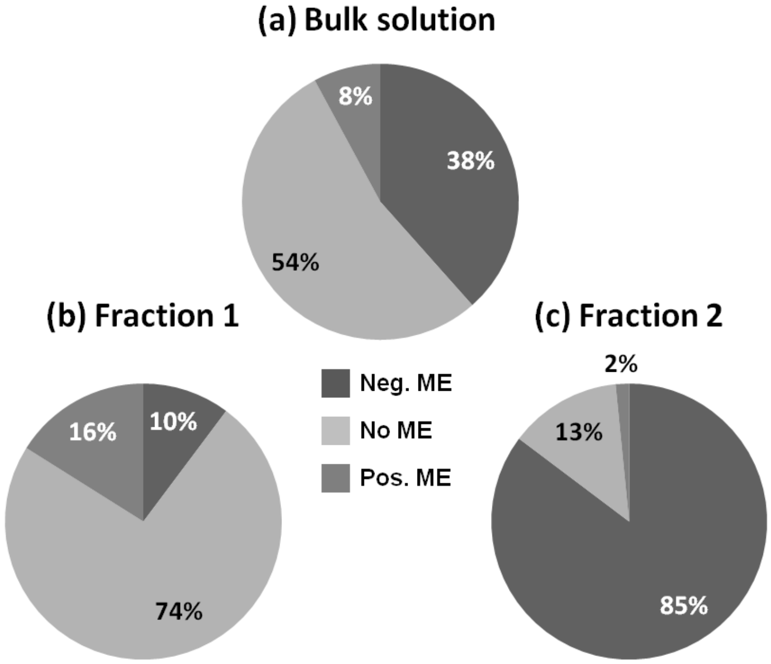

Figure 5-3: Summary of the matrix effect measured for the three preparation techniques

It was hypothesized that Fraction 1 would increase the number of measurements showing no matrix effects, 74%, as compared to Bulk, 54%. SPE is a commonly used preparation and preconcentration technique to increase the accuracy and reproducibility in elemental analysis of groundwater samples[130,131]. It is interesting to note the significant loss of accuracy in analyte response in Fraction 2. These comparisons indicate that the presence for matrix effects in Bulk is a combination of both Fraction 1 and Fraction 2, but to a larger extent from the organic compounds in Fraction 2. Such studies, in the context of these samples having unknown matrix compositions reinforces the use of best practices reported previously.

5.4.2 Cumulative Sample and Metal Summaries

Some applications may be interested in a sum of metal concentrations rather than that of individual metals specifically. The recovery of analyte is affected by sample preparation, sample introduction, and detection. Our response calculations are functions of sample introduction and detection influences. We calculate a cumulative metal response which is the average analytical response of all metals for a single sample. This metric assesses the analytical influence on measured recovery and not that of sample preparation. Based on the measurements taken of the samples as Bulk and Fraction 1, good total response recoveries are measured. The average of the cumulative metal response for the 19 metals of each of the Bulk sample solutions was 87%, ±3% between the sampled wells. Fraction 1 showed an increased average cumulative metal response to 104%, ±6%. The consistency of the cumulative response between all the water wells shown in Bulk and Fraction 1 was not the case for Fraction 2, resulting in only a 54% average cumulative metal response with a ±23% deviation between samples.

When working with multiple samples, it is important to be able to speculate the outcome of the accuracy of the measurements for a given sample preparation. We compare the averages of the absolute value of response deviation, positive or negative, from 100% analyte response to estimate how near our quantitative measurements would be to an external calibration curve for a given metal. Absolute values of each deviation allow for the two responses of 120% and 80% to give an average of 20% deviation, rather than 0%. This data for each metal and three sample systems is compiled in Figure 5-4a. The median deviation in response for the Bulk sample solutions was 20%, which was reduced to a median deviation of only 10% in Fraction 1. The matrix system of Fraction 2 generated a median of a 46% deviation in response across the 19 metals. An improvement in average response accuracy between Bulk and Fraction 1 was recorded for antimony, chromium, copper, iron, manganese, molybdenum, nickel, potassium, titanium, and zinc across the sampled wells. Little or no change occurred in the response for barium, beryllium, boron, cobalt, thallium, and vanadium. The greatest amount of matrix effect observed for any given metal was found in Fraction 2, except for potassium which showed the Bulk Solution having the greatest average deviation of 75%, ±23%, notably in the positive direction.

Nearly all of the first row *d*-block metals showed an improvement in accuracy when analyzed as Fraction 1, after being passed through the SPE cartridge. The average response deviation with one standard deviation is plotted in Figure 5-4b. The average deviation of titanium through zinc in the Bulk Solution was 24.7%, which was reduced more than half in Fraction 1 to only 11.2% away from the response of the standard solution. Precision between each sample for the given metals also improved in Fraction 1, bettered from 6.3% to 5.2% average of the standard deviations of titanium through zinc.

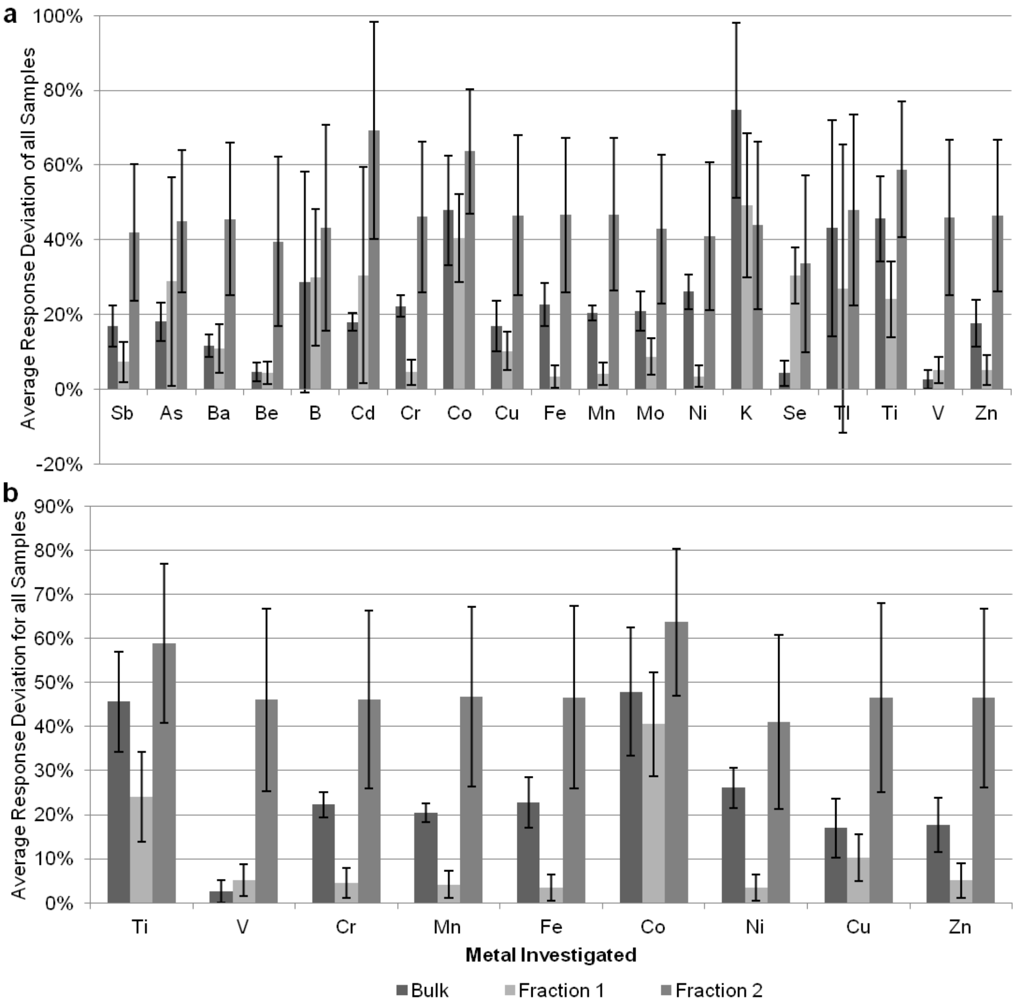

Figure 5-4: Average of the absolute response deviation from 100% for (a) each metal and (b) first row *d*-block metals

5.4.3 Water Quality Effects

The average matrix effect for each water sample was compared to water quality parameters measured at the time of sample collection. Values of the physical properties anticipated to possibly affect analytical results are listed in Table C-2. It is notable that samples of increased salinity up to 1.49 g/L have increased average matrix effects present (as shown in Figure 5-5a). This phenomenon has been reported previously[132,133]. Ionic species are the likely culprit. The ionic strength of the solution, whether from salts or acids/bases, can induce ion suppression or enhancement through different mechanisms[54]. A study of ionic matrices revealed that ion suppression in K and Cs matrices across all elements studied could be counteracted with a Na matrix due to a Coulomb fission mechanism[124]. While samples with less than 0.4 g/L (n = 12) include the highest and lowest average matrix effects per well, 32.9% and 22.2% respectively, the 5 samples with less than 25% average response deviation are among the 8 lowest salinity measurements. The range of average absolute matrix effects at the low salinity concentrations indicates additional driving forces than just solution salinity for the response deviation.

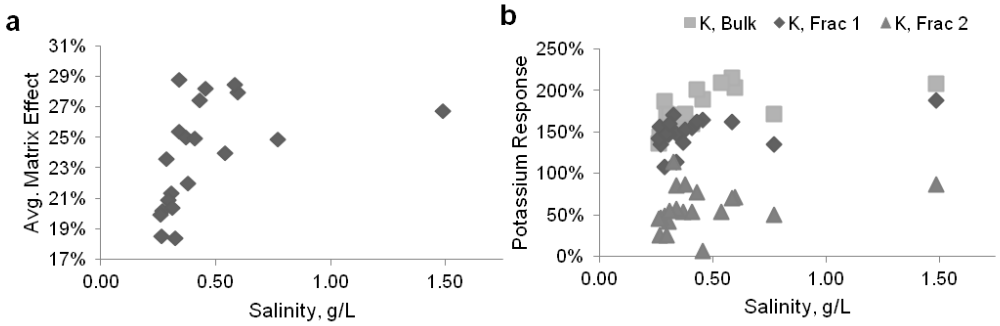

Figure 5-5: Salinity influence for the observed matrix effects for (a) all samples as a function of averaged matrix effect of all metals and (b) the response of potassium under the three preparation approaches

The responses for potassium and thallium in the bulk solution revealed similar correlations with multiple ground water quality measurements. The least degrees of matrix effects for each element were present at the lowest concentrations of TDS and salinity for the water samples. Conversely, matrix effects for the two elements decreased as the turbidity of the solution increased. High concentrations, ≥ 10 mM, of any element efficiently ionized generally results in analyte signal suppression [111]. These statements are supported with plots provides in Figure C-1.

The direct relationship observed between TDS and potassium and thallium matrix effects in the Bulk solution was the opposite for selected metals in Fraction 1. Antimony, molybdenum, nickel, selenium, thallium, and vanadium all had the lowest degree of matrix effects with the highest concentrations of TDS in the original sample. On the contrary, potassium measurements continued to behave similar to the Bulk solution with the least degree of matrix effect in samples of lowest TDS, but with a weaker Spearman correlation ($\rho = 0.306$ vs. $\rho = 0.756$).

Zinc and cadmium, two group 12 elements, had almost identical responses for each sample, with 17 of the 20 within 5% of the other in the Bulk Solution. After SPE treatment, only 4 samples had responses within 10% of the other group 12 metals. In general, the zinc measurements show a reduced matrix effect in Fraction 1 as anticipated. Fraction 1 measurements for cadmium are quite sporadic, with PW71 showing a 50% decrease in response and PW77, 78, and 97 each showing an increase of greater than 100%. These responses also show that the samples with the highest turbidity were among the lowest matrix effects observed. This was also observed for potassium, thallium, and copper. Zinc and cadmium each show positive Spearman correlations, 0.465 and 0.642 respectively, between analyte response and turbidity as the analytes approach 100% response. After SPE, the majority of samples showed decreased matrix effects for these 5 metals mentioned, but independent of the initial solution's turbidity. Suspended solids will be removed from the Fraction 1 solution after passing through the SPE column, indicating that another physical property of the solution has a greater positive effect in response accuracy than that lost by reduced turbidity.

5.4.4 Metal Summaries

The emission responses for arsenic in the Bulk solutions were reasonably uniform throughout all twenty samples, ranging from 70.6% to 89.8%. From a previous study involving a matrix of 0.1 M of either Na, K, Ca, or Mg, measurements for arsenic revealed a recovery response ranging between 72% and 93%, while the mixture of these four elements to the same 0.1 M concentration gave a synergistic decrease in signal ranging from 50% to 67%[112]. Analysis of arsenic for Fraction 1 of the given samples resulted in a net increase in response, ranging from 104.8% to 179.7%. When considering the conclusions by Pereira et al.[112], it is suspected that a combination of Na, K, Ca, and Mg may be removed by the SPE sorbent, causing less emission suppression for arsenic. At least one of these four elements resulted in reduced recoveries for each of the samples after being passed through the RP-SPE. It has been shown by others that metals can be deposited and accumulate onto C18 silica support, supporting this hypothesis[134].

Beryllium shows no matrix effects present for the Bulk and Fraction 1 samples across all twenty well water samples. Beryllium is not expected to form oxides during residence time in the plasma, a chemical interference for which other metals are more susceptible and is well known to induce signal suppression. All but five samples show noticeable matrix effects in Fraction 2.

Resulting responses for boron were quite varied across the twenty wells. Thirteen Bulk solution samples showed no matrix effects, but after SPE, only 3 of those 13 still showed no matrix effects after SPE. Fourteen samples showed an improvement in response for the Fraction 1 measurement, while 3 showed a decrease in response of the Bulk solution to Fraction 1 measurements. Of the Bulk measurements, the four reference wells had the greatest degree of matrix effect present. This effect was resolved in three of the reference samples, yielding a response between 80 and 100% in Fraction 1. All 4 of the reference samples were of the nearest samples to ideal response, while half of the remaining samples yielded an increased response near 150% of the standards.

Cadmium showed a matrix effect present in only three wells in the Bulk solution, but only to a slight degree with the greatest effect being PW9 with 78% response. Fraction 1 showed a reduction of sample matrix, except for in PW71, PW77, PW78, and PW97. The response change for each of these wells ranged from a Bulk response of at least 79% to a Fraction 1 response of less than 27%. PW77 and PW78 are in near proximity to each other, being located in neighboring small counties on the southwest portion of our sampling region.

Potassium showed positive matrix effects in all Bulk samples, with the greatest degree having over 200% response. Fraction 1 reduced the positive matrix effects, but still all except PW9 (108%) and PW74 (113%) displayed these positive effects. It is not until Fraction 2 that the source for the response enhancement is removed from all samples. The SPE-retained matrix in Fraction 2 results in response suppression in all samples except PW41, PW50, PW55, and PW102. The significant difference between the matrices of Fraction 2 and that of Bulk or Fraction 1 is that Fraction 2 contains no ionic species. These results indicate that in general, there is an ionic cause present in all the samples that gives to the enhanced sensitivity of the K measurements. Figure 5-5b reveals a relationship between the solution salinity and responses in Bulk and Fraction 1, but a loss in salinity influence in Fraction 2. Nebulized droplets of a solution with a high ionic matrix will reach the Rayleigh limit quicker than less charged droplets, inducing an explosion of smaller droplets to evaporate more easily, resulting in more usable droplets reaching the plasma than with a matrix-free solution, e.g. standard solution[54]. A spectral interference would give rise to the increased emission, but no interferences are listed near the K monitored wavelength of 766.49 nm.

Selenium revealed a consistent response across all wells in the Bulk measurements, having all responses between 80% and 110%. All wells increased response in Fraction 1, 15 of which improved to over 120% the calibration response, reported as a positive matrix effect. The reconstituted matrix of Fraction 2 reduced the response for all wells below 100% except for PW50, which was further enhanced to 155% response. Only 6 of the 20 wells in Fraction 2 showed no matrix effects.

Zinc showed moderate response inhibition across all twenty Bulk samples with an average response of 82.4% with 8 wells exhibiting matrix effects. Treatment of the sample via SPE resulted in improved responses for all wells except PW97 which showed only a 1.6% response deviation in Bulk and an 11.1% response deviation in Fraction 1.

5.5 Conclusion

This study investigated the analyte-specific tendencies of the groundwater matrix from the Barnett Shale region of North Texas. Data shows that the resulting matrix does not affect each elemental analyte to the same degree. For many metals, the matrix effect in Bulk sample solutions is considerable, while it is negligible for other metals. The use of reversed-phase solid phase extraction to remove hydrophobic organic molecules reduced the sample matrix compared to Bulk for almost all measured samples, resulting in 74% of all measured metals in all samples showing no matrix effects. These results indicate that there is an effect from the hydrophobic constituents of the water when the Bulk was measured without pretreatment beyond simple acidification. This notion can be confirmed by Fraction 2, the retained matrix, which when isolated, has quite unpredictable effects on each metal in each collected sample. Even though these samples were collected from two aquifers in North Texas, each sample was found to have varying unknown constituents through calculating a degree of matrix effect. Wells within the localized area of the same county still showed different characteristics of response impact. In general, all metals, except arsenic, sampled from the twenty samples across North Texas revealed either reduction or minimal change in matrix effect after RP-SPE treatment. Collectively, these data indicate that it is important to optimize sample preparation depending on the analyte of interest, for each and every sample to account for unknown or unanticipated matrix effects, unless a standard addition protocol can be used to ensure quantification is carried out in the exact same matrix as the sample of interest.

Chapter 6

Rapid Analysis of Eukaryotic Bioluminescence to Assess Potential Groundwater Contamination Events

6.1 Abstract

Here we present data using a bioluminescent dinoflagellate, *Pyrocystis lunula,* in a toxicological bioassay to rapidly assess potential instances of groundwater contamination associated with natural gas extraction. *P. lunula* bioluminescence can be quantified using spectrophotometry as a measurement of organismal viability, with normal bioluminescent output declining with increasing concentration(s) of aqueous toxicants. Glutaraldehyde and hydrochloric acid, components used in hydraulic fracturing and acidization, triggered significant toxicological responses in as little as four hours. Conversely, *P. lunula* was not affected by the presence of arsenic, selenium, barium, and strontium – naturally occuring heavy metal ions potentially associated with unconventional drilling activities. If exogenous compounds, such as glutaraldehyde and HCl, are thought to have been introduced into groundwater, quantification of *P. lunula* bioluminescence after exposure to water samples can serve as a cost-effective detection and risk assessment tool to rapidly assess the impact of putative contamination events attributed to unconventional drilling activity.

6.2 Introduction

Unconventional drilling techniques, such as hydraulic fracturing and shale acidization, have made the extraction of oil and natural gas from previously inaccessible deep shale formations both practical and economically advantageous[107]. Hydraulic fracturing involves a highly pressurized injection of water, sand or ceramic-based proppants, and chemical additives to expand fissures or fractures in the shale formation to release the trapped gases. Shale acidization uses large quantities of hydrochloric and/or hydrofluoric acid under low pressure to dissolve sediments and solids, increasing the permeability of the shale formation. Despite the effectiveness of these technologies, they are not without environmental risk. Concerns about environmental stewardship, in conjunction with using natural gas to achieve energy independence, have provided the impetus for a number of recent investigations to characterize the potential effects of unconventional drilling on groundwater quality[7,10,34].

Groundwater can potentially be contaminated by unconventional drilling activities through several direct and indirect mechanisms. Chemical contamination can occur as a result of flaws in the well casing such as loss of integrity between the cement and casing and/or the formation of fractures or gaps in the cement annulus[1]. Hydraulic fracturing can also introduce fracturing fluid, flowback, and produced waters into the aquifer as a result of induced changes in hydraulic conductivity and the presence of cavernous, water-filled voids in the geological formation[135]. Unconventional drilling may also be associated with elevated levels of arsenic, selenium, strontium, and other trace mineralogical elements in the groundwater[10].

While many potential pathways leading to chemical and heavy metal contamination have been proposed, it is difficult to predict the risk for an individual site given varying geological conditions and unconventional drilling practices[1]. Here, we present an assay (QwikLite™ 200 Biosensor Sytem, Assure Controls, Inc., Vista, California, USA) using the bioluminescent dinoflagellate *Pyrocystis lunula* as a tool for the rapid characterization of groundwater quality, indicating both the presence and severity of toxicity. Moreover, we quantify *P. lunula* toxicological response to exogenous chemicals and endogenous groundwater constituents that have previously been linked to unconventional oil and natural gas extraction[49].

6.3 Methods and Materials

6.3.1 QwikLite™ Procedure

QwikLite™ experiments were performed according to ASTM method E1924 and are based on previously published methods[13]. Briefly, 22.5 mL of sample was adjusted to a salinity of 30 ppth with a negligible amount of sample dilution by using crystallized Ocean Salt. Salt concentrations were confirmed by refractometry. A homogenous suspension of 4.0 mL *Pyrocystis lunula* (obtained from Assure Controls Inc., Vista, California, USA) were added to each salinity-adjusted sample, gently mixed, and 3.25 mL of the mixture pipetted to each of six replicate cuvettes in the measurement cartridge, then incubated in a light box with a 12 hour on/off light cycle. After 24 hours, the bioluminescent light output was measured using the QwikLite™ 200 Biosensor System instrument (spectrophotometer and microprocessor). All spectrophotometry data was represented as percent decline in light output of a sample to that of total bioluminescence from control samples (percent inhibition). Measurements with a value of zero to 10% correspond to no observed effect, values ranging from 20-40% require further review, and values between 50-100% suggest significant organismal stress associated with toxicity; potentially leading to cell death and/or the reallocation of cellular resources away from the enzymatic production of bioluminescence[13]. The coefficient of variation (CV) was calculated as a function of light output observed in the six replicate measurements.

6.3.2 Selected Analytes and IC_{50} Determinations

Individual solutions for arsenic, barium, glutaraldehyde, hydrochloric acid (HCl), naphthalene, selenium and strontium were prepared in 30 ppth ocean salt solutions, for toxicological assessment of each analyte. Initial dosing and serial dilution measurements were taken to determine the concentration required to elicit a 50% inhibition of bioluminescence in vitro (IC_{50}) for each individual analyte under the standard protocol of a 24-hour exposure[13] (Table 6-1).

Table 6-1: Concentrations of selected endogenous groundwater constituents and exogenous chemicals required to produce toxic effect on *Pyrocystis lunula* after a 24-hour exposure

Endogenous Compounds							
Arsenic		Barium		Selenium		Strontium	
Concentration (mg/L)	Percent Inhibition	Concentration (mg/L)	Percent Inhibition	Concentration (mg/L)	Percent Inhibition	Concentration (mg/L)	Percent Inhibition
Control	0	Control	0	Control	0	Control	0
5	98	40	13	25	0	4000	62
10	99	60	39	50	0	10000	59
30	98	80	72	100	0	20000	0
50	99	125	100	250	43	25000	0
100	98	250	100	500	74	-	-

Exogenous Compounds			
Glutaraldehyde		Hydrochloric Acid	
Concentration (mg/L)	Percent Inhibition	Concentration (mg/L)	Percent Inhibition
Control	0	Control	0
0.75	0	25	0
1.5	0	50	0
3	0	100	0
5	47	200	55
7.5	98	300	99

Prepared solutions with concentrations above and below the previously determined IC_{50} values were used for each individual analyte, in conjunction with 4, 6, 8, 12, 24, 48, 72 and 96 hour exposures. Time-lapse IC_{50} values were interpolated graphically to determine the concentration responsible for a 50% reduction in light production during each of the 8 different exposure periods.

6.3.3 Sample Source

To test the efficacy of the assay for groundwater contamination evaluations, a total of 100 water samples were collected from private drinking water wells that draw from the Trinity, Woodbine and Nacatoch aquifers in and around the Barnett Shale in North Texas as described previously[10]. Briefly, samples were collected from private water wells drawing from underlying aquifers in areas of active natural gas extraction in the Barnett Shale formation (one or more gas wells located within a 5 km radius of the private well; $n = 91$), non-active natural gas extraction areas within the Barnett Shale formation (no gas wells located within a 14 km radius of the private well; $n = 4$), and reference sites without natural gas extraction lying outside of the Barnett Shale formation (no gas wells located within a 60 km radius of the private well; $n = 5$). To account for variability in purging flow rates between private wells, samples were collected after purging private wells for a minimum of 20 minutes to ensure that measured water quality parameters had stabilized (determined by a multi-parameter YSI Sonde), indicating that fresh well water was being sampled. All private water well samples were collected from as close to the well head as possible, bypassing any treatment or filtration systems. For each private well, we obtained four duplicate 40 mL water samples in glass vials with no headspace and kept them at 4°C during transport to The University of Texas at Arlington.

6.3.4 Elemental Analysis

Elemental analysis of arsenic, barium, selenium and strontium was performed as described previously[10]. Briefly, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was performed on a Varian 820 coupled with a SPS 3 Varian autosampler, using Argon as the plasma source. MS data was acquired in scan mode with 5 replicates and 30 scans per replicate.

6.4 Results and Discussion

6.4.1 Time-lapse Monitoring of Response at IC_{50} Concentration

Time-lapse analyses of *Pyrocystis lunula* bioluminescence were performed in the presence of exogenous chemical compounds that have been identified as contaminants of concern in a congressional report on hydraulic fracturing fluid components[49]. Measurements were taken at multiple time points to identify the shortest incubation duration required to elicit a reliable toxicological response. Bioluminescence in *P. lunula* is enzymatically produced as a burst of blue-green light (490nm wavelength). In a nearly linear fashion, bioluminescent light production is reduced relative to the toxicity of the tested sample – the greater the level of contamination, less light is emitted, indicating that the *P. lunula* cultures are either severely stressed or have died from toxic exposure[13]. Glutaraldehyde and hydrochloric acid (HCl) were selected for analysis as they both embody important aspects of some unconventional drilling procedures[1]. Glutaraldehyde and HCl are used in hydraulic fracturing fluids in certain regions as an antimicrobial agent to inhibit bacterial growth throughout the well casing, and as an acidizing agent to initiate fissures in the shale rock during shale acidization, respectively[1]. Other components of hydraulic fracturing fluids include, but are not limited to, friction reducers, iron-controlling compounds, gelling agents, crosslinkers, breaking agents, oxygen scavengers, pH buffering agents, fissure expanding sands or proppants, scale inhibitors, and surfactants[1]. However, these compounds were not tested due to their limited availability or poor solubility.

In particular, naphthalene, a compound found in diesel fuel used to help solubilize surfactants used in hydraulic fracturing, has a maximum solubility in water of 30.0 mg/L, and when tested at 22.5 mg/L per the standard protocol, showed no evidence of organismal stress (0% inhibition). As a result, the effect of this exogenous compound on *Pyrocystis lunula* bioluminescence could not be determined by increasing the concentration of naphthalene.

Glutaraldehyde elicited a 50% reduction in *Pyrocystis lunula* bioluminescence at a concentration of 5.14 mg/L after a 24-hour exposure with consistent sensitivity throughout the 4, 6, 8, 12, 24, 48, 72 and 96 hour solution exposures (Table 6-2, Figure 6-1A).

Table 6-2: Concentrations of endogenous groundwater constituents and exogenous chemical compounds required to produce a 50% reduction in *Pyrocystis lunula* bioluminescence light output during eight different exposure periods

Endogenous Compounds							
Arsenic		Barium		Selenium		Strontium	
Exposure (hours)	IC_{50} Conc.* (mg/L)	Exposure (hours)	IC_{50} Conc* (mg/L)	Exposure (hours)	IC_{50} Conc* (mg/L)	Exposure (hours)	IC_{50} Conc* (mg/L)
4	2.55	4	40	4	200	4	5400
6	2.53	6	65	6	451	6	7650
8	2.52	8	68	8	493	8	10010
12	2.65	12	88	12	314	12	3600
24	2.55	24	68	24	307	24	3200
48	2.50	48	68	48	400	48	4000
72	2.55	72	62	72	378	72	4490
96	2.55	96	70	96	359	96	5100

Table 6-2 *(Continued)*

Exogenous Compounds			
Glutaraldehyde		Hydrochloric Acid	
Exposure (hours)	IC_{50} Conc* (mg/L)	Exposure (hours)	IC_{50} Conc* (mg/L)
4	4.60	4	136
6	5.96	6	178
8	4.36	8	182
12	4.24	12	199
24	5.14	24	194
48	4.10	48	235
72	4.28	72	276
96	4.46	96	274

*IC_{50} values were interpolated graphically from measurements collected with varying concentrations during each exposure period

These data are similar to the responses rendered by the herbicide diuron and the biocide tributyltin, with respective EC_{50} concentrations of 19.0 and 0.226 mg/L[136]. *P. lunula* was found to be most sensitive to HCl during the shortest exposure (Figure 6-1B, 4 hours) in which 136 mg/L HCl elicited a 50% reduction in bioluminescence.

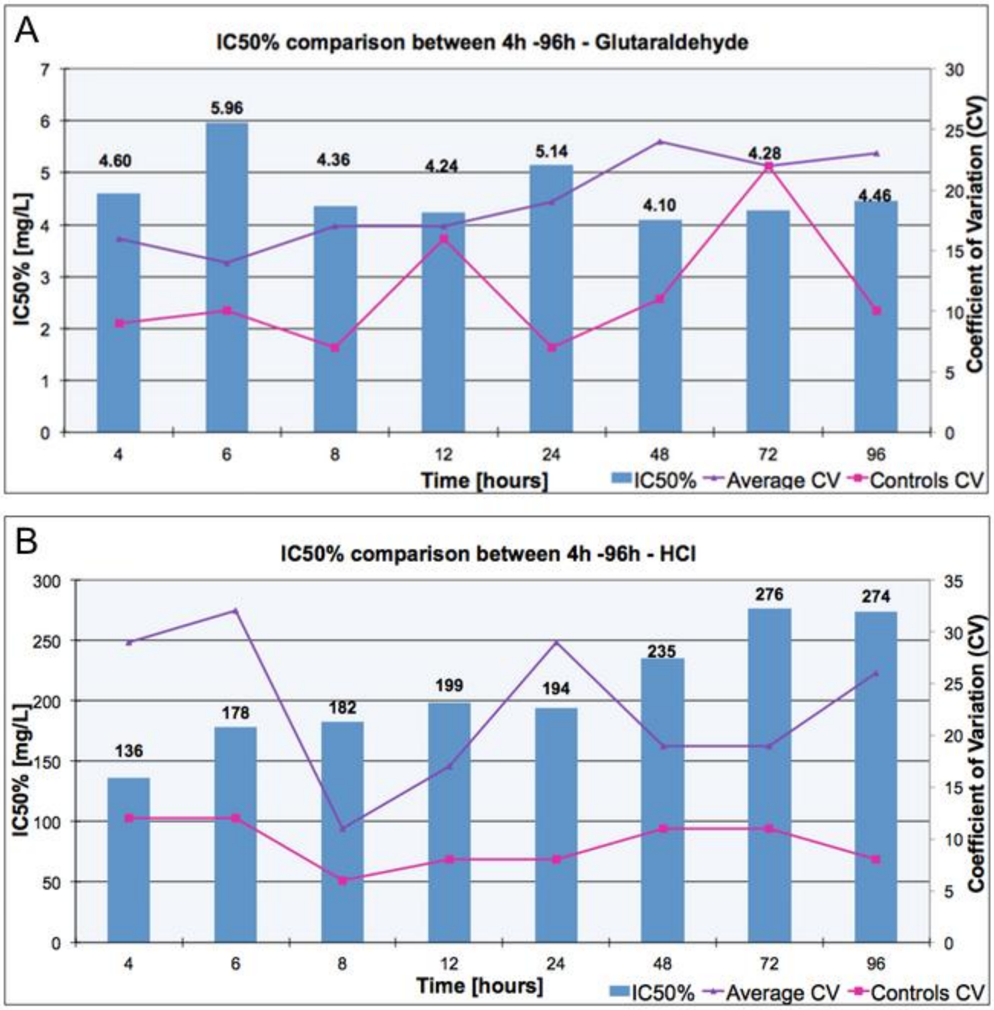

Figure 6-1: Pyrocystis lunula decrease in bioluminescence in response to exogenous chemicals A) glutaraldehyde and B) hydrochloric acid used in unconventional drilling

These data corroborate previous observations that external acids stress the cell to the point where *in vitro* bioluminescence is greatly inhibited[137]. Notable hormesis was observed throughout the 96-hour time course as *P. lunula* exhibited decreased sensitivity to HCl with increased exposure time (136 mg/L vs. 274 mg/L, during 4 and 96 hour exposures, respectively).

Collectively, the observed sensitivities of *Pyrocystis lunula* to glutaraldehyde and HCl make them useful indicators for risk assessment in alleged contamination events involving unconventional drilling activities that use glutaraldehyde and HCl. Hydraulic fracturing fluid has been documented to contain up to 0.01% glutaraldehyde by mass and 0.13% HCl by mass, corresponding to approximate concentrations of 100 and 1300 mg/L, respectively (www.fracfocus.org). If glutaraldehyde and HCl are present at these concentrations in unconventional drilling fluids, samples collected during a putative contamination event (e.g., a leak through a faulty casing or the mishandling of waste/produced water), would likely trigger a toxicological response in *P. lunula*, even during a short exposure period.

6.4.2 Application to the Barnett Shale Formation

Pyrocystis lunula bioluminescence was also characterized in samples of private well water previously described as having elevated levels of arsenic, barium, selenium and strontium[10]. Historically, these heavy metal ions are generally found at very low concentrations in many private water wells in Texas[69,82,87]; however, elevated levels of these ions may be indirectly associated with unconventional drilling in the Barnett shale of North Texas[10].*Pyrocystis lunula* inhibition values ranged from 0 to 70% inhibition of bioluminescence with a mean value of 24% within the 100 private water wells that were collected (Figure 6-2A).

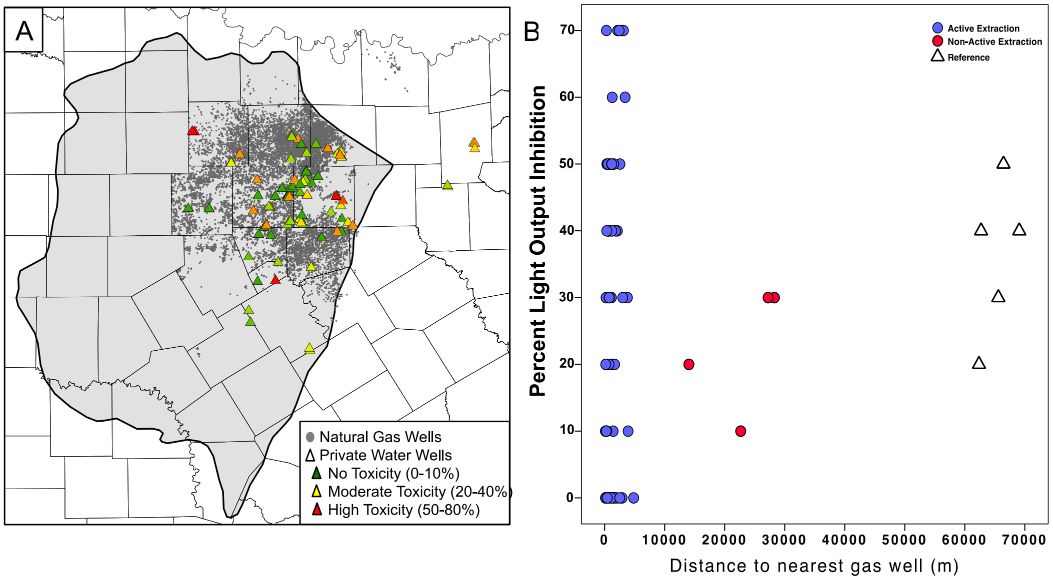

Figure 6-2: Groundwater quality from private wells in and around the Barnett Shale formation according to *Pyrocystis lunula* toxicological response and the relationship between registered toxicity and distance to the nearest gas well

A) Map of private water well sampling sites and their respective toxicity values in relation to unconventional drilling sites in the Barnett Shale Formation in north Texas, USA. B) Scatterplot of the relationship between private water well toxicity and distance to the nearest natural gas well

Percent inhibition values of samples collected within the active extraction regions (mean=24%, n=91), non-active extraction regions (mean=23%, n=4) and reference sites outside of the Barnett Shale (mean=36%, n=5) were similar, in that none of the three groups had mean values that exceeded the 50% inhibition threshold indicative of significant organismal stress. There was no significant correlation between percent inhibition values and the distance of the private water well to the nearest natural gas extraction site (Figure 6-2B, r=0.133), and there were no correlations between percent inhibition and the concentrations of arsenic, barium, selenium and strontium, as detected by ICP-MS (Figure 6-3).

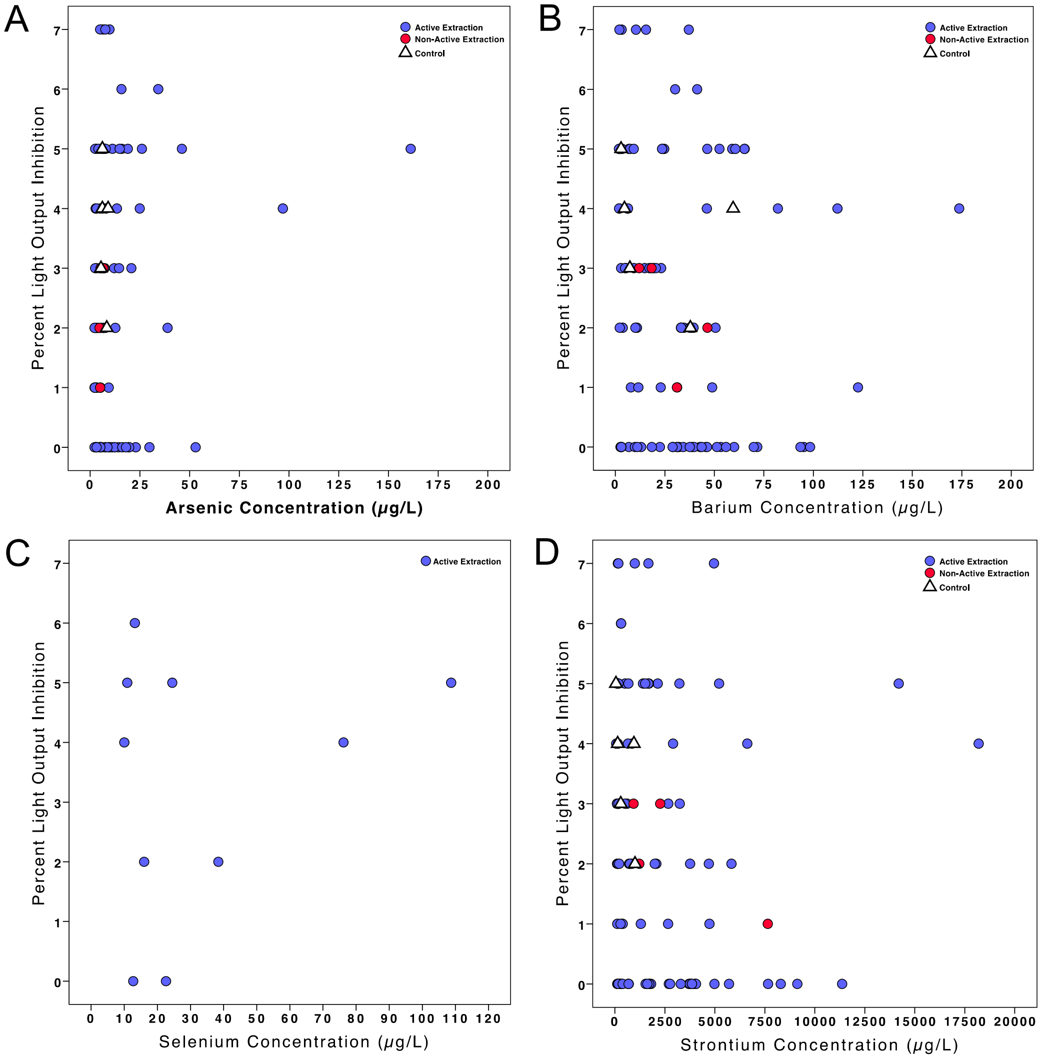

Figure 6-3: Scatterplots of the relationship between the percentage decrease in light output (compared to controls) and sample concentrations of (A) arsenic, (B) barium, (C) selenium, and (D) strontium

These data suggest that *P. lunula* either has a high tolerance for heavy metal ions in the concentrations present in the well water samples or there are varying degrees of *in situ* matrix effects in the groundwater samples mitigating the toxic effects of heavy metals on *P. lunula*. It is important to note than none of the private well samples contained detectable amounts of glutaraldehyde or had extremely low pH values that would indicate acid contamination[10].

To explore these results further, *Pyrocystis lunula* response was also quantified in prepared solutions of arsenic, barium, selenium and strontium of varying concentrations. Measurements were taken during 4, 6, 8, 12, 24, 48, 72 and 96 hour solution exposures to assess *P. lunula* toxicological response over an elongated time course. Initial IC_{50} determinations for arsenic, barium, selenium and strontium revealed concentrations well above their respective Drinking Water Maximum Contaminant Limit (MCL) and recommended levels (in the case of strontium) suggested by the US EPA of 10, 2000, 50 and 4000 μg/L, respectively. Elevated tolerances were observed for each of the heavy metals throughout the 4 to 96 hour exposure spectrum with no evidence of decreased sensitivity or hormesis during the longer time periods (Table 6-2). Toxicity response in *P. lunula* has not been previously characterized in the presence of heavy metal ions; however, the IC_{50} values reported here are orders of magnitude greater than EC_{50} value of 0.128 mg/L reported for copper[136]. Collectively, the heavy metals data presented here suggest that *P. lunula* has a tolerance for elevated levels of arsenic, barium, selenium, and strontium, and that these characteristics of the dinoflagellate may have contributed to the limited toxicological response observed from the private water well samples.

Together, these data were used to assess the toxicity of groundwater in private water wells located in the Barnett Shale region. This risk assessment technique takes advantage of the life history characteristics of a bioluminescent dinoflagellate to function as a bioindicator. Glutaraldehyde and HCl were found to elicit rapid toxicological responses (4 hours exposure) at concentrations well below those found in many drilling fluid recipes. *Pyrocystis lunula* response to glutaraldehyde was also found to be more sensitive and more rapid than equivalent observations previously recorded with *Daphnia magna* (EC_{50} value of 18.0 mg/L after a 48 hour exposure) and *Pimelphales promelas* (LC_{50} value of 22 mg/L after a 96 hour exposure; http://www.pesticideinfo.org/). Conversely, *P. lunula* showed little toxicological response to high levels of heavy metals such as arsenic, selenium and strontium that could be indirectly linked with unconventional drilling[10]. While *P. lunula* exhibits tolerance for heavy metals, the observed responses to these ions are more sensitive than that of other bioassays. For arsenic, *Procambarus clarkia*, *Aplexa hyprorum* and *Morone saxatilis* each exhibit LC_{50} values orders of magnitude greater than that of *P. lunula* (1019, 24.5 and 30.0 mg/L, respectively; http://www.pesticideinfo.org/). Common assays using *P. promelas*, *D. magna,* and *Vibrio fisheri* exhibit similar sensitivities to arsenic when compared to *P. lunula* (EC_{50} values of 2.81, 4.30 and 1.52 mg/L, respectively), but require at least 96 hours of exposure to quantify a response (http://www.pesticideinfo.org/).

6.5 Conclusion

These data show that the QwikLite™ algal bioluminescence test is rapid, cost efficient, and sensitive to some of the acidic compounds commonly associated with natural gas extraction. However, there are some potential issues to consider when using this approach to assess potential groundwater contamination. Using *Pyrocystis lunula* to assess freshwater samples requires the addition of salt to the samples to simulate the saltwater environment of the organism. For the purposes of this study, we followed the prescribed protocol for this assay in order to evaluate its efficacy as a rapid risk assessment tool, but it is possible that increasing the salinity of the groundwater samples could influence the speciation of potential contaminants as well as their toxicity, so future studies should focus on how changes in salinity may influence these factors. We were also unable to obtain whole fracking fluid samples from industrial sources so our study was limited to examining selected potential contaminants. It is possible that matrix interactions in whole fracking fluid could also influence toxicity in contaminated groundwater. Additionally, fracking fluid contamination events would likely result in at least some of the contaminants being present in low concentrations due to aquifer dilution, thus limiting the utility of the assay. However, in some regions natural gas extraction often requires shale acidization which utilizes much higher concentrations of acids and this assay could prove very useful in detecting potential contamination events in regions where shale acidization is widely used[1]. For these reasons, QwikLite™ may best be utilized as a rapid response, risk assessment tool in conjunction with a larger suite of toxicity tests if initial results indicate potential contamination.

The recent expansion of hydrocarbon extraction across the continental United States has provided incentive to explore the relationship between groundwater quality and unconventional drilling. The results presented here provide an initial characterization of *Pyrocystis lunula* as a cost-effective preliminary screening and risk assessment tool that can be used to rapidly detect instances of groundwater contamination by some common exogenous compounds used in unconventional drilling. Furthermore, this assay provides a response in as little as 4 hours which makes it desirable for rapidly assessing putative groundwater contamination events that could have political, legal and human health consequences. Combined with onsite pH measurements, *P. lunula* toxicological assays can be used to assess the immediate effects of shale acidization, while subsequent gas/liquid chromatography and mass spectrometry can be used to detect and quantify exogenous compounds used in hydraulic fracturing. Forthcoming studies with these technologies will further evaluate the anthropogenic effects of unconventional drilling and may aid the development of best management practices for the oil and gas industry.

6.6 Ethical Standards

All experiments in this study were conducted in accordance with the laws of the United States of America.

Chapter 7

Future Prospects and Advances for Gas Chromatography Methodologies

7.1 Introduction

The approaches in analyte selection and method development were established in the early research surge of environmental effects of unconventional drilling techniques. The lack of information available of constituents present in HF fluids, produced waters, and recovered drilling muds slowed early work for analytical approaches specific to unconventional drilling techniques. Current regulatory methods[138] have been retrofitted to be applicable to these unique systems, but are having difficulties. This past year has shown rapid development of application notes[139,140] through instrument vendors demonstrating techniques for characterizing primarily produced waters for metals or ions. These applications have been valuable in demonstrating an instruments ability to handle the extreme systems with high salts, TDS, and metal content, but add little new advice about studying groundwater.

To date, there are not universal methods or accepted indicators for identifying groundwater contamination from unconventional drilling techniques[5]. Colorado and Illinois recently enacted state legislation for baseline monitoring of groundwater, to include, but not limited to pH, specific conductance, TDS, dissolved gases (methane, ethane, and propane), and BTEX. Colorado would also require total petroleum hydrocarbon (TPH) measurements. California also instated an oil and gas-related law requiring groundwater monitoring, SB4. No water monitoring criteria is stated in the law, but it requires the Water Quality Control Board of the state to have stipulations in place by July 1, 2015. Act 13 in Pennsylvania requires that if the PA Department of Environmental Protection deems a water well to be contaminated within 12 months of drilling, the gas well operator is required to provide an alternate source of water for the affected well owner. The well operators can rebut the accusations by collecting baseline water samples, but this act is voluntary and the law does not specify required analytical parameters.

The major reports published by academic institutions initiating targeted analytes or techniques are quite limited. Coupled to the limited information is the fact that the teams are still investigating possible contamination events based up their own expertise. In general, Duke University measures dissolved gas[6-8,34] concentrations through a contract laboratory and isotopic analysis[6-9,34] of the gas, water, and NORMs within the University. Our research team at The University of Texas at Arlington, while surveying groundwater from many angles, has analytical expertise is in gas chromatography and mass spectrometry[10]. Very few other investigators are using GC, and if they are, established methods for BTEX or other general regulatory methods are employed. No others have taken the time to step away from retrofitting general drinking water methods and develop GC methods specific to hydraulic fracturing or other unconventional drilling processes.

7.2 Proposed Progression of the Current Analytical Methods for the Texas Well Study

7.2.1 GC-MS for Known and Unknown Compounds

To investigate organic constituents in groundwater, GC analysis is almost mandatory. Many of the compounds identified as fracturing fluid ingredients and listed in the EPA SWDA are volatile or semivolatile. Some other ingredients can be derivatized to be semivolatile or improve separation capabilities by GC. A MS detector for compounds with a molecular weight greater than 40 Da and sufficient ions also greater than 40 *m/z* is an appropriate choice for quantification and qualitative identification. Below 40 *m/z*, signals from inherent atmospheric gases, e.g., N_2, O_2, and Ar, increase the chromatographic noise and convolute the resulting spectra for identification. The current

GCMS approach with the Rxi-5ms column, electron ionization-MS, and ethyl acetate solvent extraction was an attempt to analyze a wide variety of compounds with minimal preparation and analysis time. The select analytes that have been quantified with this method, including dichloromethane and BTEX, have a detection limit near 1 mg/L, higher than many established regulatory limits and method capabilities. It has been advised[141] that the compounds need to be prioritized based on their occurrence, environmental/health risk, and chromatographic capability. We should then develop the most sensitive method for the top ten compounds. If remaining compounds on the list can be added into the method, then so be it. This prioritization will most likely result in multiple methods either with different extraction approaches, GC columns, or even detector ionization techniques. Table 7-1 lists a few parameter options, their applications, and advantages/disadvantages for our research. Expanding the one method to multiple methods would increase preparation and analysis which would only become productive with additional researchers to maintain the current and expanding workload.

Table 7-1: Suggested GC method parameters to be considered for future development

Method Option	**Application**	**Advantages (A) / Disadvantages (D)**
Extraction		
Headspace sampling	Volatile and semivolatile compounds	A: Reduces detection background; reduces sample prep steps; Less GC maintenance D: Many parameters to optimize (heating temperature, time, sample volume, vial volume); increased time per sample if manual; Automation is expensive
Multi-step liquid-liquid extraction	Class specific based upon chosen solvent	A: Increased analyte extraction D: Increased solvent consumption; drying time to reduce solvent
Solid phase extraction – cartridges (C), disks (D), or pipette tips (T)	Class specific based upon chosen phase	A: Preconcentration of analytes (C,D,T) D: Increased time (C,D); increased solvent consumption (C); added expense per sample (C,D,T)
Multi-phase SPE cartridges	Potentially 3 classes of compounds able to be extracted	A: Preconcentration of analytes, less time than 3 separate SPE D: Increased time; increased solvent consumption; added expense per sample
Solid phase micro-extraction	Class specific based upon chosen phase	A: Preconcentration; reduces background; sample unaltered to extract complementary compounds D: Increased time per sample; automation is expensive
Headspace – solid phase micro-extraction	Class specific for volatiles and semivolatiles based upon chosen phase	A: All advantage for both HS and SPME; more selective than either technique alone D: All disadvantaged for both

Table 7-1 *(Continued)*

		HS and SPME
GC Column		
5% diphenyl, 95% PDMS	Non-polar, general purpose	A: Common column; retention indices characterized; high temperature limit D: Poor retention, selectivity for light alcohols, acids; poor peak shape for alcohols, acids, amines
50% diphenyl, 50% PDMS 14% cyanopropyl, 86% PDMS	Mid-polarity column, mostly for inorganic functional groups	A: Added selectivity and retention for alcohols, acids, amines; high temperature limit; quicker elution of large hydrocarbons D: Database retention indices cannot be used
PEG or Ionic Liquid	High-polarity column	A: Exceptional retention of small, polar compounds; complementary selectivity for confirmation analyses D: Lower temperature limits; database retention indices cannot be used
Detector		
Electron Ionization (EI)	Any volatile or semivolatile	A: Extensive database library of spectra; universal ionization D: Similar spectra between some compounds; molecular ion may not be distinguishable
Chemical Ionization (CI)	Nearly all volatile and semivolatile comounds	A: Prominent molecular ion D: Few standard databases; less structural information
Negative Chemical Ionization (NCI)	Acidic or electronegative compounds	A: Selective ionization source; very little detector noise D: Lose detection of other compounds
Quadrupole MS	Database searching of unknowns	A: Most common; fast D: Only scan or selected ion monitoring for detection
Triple Quadrupole MS	Tandem MS (MS/MS) for quantification	A: Specific transitions for compounds; scan or MS/MS;

Table 7-1 *(Continued)*

		greater sensitivity with MS/MS D: MS/MS transitions must be developed for each compound; collision gas may skew scan spectra for unknown ID
Ion Trap MS	MS^n of compounds	A: Multiple stages of fragmentation to ID unknowns; scan or MS^n D: Small dynamic range; slower than quadrupole MS
Time of Flight MS	High mass resolution, high mass accuracy measurements	A: Fastest MS, mass accuracy for unknown ID; scan or selected ion monitoring; no MS detector skewing D: Cost; large data files

The selection process for a condensed list of possible targets should also be revisited. The Congressional report generated in 2011 presents a large list of approximately 750 ingredients used in products sold at any time through 2005-2009 for hydraulic fracturing. There is a count of how many products a given chemical can be found in, but there is no information about the final concentrations of these compounds after recommended dilution or mixing. Also, different shale formations require different strategies for unconventional drilling, such as water volume and types of chemical additives for hydraulic fracturing. Additive recipes also vary by operator, and multiple operators will be working within a shale play. One could see the difficulties in developing regulatory methods governed at the national level with such variability of possible target compounds.

It is proposed that the best way to generate a “suspected target” list would be to obtain actual hydraulic fracturing fluid mixtures and flowback water and then analyze via GC-MS or other technique of choice. Ideally, the provided fluid could also be tied to which shale formations in which it is being used. After identifying compounds within a set of fluid variations for a given formation, a more robust hypothesized list of compounds that could possibly contaminate the surrounding environment could be generated. Accessibility to these fluids is quite difficult because their mixtures are deemed proprietary by the operators and final blends are only available through them.

7.2.2 Headspace – GC Analysis

The current method for alcohol and light solvent detection in water by static headspace analysis[142] works well. The resolving power of the ZB-BAC2 column is sufficient for our suspected analytes of methanol and ethanol, yet still allows for quick analysis. One limitation of the method is using a flame ionization detector (FID). The limitation does not come from a lack of sensitivity compared to MS. In actuality, we feel the FID has a detection advantage over MS for methanol and ethanol since it does not detect atmospheric compounds. The shortcoming of FID in general is that no spectral information is provided to confirm the identity of the eluted compound, only a retention time. Because of the lack of confirmation, many EPA methods using FID or other non-specific detectors require confirmation either by MS or by the retention time on a column with complementary selectivity[143]. The confirmatory analysis can be performed by a separate injection on a different column or detector or through a single injection that is split to two columns, each with a detector.

I propose expanding the current method to a single injector/dual detector configuration where a single injection is split to two chromatographic columns, each with a detector. The dual detector configuration is currently 2 FID detectors because of achieved sensitivity and public availability and familiarity, general considerations for standard methods. Our method would not be restricted by all of these considerations since the measurements would not need to be certified or defensible in court. Unrelated collaborations within our laboratory have been application development for a universal vacuum ultraviolet detector, the VGA-100 (VUV Analytics Inc., Austin, TX) for GC[144,145]. Work has shown sufficient sensitivity and spectral specificity between the light alcohols.

The ZB-BAC2 column is the second column of a two column pair[61]. Its counterpart, the ZB-BAC1 column, would be an appropriate selection for a confirmatory column set. This column set with the suggested single injector/dual detector arrangement is the typical hardware arrangement for measuring blood alcohol content by law enforcement. Between the columns, the retention time and elution order is different due to different stationary phases. This allows for analyte confirmation without added analysis time. This would increase the confidence of our current measurements without increasing analysis time after method development has been performed.

7.3 Conclusion

Implementing any one of the aforementioned techniques has the potential to increase detection sensitivity or the confidence of compound identification. Selecting appropriate proposed parameters can only be made possible after selecting a class of target analytes. The most effective lists of target analytes will only come through industrial collaboration or public access to chemicals and final concentrations expected for a given shale formation. Regretfully so, these relationships or accessible information are not present.

Appendix A

Supporting information for Chapter 3:

An Evaluation of Water Quality in Private Drinking Water Wells near Natural Gas Extraction Sites in the Barnett Shale Formation

A.1 Methods

A.1.1 Aquifer Description

The most heavily sampled aquifers in this study are the Trinity and Woodbine aquifers. These Cretaceous formations collectively extend from southwest Arkansas to central Texas with a combined total area over 48,000 km^2 [86]. A model of groundwater dynamics[84] in the Trinity and Woodbine aquifers describes a large underground aquifer system with the smaller Woodbine aquifer overlying the larger Trinity aquifer which itself is composed of subunits (the Trinity group includes the Antlers, Glen Rose, Twin Mountains, Travis Peak, Hensell, Hosston, and Paluxy aquifers). These aquifers are characterized by permeable, water-bearing sandstone, shale, clay, and/or limestone, with the Trinity and Woodbine aquifers separated by less permeable clay and carbonate layers[84]. The respective western portions of both the Trinity and Woodbine aquifers are closer to the surface and act as unconfined outcrop zones where the aquifers can receive infiltrated precipitation. Outcrop zones also receive water from and discharge water to surface features such as streams and the twenty large reservoirs in the study area[84]. The respective eastern portions of the Trinity and Woodbine aquifers reach lower depths and act as confined artesian units with a limited amount of hydraulic connectivity to one another owing to the less permeable clay layers that form their boundaries. Upward flow between aquifer subunits as well as horizontal flow from the outcrop zones to the artesian zones was traditionally very low in the eastern portions of these aquifers because of the less permeable layers separating features[84]. Historical groundwater pumping in the area led to a decrease in artesian pressure as drinking water wells pumped large amounts of water out of the aquifer[84,146]. Water table levels have dropped as much as 550 feet in some portions of the Trinity aquifer, but the water table has risen slightly in recent years as groundwater usage has massively decreased and surface reservoirs have increasingly been used as drinking water sources for the rapidly expanding population[84,146] (See Supporting Information Table 3). Groundwater withdrawals in these aquifers for irrigation and livestock use have reduced artesian pressure, especially in confined portions of the Woodbine aquifer. This has increased the rate of horizontal flow from outcrop to artesian zones, but the clay layers surrounding the units have kept the upward interformational flows between the Trinity and Woodbine at a minimum similar to predevelopment levels[84].

Four samples were obtained from the Mineral Wells and Palo Pinto Limestone formations, Paleozoic formations of limestone, sandstone, and shale overlying the Barnett Shale formation in Palo Pinto County that contain small amounts of groundwater. Additionally, reference samples were obtained from the Nacatoch aquifer, a Cretaceous aquifer composed of sand beds separated by layers of impermeable clay that does not overly the Barnett Shale formation and is primarily used for rural drinking water and livestock irrigation[146].

A.1.2 Gas Chromatography – Mass Spectrometry (GC-MS)

Specific semi-volatile compounds to be analyzed using GC-MS were selected based upon suspected health or environmental effects and their inclusion in hydraulic fracturing fluid component lists freely available on the website fracfocus.org. The diversity of these compounds encompasses alcohols, aromatics, aldehydes, and others, all separated on a SHRXi-5ms column (30 m x 0.25 mm; 0.25 µm df). Oven programming and detection were performed using a GCMS-QP2010 SE (Shimadzu Scientific Instruments, Inc.; Columbia, MD). The GC inlet, interface, and MS temperatures were set to 300 ºC, 260 ºC, and 260 ºC, respectively. Selected compounds were detected by selected ion monitoring of the base peak of each analyte, as shown in Supporting Table 1.

A.1.3 Headspace Gas Chromatography (HS-GC)

Methanol and ethanol detection was performed using static headspace – GC with a flame ionization detector. Headspace operations were controlled with the AOC-5000 Plus headspace autosampler. 1 ml of sample was mixed with 1 ml of 0.5 M NaCl (aq) in a 20 ml screw-top headspace vial. Automated incubation at 90 °C for 15 minutes and agitation were performed before 2.5 ml of headspace was sampled. Separation and detection was achieved using a Shimadzu GC-2010 Plus equipped with a Phenomenex ZB-BAC2 column (30 m x 0.32 mm; 1.2 μm df) held isothermally at 40° C. Inlet and detector temperatures were set to 200° C.

A.1.4 Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

Elemental analysis of heavy metals was achieved using a Varian 820 ICP-MS coupled with SPS 3 Varian autosampler and Argon as the plasma source. MS data acquisition was performed in scan mode with 5 replicates, 30 scans per replicate.

A.1.5 Geospatial and statistical analyses

Geospatial analyses were conducted using the software package ArcGIS 10.1 (ESRI 2011. ArcGISDesktop: Release 10. Redlands, CA: Environmental Systems Research Institute). The distance in kilometers from each sample to the nearest natural gas well as well as the number of gas wells in a one kilometer radius around each sample were calculated to assess whether or not there is a relationship between proximity to natural gas extraction activities and private well water quality. Relationships among the data were assessed using Spearman's rank correlation and Mann Whitney U pairwise analysis.

A.1.6 Historical data: Data source and statistical methods

Historical arsenic, selenium, strontium, barium, and total dissolved solids (TDS) concentrations in private well water samples from 1989 – 1999 were obtained from the Texas Water Development Board's online database of private well water quality for each of the counties sampled in the present study (http://www.twdb.state.tx.us/groundwater/data/gwdbrpt.asp#F). These data served as a baseline measure of contaminant concentrations in Barnett Shale private water wells before widespread natural gas extraction activities had occurred. Historical data for these analytes were compared with the levels observed in this study using Mann-Whitney U pairwise analysis.

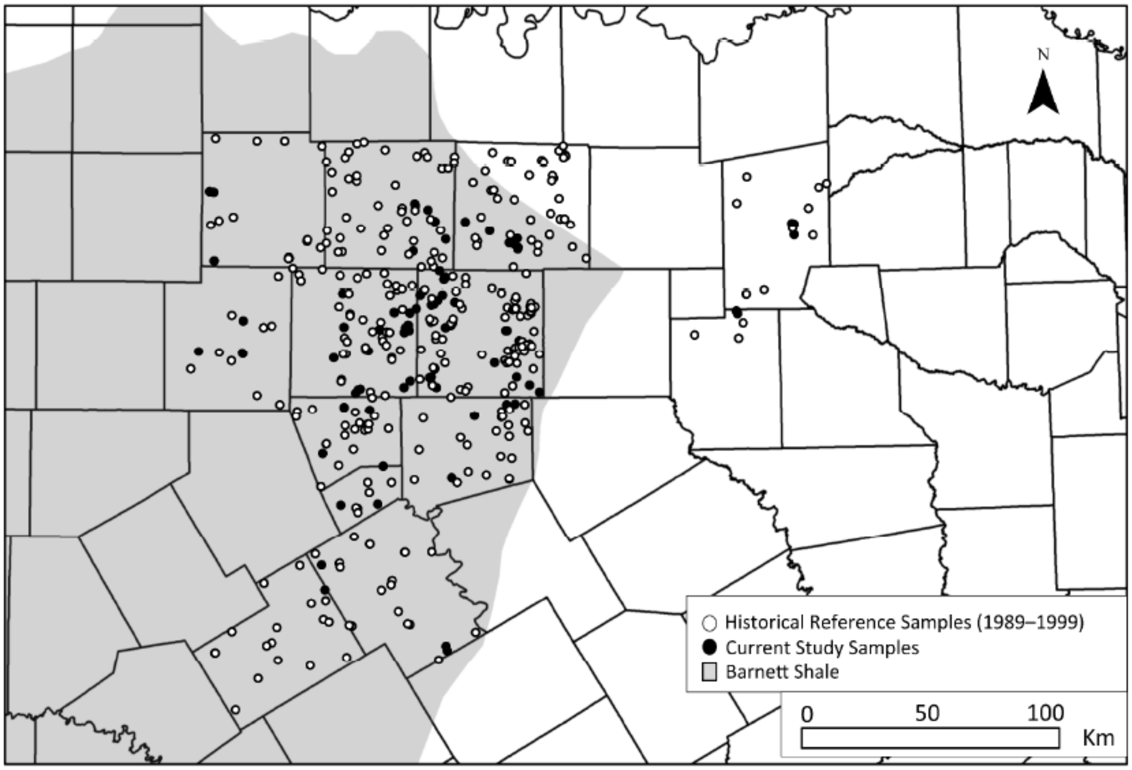

Figure A-1: Location of private water wells sampled in the current study (*n* = 100) and historical reference private water wells (TWDB 1989-1999) from the same counties (*n* = 330)

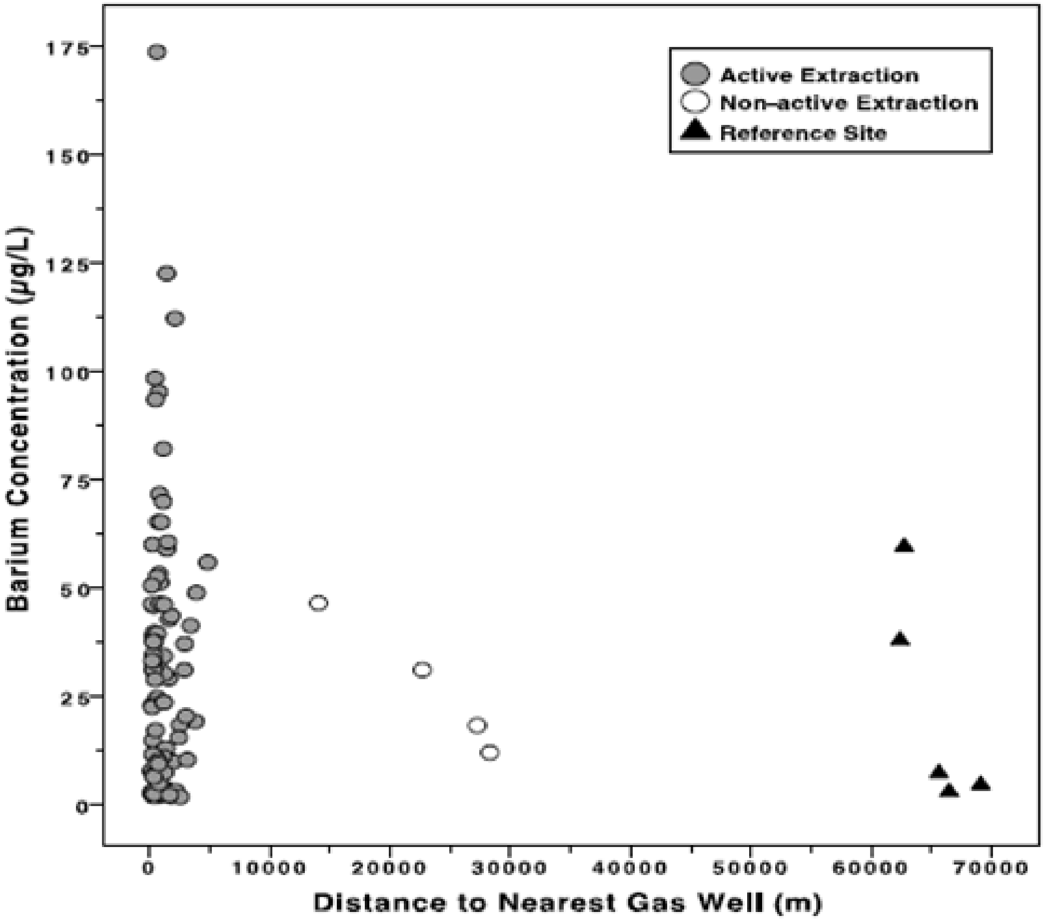

Figure A-2: Barium concentration versus distance to the nearest natural gas well in Barnett Shale private water well samples

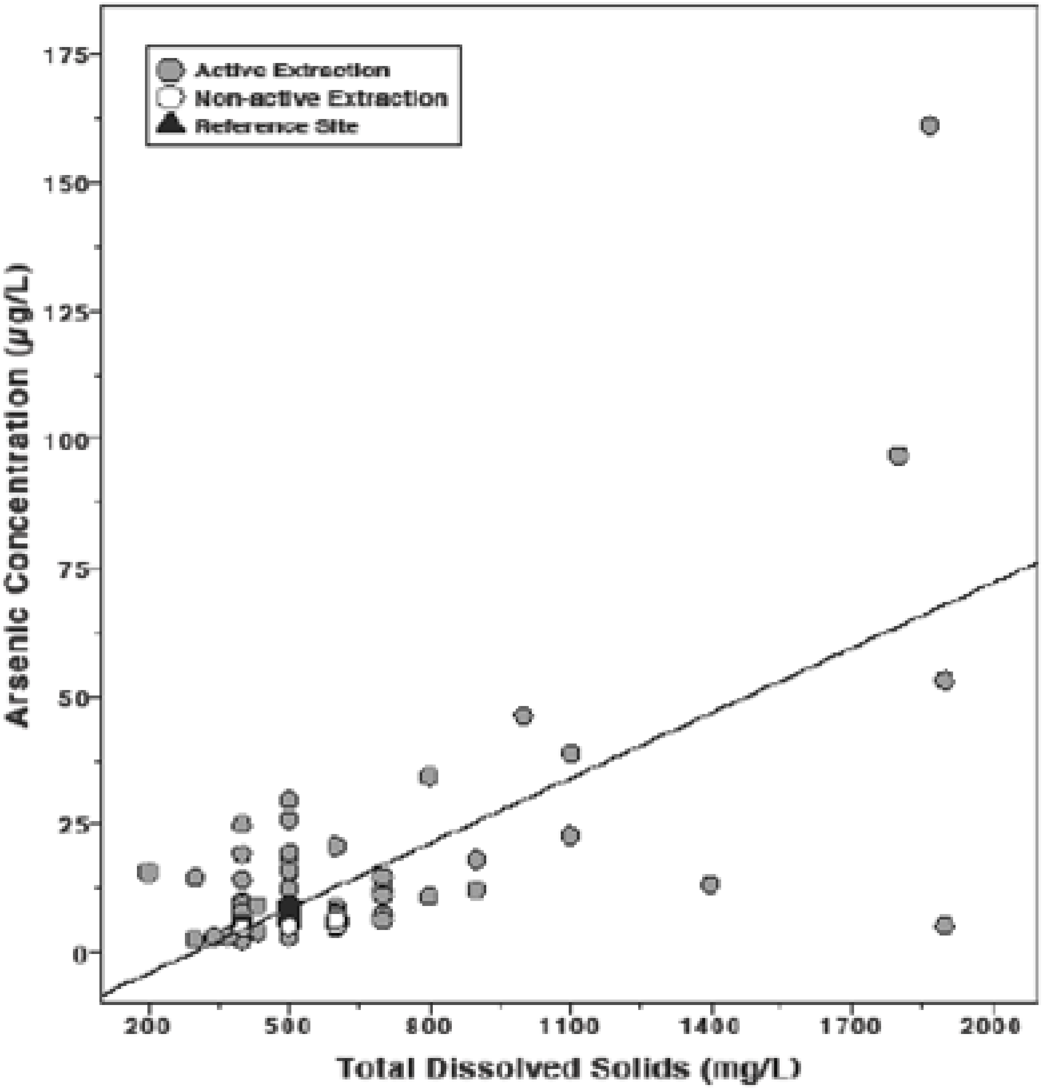

Figure A-3: Arsenic concentration versus the amount of toatal dissolved solids in Barnett Shale private water well samples

Table A-1: Contaminants of concern selected for GC-MS screening in Barnett Shale private well water samples[49]

Compound	CAS Number	SIM Ion
Methanol	67-56-1	31.1, 29.1
Ethanol	64-17-5	31.1, 29.1
Isopropanol	67-63-0	45.1, 29.1
n-Propanol	71-23-8	31.1
Propargyl Alcohol	107-19-7	55.1
n-Butanol	71-63-3	56.1
Ethylene Glycol	107-21-1	31.1
2-Butoxy Ethanol	111-76-2	57.1
Benzene	71-43-2	78.1
Toluene	108-88-3	91.1
Ethylbenzene	100-41-4	91.1
m-Xylene	108-38-3	91.1
p-Xylene	106-42-3	91.1
o-Xylene	95-47-6	91.1
Mesitylene	108-67-8	105.15
Benzyl Chloride	100-44-7	91.1
Formaldehyde	50-00-0	29.1
Acetaldehyde	75-07-0	29.1
Glutaraldehyde	111-30-8	44.1
Dimethyl Formamide	68-12-2	44.1
Naphthalene	91-20-3	128.1
1-Methyl Naphthalene	90-12-0	142.15
2-Methlyl Naphthalene	91-57-6	142.15
1-Naphthol	90-15-3	144.15
2-Naphthol	135-19-3	144.15
PEG 200	25322-68-3	45.1
Bisphenol A	80-05-7	213.1
d-Limonene	5989-27-5	68.1
Acetophenone	98-86-2	105.1

Appendix B

Supporting Information for Chapter 4:

Time-Course Monitoring of Groundwater Quality Relative to Increased Unconventional Drilling in Nolan County, Texas

B.1 Methods

B.1.1 Gas Chromatography – Mass Spectrometry (GC-MS)

Specific semi-volatile compounds to be analyzed using GC-MS were selected based upon suspected health or environmental effects and their inclusion in hydraulic fracturing fluid component lists freely available on the website fracfocus.org. The diversity of these compounds encompasses alcohols, aromatics, aldehydes, and others, all separated on a SHRxi-5ms column (30 m x 0.25 mm; 0.25 μm df). Oven programming and detection were performed using a GCMS-QP2010 SE (Shimadzu Scientific Instruments, Inc.; Columbia, MD). The GC inlet, interface, and MS temperatures were set to 300 ºC, 260 ºC, and 260 ºC, respectively. Selected compounds were detected by selected ion monitoring of the base peak of each analyte, as shown in Table B-1.

Table B-1: Selected compounds targetted for GCMS analysis

Compound	**CAS Number**	**SIM Ion**	**Compound**	**CAS Number**	**SIM Ion**
Methanol	67-56-1	31.1, 29.1	1,3,5-Trimethyl Benzene	108-67-8	105.15
Ethanol	64-17-5	31.1, 29.1	1,2,4-Trimethyl Benzene	95-63-6	91.1
Isopropanol	67-63-0	45.1, 29.1	Isopropyl Benzene	98-82-8	105.1
n-Propanol	71-23-8	31.1	Benzyl Chloride	100-44-7	91.1
Propargyl Alcohol	107-19-7	55.1	Acetaldehyde	75-07-0	29.1
n-Butanol	71-63-3	56.1	Glutaraldehyde	111-30-8	44.1
Ethylene Glycol	107-21-1	31.1	Dimethyl Formamide	68-12-2	44.1
Propylene Glycol	57-55-6	45.1	Naphthalene	91-20-3	128.1
2-Butoxy Ethanol	111-76-2	57.1	1-Methyl Naphthalene	90-12-0	142.15
2-Ethyl Hexanol	104-76-7	57.1	2-Methyl Naphthalene	91-57-6	142.15

Benzene	71-43-2	78.1	1-Naphthol	90-15-3	144.15
Ethylbenzene	100-41-4	91.1	2-Naphthol	135-19-3	144.15
Toluene	108-88-3	91.1	Bisphenol A	80-05-7	213.1
o-Xylene	95-47-6	91.1	d-Limonene	5989-27-5	68.1
m-Xylene	108-38-3	91.1	Acetophenone	98-86-2	105.1
p-Xylene	106-42-3	91.1			

B.1.2 Headspace Gas Chromatography

Methanol and ethanol detection was performed using static headspace – GC with a flame ionization detector. Headspace operations were controlled with the AOC-5000 Plus headspace autosampler. 5 ml of sample was mixed with 1 ml of 0.25 M NaCl (aq) in a 20 ml screw-top headspace vial. Automated incubation at 90 °C for 15 minutes and agitation were performed before 750 µL of headspace was sampled. Separation and detection was achieved using a Shimadzu GC-2010 Plus equipped with a Phenomenex ZB-BAC2 column (30 m x 0.32 mm; 1.2 µm df) held at 40 °C for 4.5 min, then increased to 130 °C at 30°C /min, held for 2 minutes. Inlet and detector temperatures were set to 200° C. Injector was set for a 5:1 split ratio.

B.1.3 Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

Elemental analysis of heavy metals was achieved using a Varian 820 ICP-MS coupled with SPS 3 Varian autosampler and Argon as the plasma source. MS data acquisition was performed in scan mode with 5 replicates, 30 scans per replicate.

B.1.4 Ion Chromatography (IC)

The IC analysis protocol used an IC-25 isocratic pump with an EG40 electrodialytic eluent generator, AG20/AS20 guard and separation column (2 mm bore) sets housed in a LC30 temperature controlled oven (30 °C), ASRS-Ultra II anion suppressor in external water mode, and a CD-25 conductivity detector, all from ThermoFisher/Dionex. Eletrodialytically generated high purity KOH eluent was used at a flow rate of 0.25 mL/min as indicated by the table B-2. Eluent generation, sample injection (2 uL), electrodialytic suppression, autoranging conductivity detection and data acquisition were all conducted under Excalibur/Chromeleon software control. All data were interpreted in terms of a 5-point calibration with check standards run daily. Any sample falling outside the calibration range was reanalyzed after appropriate dilution.

Table B-2: Gradient program for IC separation of Nolan County water samples

Time (min)	Concentration (mM)	Flow (mg/L)
0.00	4.00	2.5
3.00	4.00	2.5
15.00	10.00	2.5
19.00	40.00	2.5
27.00	40.00	2.5
27.50	4.00	2.5
30.00	4.00	2.5

B.1.5 TOC/TN

Carbon and Total Nitrogen measurements were made using the Shimadzu TOC-L/TN. Sampled water was introduced into 40 mL septum-top VOA vials and loaded into the ASL autosampler. Standards and calibration curves were generated using the manufacturer’s recommendations. Samples were not filtered unless noticeable particulates were present.

B.1.6 Geospatial and Statistical Analysis

Geospatial analyses were conducted using the software package ArcGIS 10.1 ESRI 2011. ArcGISDesktop: Release 10. Redlands, CA: Environmental Systems research Institute). The distance in kilometers from each sample to the nearest natural gas well as well as the number of gas wells in a one kilometer radius around each sample were calculated to assess whether or not there is a relationship between proximity to natural gas extraction activities and private well water quality. Relationships among the data were assessed using Spearman’s rank correlation and Mann Whitney U pairwise analysis.

Appendix C

Supporting Information for Chapter 5:

Varying Matrix Effects for Elemental Analysis Identified from Groundwater in the Barnett Shale

Table C-1: Composition of the 26 metals included in the aqueous multi-metal standard mixture

Aluminum	Beryllium	Chromium	Lead	Nickel	Silver	Titanium
Antimony	Boron	Cobalt	Magnesium	Potassium	Sodium	Vanadium
Arsenic	Cadmium	Copper	Manganese	Selenium	Thallium	Zinc
Barium	Calcium	Iron	Molybdenum	Silicon[a]		
All metals present at 100 µg/mL in 4% HNO_3(aq) [a]Silicon present at 50 µg/mL						

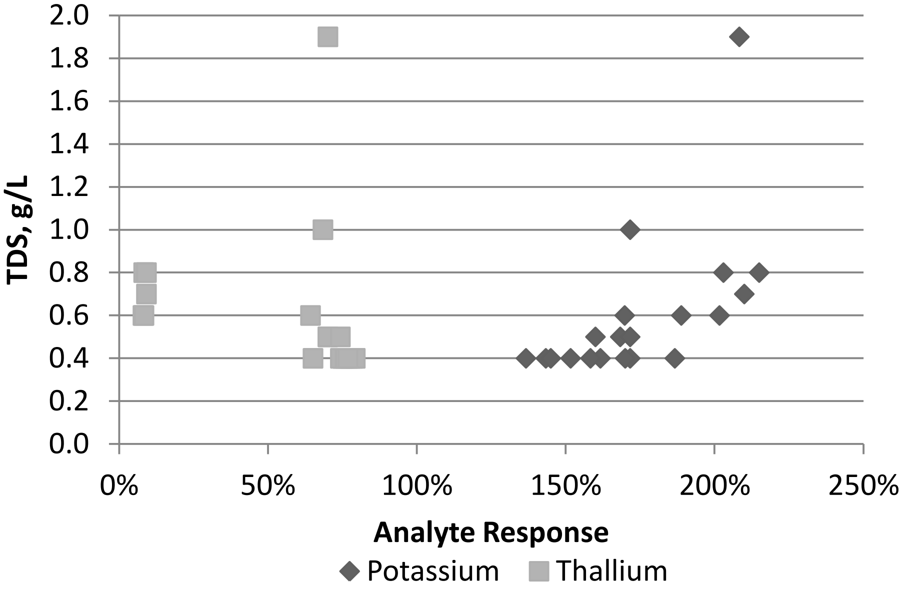

Figure C-1: Correlation between the response of potassium and thallium with total dissolved solids (TDS) in the Bulk solution

Table C-2: Water quality measurements considered in the physical properties that may give rise to the observed matrix effects

	Salinity, g/L	TDS, mg/L	Turbidity, NTU	Oxidative Reduction Potential, mV
PW9	0.29	400	0.61	319.45
PW19	0.60	800	0.78	-39.70
PW32	0.59	800		29.45
PW40	0.46	600	2.36	-85.50
PW41	0.34	400	4.5	-185.45
PW50	0.33	400	8.61	79.25
PW55	1.49	1900	0.2	-224.00
PW56	0.31	400	0.23	-25.85
PW58	0.27	400	4.17	-53.00
PW63	0.26	400	3.27	-6.45
PW64	0.27	400	6.09	-77.25
PW68	0.37	600	1.38	17.33
PW71	0.41	500	1.7	171.00
PW72	0.43	600	1.06	-916.80
PW74	0.34	500	1.28	-100.00
PW77	0.30	400	4.91	-49.35
PW78	0.31	400	3.79	-108.75
PW94	0.54	700	0.34	54.00
PW97	0.77	1000	1.09	145.90
PW102	0.38	500	0.4	-59.00

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Biographical Information

Doug spent the most of his teenage years excelling academically in science and math and surprisingly at football. In 2005 he joined the East Texas Baptist University Tigers as an undersized, but intelligent, offensive lineman. As he progressed through his Bachelor's Degree in chemistry, he was always an undersized offensive lineman. Hard work for both fields resulted in him graduating Cum Laude and starting every game all four years at ETBU. After graduation, he knew he wanted to attend graduate school to earn an advanced degree, but didn't feel the need to join a Ph.D. program because he "wasn't going to teach and didn't intend on changing the world."

After advice from professors across DFW, he did join the Ph.D. program at The University of Texas at Arlington in the Fall of 2009. He honestly believes his experience playing football for ETBU allowed him to stand out from the other applicants and instilled traits not easily found in others. He spent the first couple years studying quantitative methods for determining the binding constants between peptides and metal cations by electrospray – mass spectrometry. This work fell to the wayside with the inception of the Texas Well Study in May of 2011. Because of his gas chromatography experienced that he gained through his father and a previous internship, he was brought onto the project to supervise method development. Three years later, this side-project is now his livelihood.