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# Water Quality Near Shale Gas Development Sites In Rural Southwestern Pennsylvania

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## Introduction

The recent development of hydraulic fracturing, or “fracking” has increased the economic feasibility of drilling unconventional and previously untapped natural resources such as shale gas beds. Hydraulic fracturing is a technologically advanced form of fossil fuel extraction, differing from traditional oil and gas extraction due to horizontal drilling and a technique utilizing pressurized fluid known as “slick water” [1],[2]. In Pennsylvania and over the Marcellus shale, slick water primarily consists of water, fine-grained sand, and less than 5% of chemicals such as biocides, corrosives, and other additives to stimulate the formation and increase production [3], [4].

There are numerous stages of shale-gas development, many of which come into contact with the hydrologic cycle and could contaminate water wells. Traditional oil and gas drilling uses vertical drilling and casing to access gas reserves, largely in shallower beds. Modern oil and gas drilling necessitates surface disturbances such as land clearing and infrastructure development, as well as the storage and disposal of wastewater fluids. Shale gas well sites typically use more landmass, taking up several acres for one pad. Improper erosion control may lead to run off, which could impact local water wells and streams via above ground contact. The well is then drilled and cased vertically, followed by drilling and fracking laterally. Shale wells are typically horizontally drilled and fracked in sequential order, every 90-150 feet laterally, for the maximum quantity of gas[5]. After fracking, 30-60% of the wastewater from the well returns to the surface and is collected in storage containers or open impoundment ponds. Throughout its lifetime a well produces flowback water along with natural gas and if improperly stored or disposed of, waste may come into contact with the water table[6], [7].

The production of natural gas is expanding due to this advanced technology, an emphasis on domestic production and a countrywide move away from coal[8], [9], [10]. Geological estimates have calculated that the Marcellus shale, which occurs in the subsurface under much of Pennsylvania, New York, Ohio and West Virginia, contains about 1.9 trillion cubic feet of gas[11]. Researchers estimate this gas, when excavated and processed, may be worth over one trillion dollars[12]. In most places the Marcellus shale is over a mile underneath the ground and has been previously untapped by traditional vertical drilling. In Pennsylvania alone, the number of Marcellus wells increased from only 195 in 2008, to over 750 in 2009[13].

At present, policy makers and the public are receiving conflicting information regarding the economic, environmental, and human health effects of shale-gas development[14], [15], [16] while possessing a minimal foundation of literature on which to base decisions. Federal reports from the Government Accountability Office (GAO) and the US Geological Survey (USGS) have projected possible contamination from the drilling, casing and disposal of waste from the shale gas development process in addition to a need for more research on the risks to groundwater quality[17], [18]. The US Environmental Protection Agency (EPA) has indicated a plan for the assessment of groundwater impacts, currently due out in 2014[19].

There are few peer-reviewed papers on hydraulic fracturing, and of those published, most are under dispute[20]. Literature regarding impacts on water quality is patchy, focusing mostly on methane[21]. Modeling research has indicated possible pathways for this contamination through natural and hydraulically fractured fissures in Pennsylvania[22], [23]. Risk assessment using probability bound analysis indicated wastewater disposal had high risk of water contamination, producing large amount of contaminated fluids from each well[24]. The Pennsylvania Department of Environmental Protection (PA DEP) currently suggests testing for 26 parameters pre- and post- hydraulic fracturing, including: metals, naturally occurring radioactive minerals (NORMS), salinity, E. coli, and minerals such as calcium[25]. It is unclear if any of these parameters may change or be associated with natural gas drilling.

The objective of this research was to further the understanding of water quality near shale gas development sites in Washington County, PA. We evaluated a link between shale gas development locations in relationship to household water wells in rural southwestern Pennsylvania. We sought to determine if the proximity of gas well drilling sites impacted the concentrations of various chemicals, metals, minerals, total dissolved solids, and pH.

## Methods

*Sampling design*

Households were chosen through a Geographic Information System (GIS) randomized point matrix in conjunction with a Health Impacts Near Shale Gas Development study (Rabinowitz et al. 2013, in review). In short, 760 household points were chosen from 38 distinct areas (townships or municipalities) in Washington County with a 100-meter offset. Households were surveyed if a consenting adult was present who had lived at the household for over one year. Water was collected if the well was accessible during the visit. Some households used well water intermittently or for portions of the year and switched between municipal water, spring water, and well water depending on availability. The Yale Human Research Protection Program (HRPP) approved this research as having minimal risk to subjects.

Data on the gas well locations as well as when drilling began ("spud dates") were acquired from the PA DEP website, ranging from when Marcellus drilling began (2003) through April 2012, a month before sampling began. This gives locations for when gas drilling "broke ground", but no further information of when various portions of the shale gas development began.

Water well sampling followed EPA sampling guidelines[26]. Water was sampled as close to the water well as possible, after removing all possible filtration or hoses and letting the water run for 3-5 minutes. Blanks, spikes and duplicates were collected to validate samples. pH, temperature, and conductivity were taken at each household with handheld field meters. During fieldwork, water samples were kept insulated and on ice. The samples were then refrigerated throughout shipment until analysis. All samples were either tested within 14 days or frozen for future analysis.

*Site description*

This study was completed in Washington County, Pennsylvania, located in the southwestern corner of Pennsylvania, outside of Pittsburgh. Washington County includes many of the first drilled horizontal wells hydrofracked in Pennsylvania and is the third most densely drilled county in the state. It is a rural area of approximately 223,000 hectares with a little over 200,000 residents. Research by the USGS indicates natural gas infrastructure is currently taking up over 1,100 hectares of the county, predominantly well sites and impoundments, all of which have been built since 2003[27]. Washington County, PA also has documented complaints of water contamination and health impacts that residents believe are directly linked to the oil and gas drilling of the Marcellus nearby[28]. In addition, southwestern Pennsylvania contains higher amounts of "wet" or "rich" gas (gas containing 12-14% ethane), making drilling profitable even with the downward trend of natural gas prices[29]. Within Washington County, townships were excluded which had municipal water in all of the township, or that bordered West Virginia due to confounding factors. Twenty-one townships in total were included in this research. They are seen in Figure 1 by population gradation, with higher population around the capital of Washington.

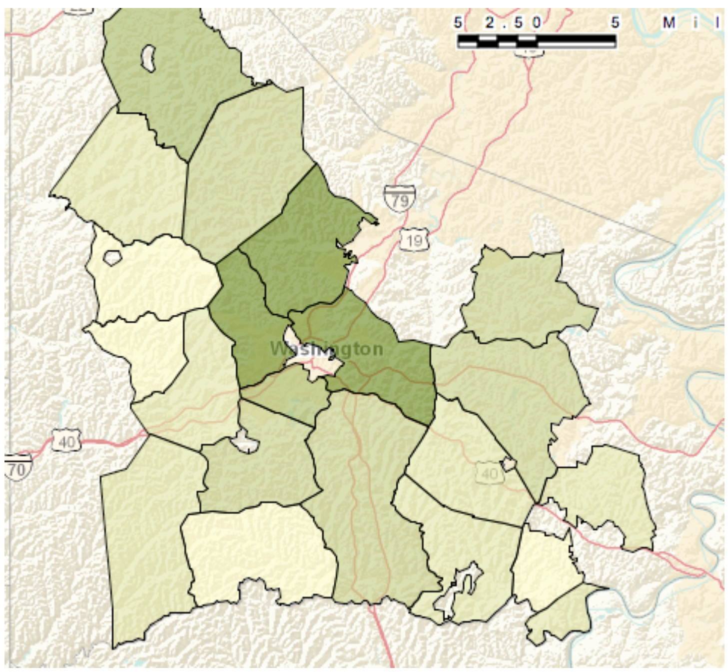


**Figure 1 Washington County Eligible Townships by Population**

Water usage and hydrology in Washington County is disparate, varied, and not well documented. Most rural residents rely on well water for at least part of their usage, but this varies widely by township and municipality, with some townships using more public water sources and residents having the option to "tap in" or not. Aquifers in Washington County include sandstone and shale and fractured sandstone and shale, with the water table averaging 80 to 200 feet below the surface[30]. Industries in this area include farming, mining, and oil and gas development.

*Analysis*

Water samples were analyzed for 36 chemical parameters: volatile organic compounds (benzene, toluene, ethylbenzene, xylene, trihalomethanes), total elements (aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, gadolinium, iron, lead, lithium, magnesium, manganese, mercury, nickel, potassium, selenium, silicon, silver, sodium, strontium, tin, uranium, vanadium, zinc), and anions (chloride, sulfate, nitrate as nitrogen). Volatile organic compound analysis followed EPA guidelines (EPA Methods 602, 624, 1624), preserving containers with half concentration hydrochloric acid. Element analysis was completed by the Connecticut Agricultural Experiment Station using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Anions were analyzed by the author at a School of Forestry and Environmental Studies laboratory using an Ion Chromatographer. Water collection and analysis was blind to proximity to gas wells.

Water quality data was assessed using Wilcoxon tests of Rank Sum means for non-normally distributed data comparing contamination concentrations less than 1 km from the nearest Marcellus well and contamination concentrations greater than 1 km from the nearest Marcellus well. All of the data analysis was conducted by the author using Statistical Analysis Software (SAS). Significance was determined by alpha=0.05. Distance from gas wells was calculated using GIS points to preserve anonymity for residents. Water results were sent back to all participants and compared to Maximum Contaminant Levels (MCLs) from Pennsylvania Drinking Water Standards where they exist and to federal agencies where they did not exist.

**Results**

148 water well samples were collected from May 2012-August 2012. Of these, 103 were reported as well water. Only these groundwater sources will be reported on, as the source of the water is known. Other sources in this sample included natural springs,

cisterns, rainwater collection, and mixes of various sources. Some water is filtered, as not as well water could be accessed unfiltered.

*Water usage*

The average water well depth was 118 feet for known wells (median: 100 feet). However, all well depths were self-reported and only 73 (70.9%) of the households knew their well depth. The average water well depth of a household was slightly higher for households that were farther from shale gas wells, but the difference was not statistically significant. 67.6% of the households reported drinking their well water at least most of the time.

*Water quality*

The households in this sample are located at varied distances from Marcellus shale wells, with some households less than 300 meters from a gas well and others over 15,000 meters away. The variability in number of wells by township is statistically significant (p= 0.01) and shown in Figure 2.

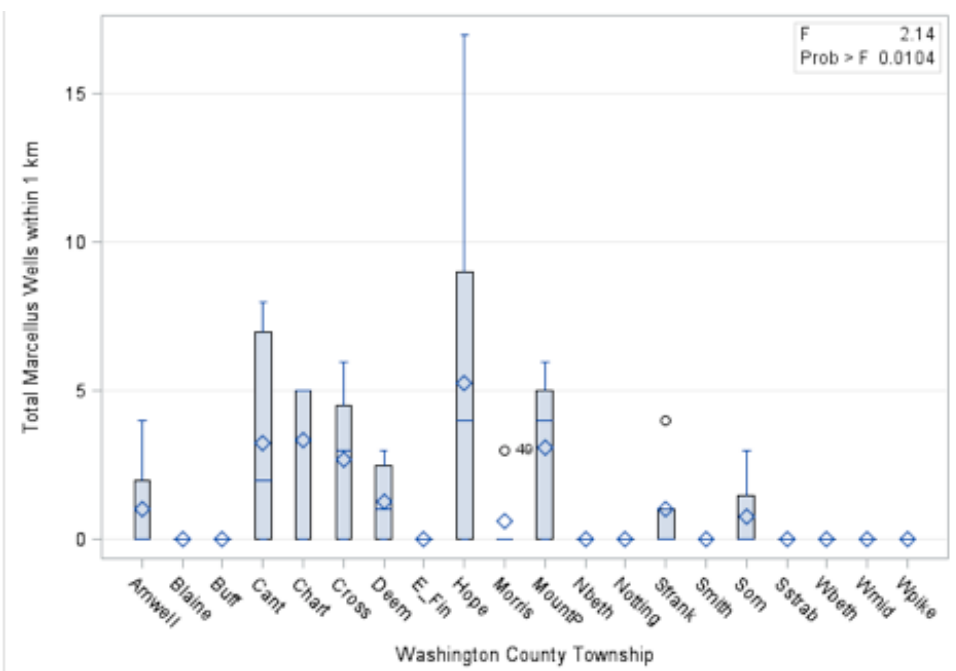


**Figure 2 Marcellus Shale Wells within 1 km of Households, by Township**

pH, temperature and conductivity show wide variation and do not appear to be associated with gas wells. pH values range from 6.48 to 9.45 (mean = 7.54, median = 7.41), some outside of the range of acceptable pH levels for Pennsylvania (6.5 – 8.5). The distribution of pH at various distances to gas wells is illustrated in Figure 3. Temperatures ranged from 13.9 to 26.8 degrees C and conductivity measurements varied from 400 u/s to 1518 u/s standardized at 25.5 degrees C.

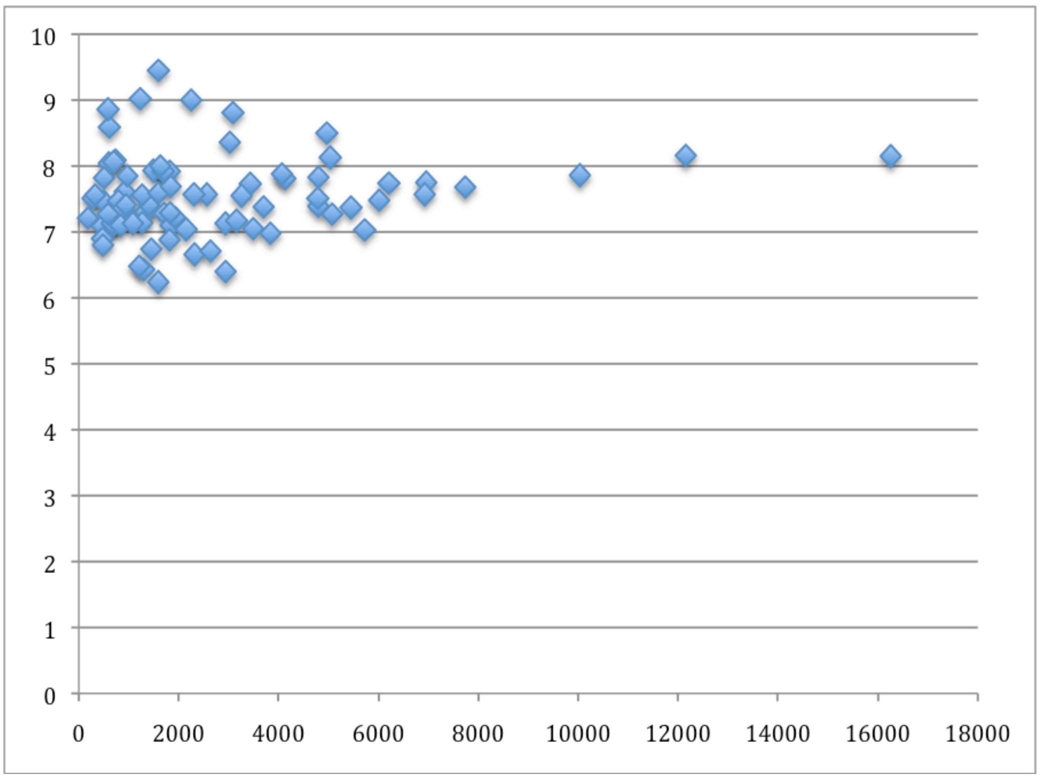


**Figure 3 pH values by distance to nearest Marcellus Gas Well**

Comparisons of groundwater contamination concentration less than 1 km away from gas wells and greater than 1 km are seen in Table 1. Lithium (p=0.005), magnesium (p=0.039) and silicon (p=0.01) show significantly greater concentrations less than 1 km from gas wells. Calcium, strontium and zinc show non-significant trends of increased contamination less than 1 km from gas wells. Iron (p=0.02) and sodium (0.03) concentrations were significantly higher greater than 1 km from gas drilling sites. Potassium and manganese show increased medians near shale gas development sites.

1

2 **Table 1 Comparisons of concentrations greater and less than 1 km***, *****

| Chemical Parameter | # Positive Samples | Mean/Median (less than 1 km) | Mean/Median (greater than 1 km) | p-value* |
|---|---|---|---|---|
| **Elements:** | | **n=30** | **n=71** | |
| Aluminum (Al) | 32 | 1.0/0** | 2.5/0 | 0.20 |
| Arsenic (As) | 15 | 0.07/0 | 0.3/0 | 0.17 |
| Barium (Ba) | 97 | 152.0/110.0 | 156.3/111.0 | 0.28 |
| Calcium (Ca) | 103 | 102914.8/77577.5 | 63197.2/69460.0 | 0.07 |
| Chromium (Cr) | 27 | 0.53/0 | 0.81/0 | 0.19 |
| Copper (Cu) | 93 | 15.1/9.6 | 22.5/8.8 | 0.38 |
| Iron (Fe) | 92 | 12.7/0.9 | 13.8/2.0 | 0.02 |
| Lead (Pb) | 84 | 0.17/0 | 0.13/0 | 0.35 |
| Lithium (Li) | 102 | 9.5/9.3 | 7.3/6.5 | 0.005 |
| Magnesium (Mg) | 103 | 14522.3/13355.5 | 12334.8/10382.0 | 0.04 |
| Manganese (Mn) | 65 | 21.4/3.1 | 29.0/0.9 | 0.21 |
| Mercury (Hg) | 12 | 0.13/0 | 0.17/0 | 0.42 |
| Nickel (Ni) | 90 | 1.5/1.1 | 1.5/1.4 | 0.16 |
| Potassium (K) | 103 | 1597.0/1335.5 | 1624.5/1230.0 | 0.13 |
| Silicon (Si) | 101 | 5911.2/5792.5 | 5435.9/5063.0 | 0.01 |
| Sodium (Na) | 103 | 43529.3/14729.0 | 69641.1/28860 | 0.03 |
| Strontium (Sr) | 98 | 674.7/506.0 | 514.3/402.0 | 0.07 |
| Uranium (U) | 24 | 0.13/0 | 0.18/0 | 0.20 |
| Zinc (Zn) | 103 | 40.5/17.0 | 37.9/16.0 | 0.25 |
| **Anions:** | | **n=20** | **n=35** | |
| Chloride (Cl-) | 55 | 21.8/9.6 | 36.7/22.8 | 0.13 |
| Nitrate as Nitrogen (N-NO3) | 55 | 0.27/0.08 | 0.51/0.12 | 0.26 |
| Sulfate (SO2) | 55 | 39.1/32.1 | 39.9/31.9 | 0.49 |

3 *Wilcoxon Rank Sum score
**0 is a value used to represent "not detected" in the statistical analysis
***Benzene, toluene, ethylbenzene, xylene, beryllium, gadolinium, and vanadium did not appear in any water results in this sample (n=0).
****Antimony, cadmium, cobalt, selenium, silver, tin, and trihalomethanes appeared in less than 10 samples; there was not enough power to perform statistical tests on these parameters.

When compared to recommended drinking water limits and Maximum Contaminant Levels (MCLs), 60% of households failed at least one water quality recommendation. Table 2 shows the average, median, minimum, maximum and failure rate for each contaminant that appeared over the MCL in the sample. Most contaminants in the sample appeared below MCLs. The only contaminant appearing both above the MCL and showing potential association with shale gas development is calcium, with 39.8% of the sample over the recommended limit of 80,000 ppb.

**Table 2 Contaminant Failures by Recommended Maximum Contaminant Levels (MCL)**

| Contaminant (ppb) | MCL (ppb) | % Fail | Mean | Min | Max | Median |
|---|---|---|---|---|---|---|
| Aluminum | 50 | 1/103 = 0.97% | 6.4 | ND | 56.3 | 3.8 |
| Calcium | 80,000 | 41/103 = 39.8% | 75,537 | 19 | 1,007,005 | 71,492 |
| Nitrate as Nitrogen | 1000 | 6/55 = 10.9% | 418.6 | ND | 3255.7 | 116.7 |
| Magnesium | 30,000 | 6/103 = 5.83% | 13,015 | 2 | 45,773 | 10,900 |
| Manganese | 50 | 14/103 = 13.6% | 41.02 | ND | 322 | 7.1 |
| Mercury | 2 | 2/103 = 1.9% | 1.31 | ND | 3.2 | 1.2 |
| Sodium | 20,000 | 54/103 = 52.4% | 61,529 | 2,524 | 361,221 | 25,142 |

*ND = Not detected*
*No recommended standard: Potassium, Silicon*

Linear trends largely back up the comparisons of ranked mean concentrations for less than or greater than 1 km, suggesting that the methodology of looking at distance as a binominal value is valid. Calcium, lithium, magnesium, silicon, strontium also show linear trend lines, with concentrations increasing as distance to gas wells decreases (Figures 4-8). Similarly, iron and sodium, which showed higher concentrations farther from gas wells, show decreasing concentrations with farther distance to gas wells (Figure 9-10). In addition, total trihalomethanes, which only appeared in water samples 6 times, show a strong linear trend (Figure 11). Nickel, tin, zinc, nitrate as nitrogen, and sulfate showed linear trends with concentrations decreasing further from Marcellus gas well sites (Appendix A). R-square values for linear trends are indicated on the graphs.

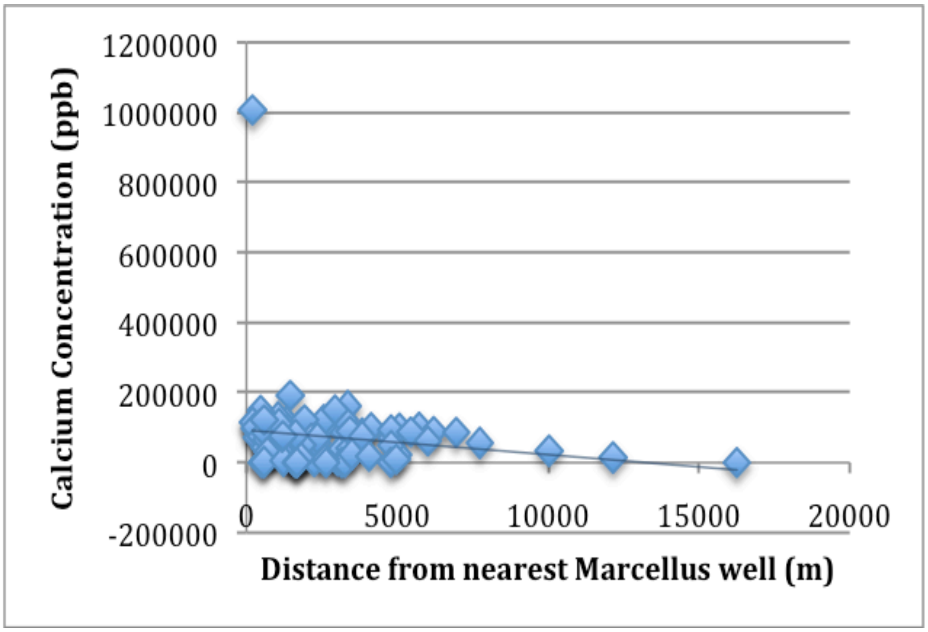


**Figure 4 Calcium Concentration (ppb) by Distance to Gas Well (R-Square = 0.029)**

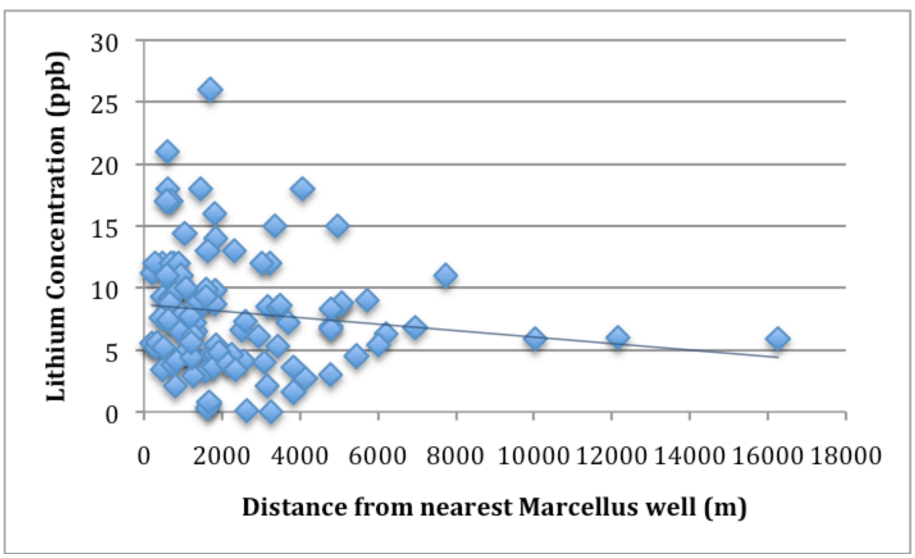


**Figure 5 Lithium Concentration (ppb) by Distance to Gas Well (R-Square = 0.019)**

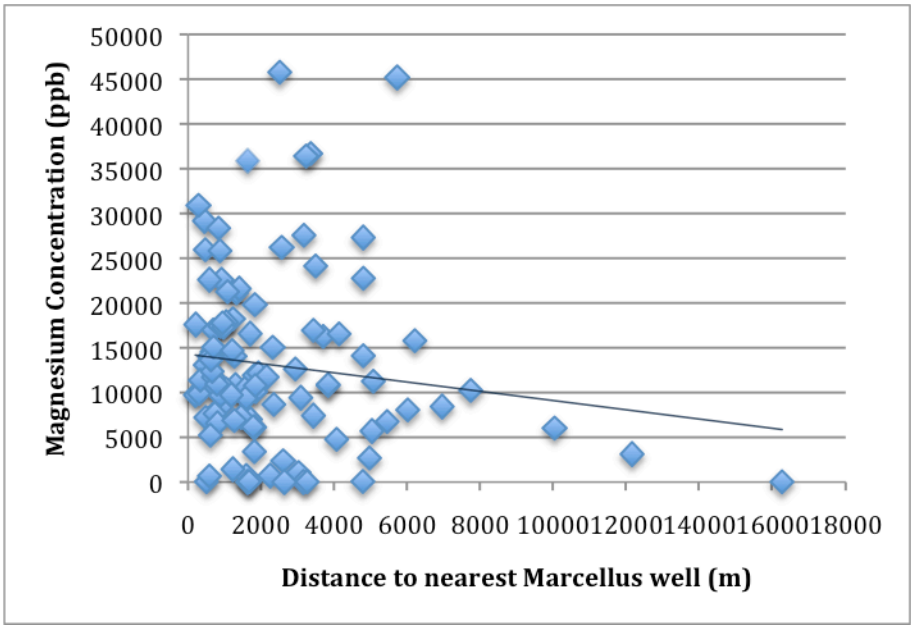


**Figure 6 Magnesium Concentration (ppb) by Distance to Gas Well (R-Square = 0.017)**

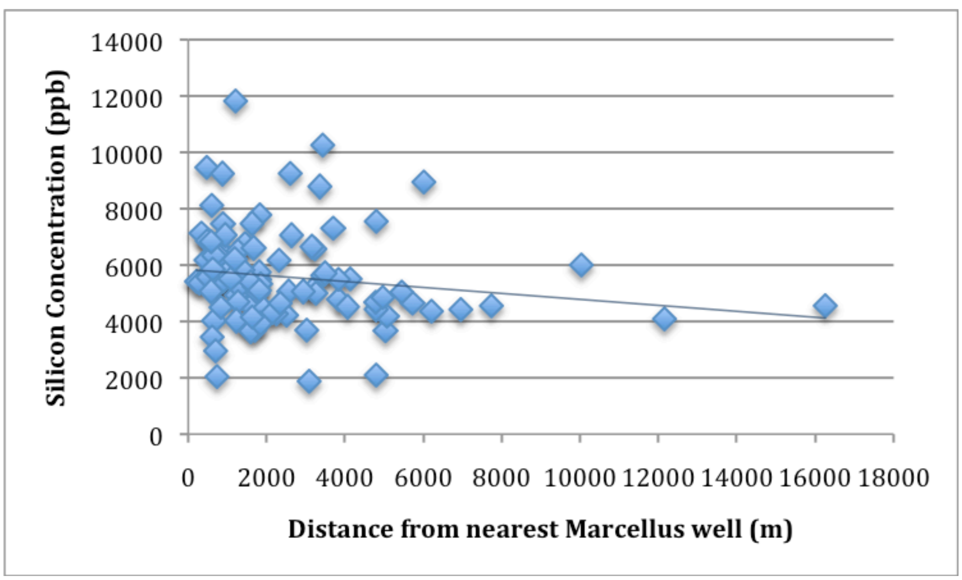


**Figure 7 Silicon Concentration (ppb) by Distance to Gas Well (R-Square = 0.025)**

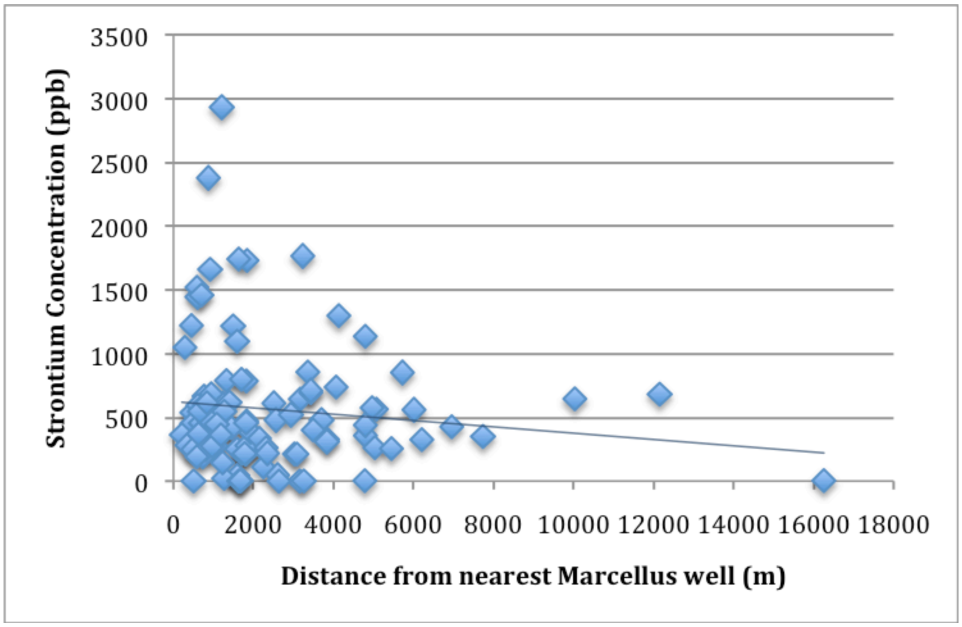


**Figure 8 Strontium Concentration (ppb) by Distance to Gas Well (R-Square = 0.015)**

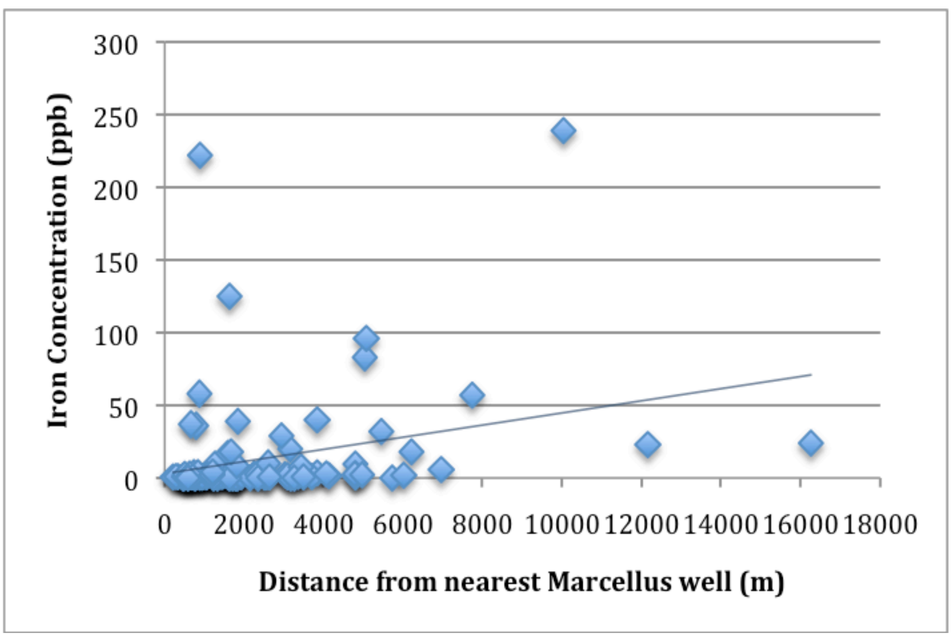


**Figure 9 Iron Concentration (ppb) by Distance to Gas Well (R-Square = 0.079)**

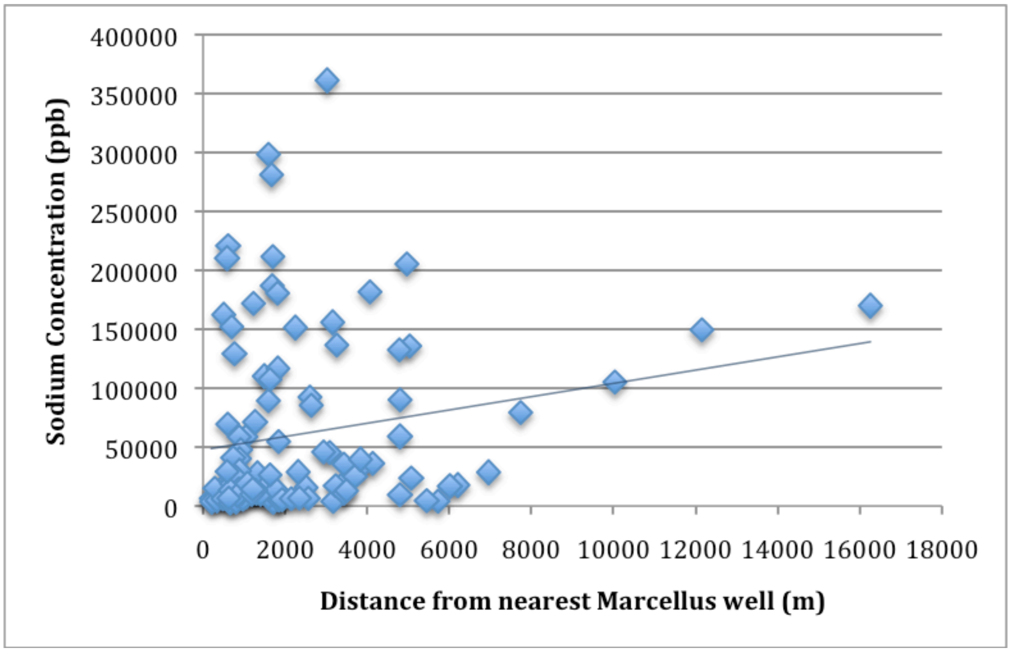


**Figure 10 Sodium Concentration (ppb) by Distance to Gas Well (R-Square = 0.035)**

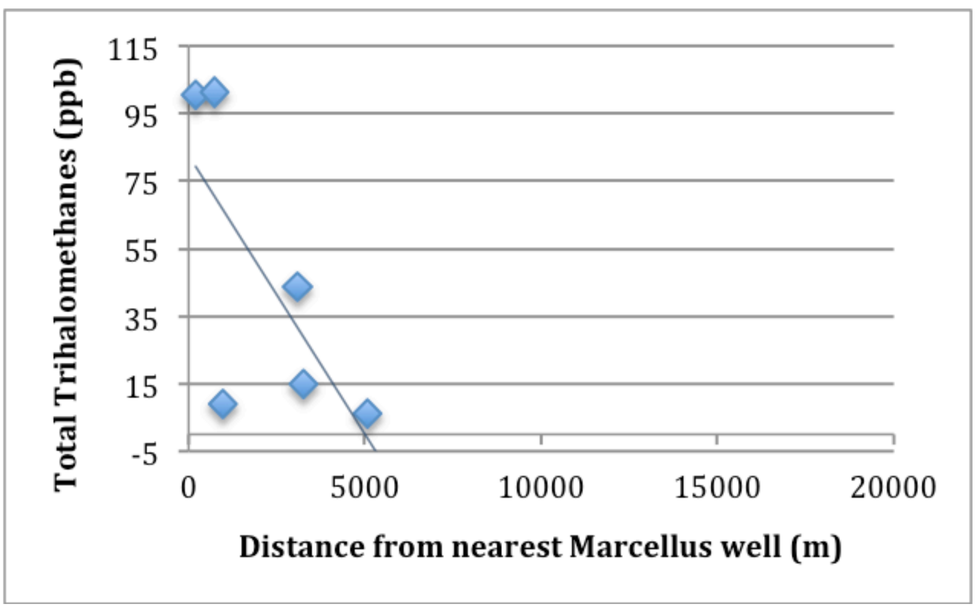


**Figure 11 Total Trihalomethanes (ppb) by Distance to Gas Well**

**Discussion**

This research shows differences in water quality closer to shale gas development sites and farther from shale gas development sites in southwestern Pennsylvania. Households near shale gas development have statistically higher concentrations of lithium, magnesium, and silicon and lower concentrations of iron and sodium than householders far from shale sites. Associations of calcium and strontium are borderline statistically higher near shale gas development sites. Barium, calcium, chloride, lithium, magnesium, manganese, silicon, nitrates, sulfates, potassium, and sodium are all found in high concentrations in typical flowback water from the Marcellus shale region[31], [32]. Silicon is present in high quantities in hydraulic fracturing fluids in this region[33], however, silicon and all other elemental parameters in this research are naturally occurring. It is therefore difficult to separate the effects of natural gas drilling on the southwestern Pennsylvania environment.

It is particularly interesting to note that the parameters that are significantly higher near shale gas drilling have the lowest atomic weights (lithium, magnesium, silicon), while those that are borderline significant or show trends are slightly heavier (calcium, strontium, potassium, manganese). A hypothesis could be that these heavier metals travel through the environment slower than lighter solutes. Barium is the heaviest of the solutes found in Marcellus shale wastewater, so it's potential this solute would take the longest to travel through the environment.

The contamination trends in this study showcase the complexity of the region's geology and hydrology. Many households had wells less than 80 feet deep, which is not recommended by the Pennsylvania Department of Environmental Protection. Improper casing and care of water wells could lead to contamination from surface waters or runoff.

Contamination from shale gas development could occur through natural or human-made fractures underground, from hydraulic fracturing, horizontal drilling, previous oil and gas development or natural fracturing. Modeling has indicated hydraulic fracturing could alter pressure and change waterway directions, causing migration of gases and liquids up to the subsurface. In addition, poor casing or high pressures from hydraulic fracturing could contaminate the groundwater directly from the casing, either while drilling and casing, during hydraulic fracturing, or during removal of flowback and produced waters. Marcellus wells undergo large amounts of pressure during drilling and fracking, with casings withstanding high pressures for long periods of time. If casing is damaged or cracked during the hydraulic fracturing period (days or weeks), wastewater coming back up could seep into the water table. Moreover, the large quantities of wastewater produced must be dealt with and stored properly. Some companies in southwestern Pennsylvania store wastewater in open impoundment pits with plastic liners; these can leak or be subject to flooding events. A history of mining as well as oil and gas development has left southwestern Pennsylvania especially vulnerable to contamination of groundwater due to undocumented fractures in the subsurface. It is uncertain whether groundwater contamination may be more likely in this area, since the Marcellus shale has been previously drilled through to reach other natural gas reserves.

Depending on the rate of transport of dissolved solutes, the concentrations of some of these may increase or decrease with time. If groundwater contamination could occur from Marcellus shale drilling, solute concentration would likely vary depending on the stage of shale gas development a leak occurred during. The information on the timing of various processes, such as drilling, casing, hydraulic or horizontal fracturing, or wastewater impoundment usage is not publically available. We used PA DEP data up until April 2012 to locate Marcellus shale wells, however, groundwater solutes would take a longer timeline to move 1 km. It may be interesting to look only at groundwater near older wells, which allows a latency period for solutes to move through slow groundwater transport. The dilution of solutes by groundwater transport to low concentrations would match with the data in this study.

*Limitations*

There are a few limitations that may restrict statistical and extrapolation power of these results. This research needed to rely on a constructed “exposed” (<1 km) and “unexposed” (>1 km) distance to gas wells to look at various chemical associations, as there is no true baseline data for most of these households. When baseline data for the individual households wasn’t available, an attempt was made to look at pre-Marcellus drilling for the region. Washington County has only 3 USGS groundwater tests available, and the last test is from 1992. In addition to being potentially outdated and having a small sample size, these analyses did not test for many of the chemical parameters of interest in this research, including barium, chloride, lithium, and uranium, and not all years were tested for each parameter (for instance, the last tests for arsenic, lead, strontium, aluminum, and mercury were in 1983). This research is also limited by a lack of understanding of groundwater flow and aquifers in Washington County.

There is little mapping of the aquifers and it is unknown if some of these water tests were in confined or unconfined aquifers, what the direction of flow was, and what the speed of flow was. It is not known how long it would take some of these metals or anions to travel 1 km in this geographic area. It likely also varies greatly throughout the water samples and the different townships. Merely testing the substrate and making these analyses is not enough to be conclusive in the risks to water contamination from hydraulic fracturing and shale gas development.

Finally, this is a pilot study conducted to further the understanding of water quality near shale gas sites in southwestern Pennsylvania. The sample size was limited additionally due to fewer households than anticipated having well water, and due to breakage from transport and freezing methods throughout the study. Unfortunately, due to a transport failure of many samples, there are only 55 for each of the anions, reducing the scope and potential statistical significance. This research also relied on self-report by homeowners. Unfortunately, most homeowners did not have the information on their water wells that would make this research stronger. Modeling of parameters together including well depth, well casing and design, distance and density of gas wells with chemical concentrations is highly limited due to lack of homeowner knowledge.

*Further Research*

More research is needed on water quality in relationship to shale gas development sites. Hopefully this paper can assist researchers, landowners and policy makers on what to test pre- and post- development. Research could also benefit from knowledge on the chemical agents used to drill and hydraulically frack for gas, including their concentrations, and information on the life cycle of the shale gas process. Collecting real-time data and allowing environmental hydrologists and geologists to analyze monitoring data from hydraulic fracturing sites would contribute rigorous data to the field. Public health practitioners and exposure assessment experts are in particularly good positions to work with oil and gas industry personnel due to their experience handling confidential data sets. Real-time monitoring of pressure gauges, water quantities, and concentrations of particular contaminants could be cost-effective strategies. Pre- or post-tracers in hydraulic fracturing fluid to "fingerprint" the drilling process would also be a good tool. Isotopic analysis has been an experimental way of accomplishing this with methane, but it doesn't reveal the full picture. In addition, it's likely methane would travel much more quickly and much differently than solutes such as silicon or heavy metals such as barium.

**Conclusions**

This research shows potential associations with some chemical parameters and short distances to shale gas development sites. More research on groundwater near hydraulic fracturing is needed.

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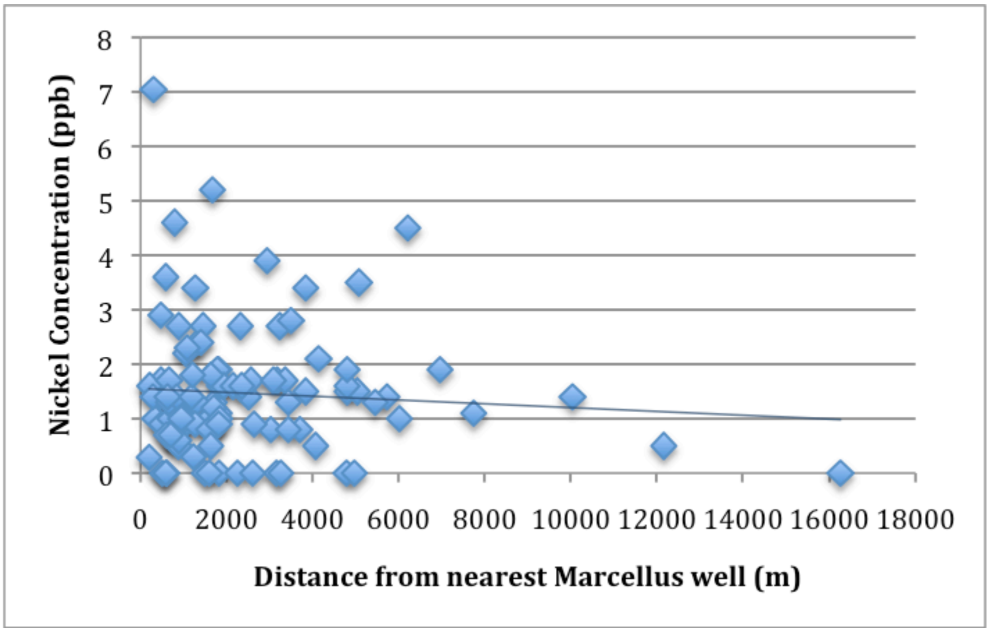
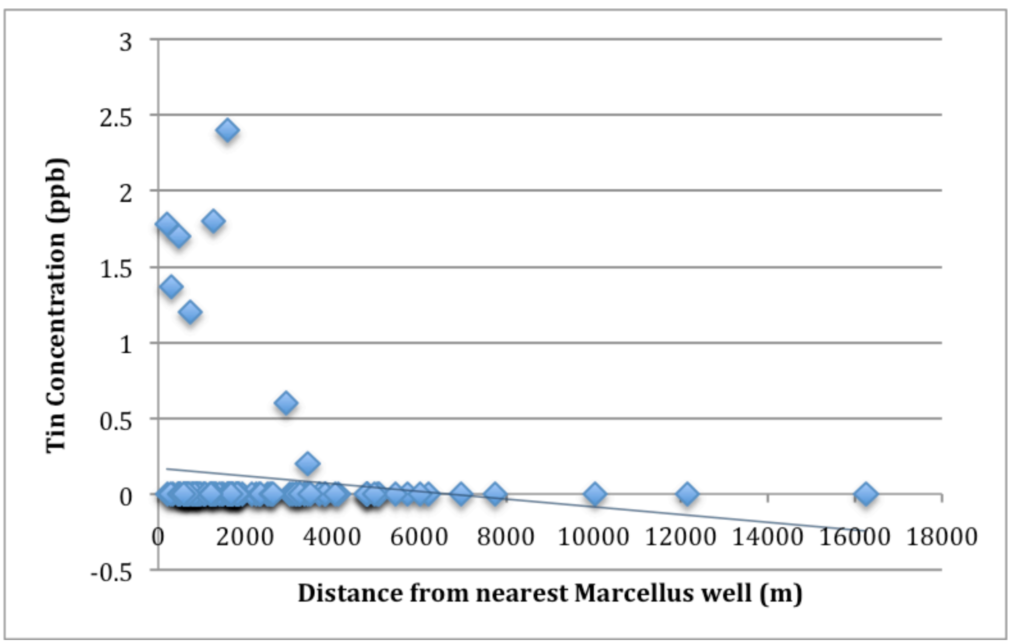
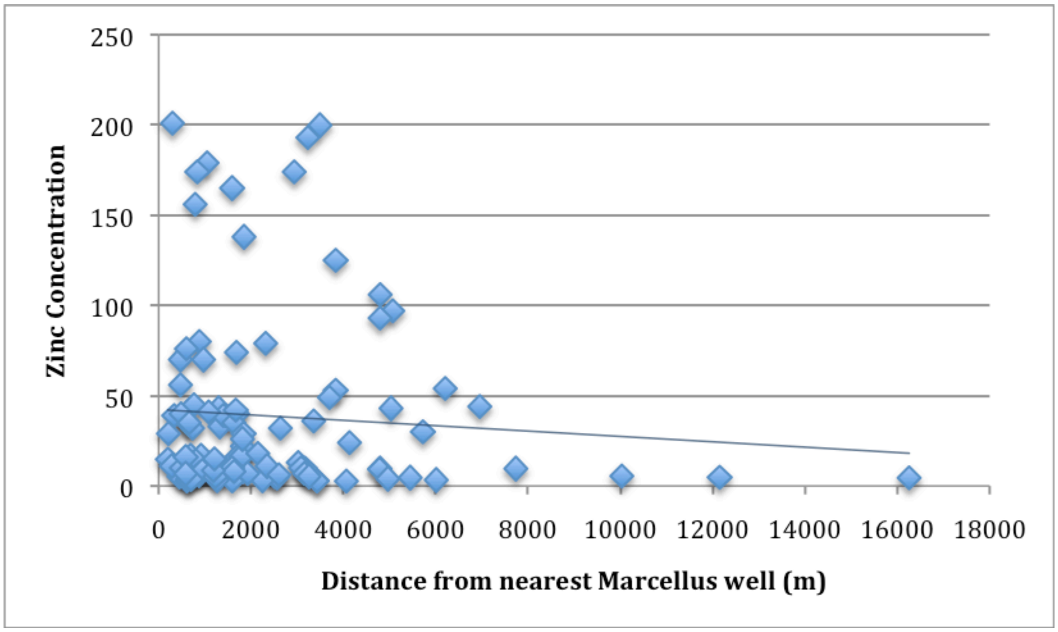
## Appendix A



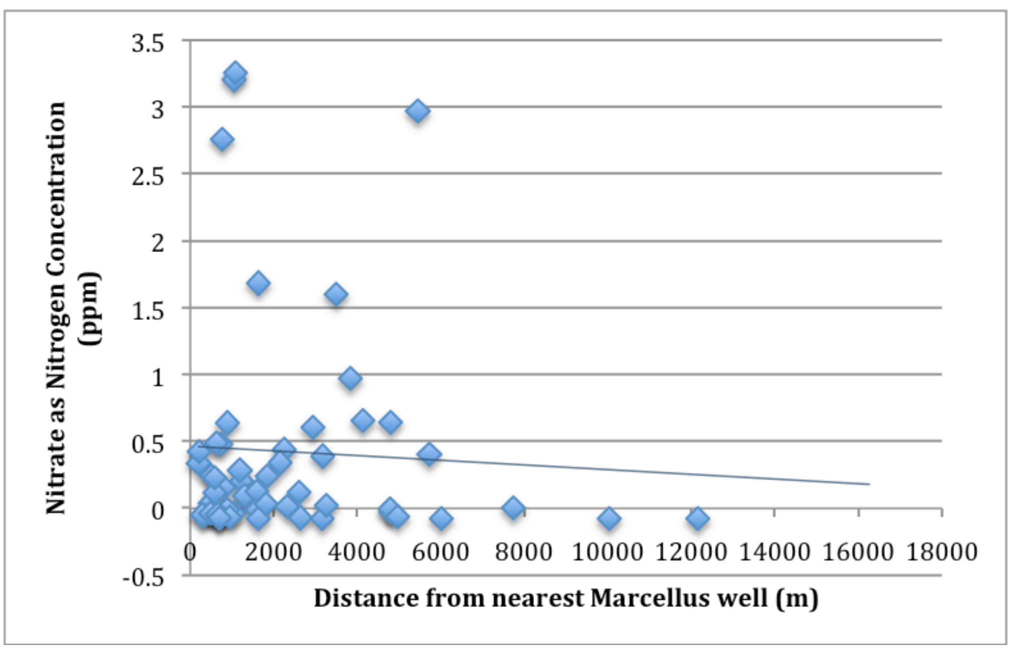

**Nickel Concentration (ppb) by Distance to Gas Well (R-Square = 0.005)**



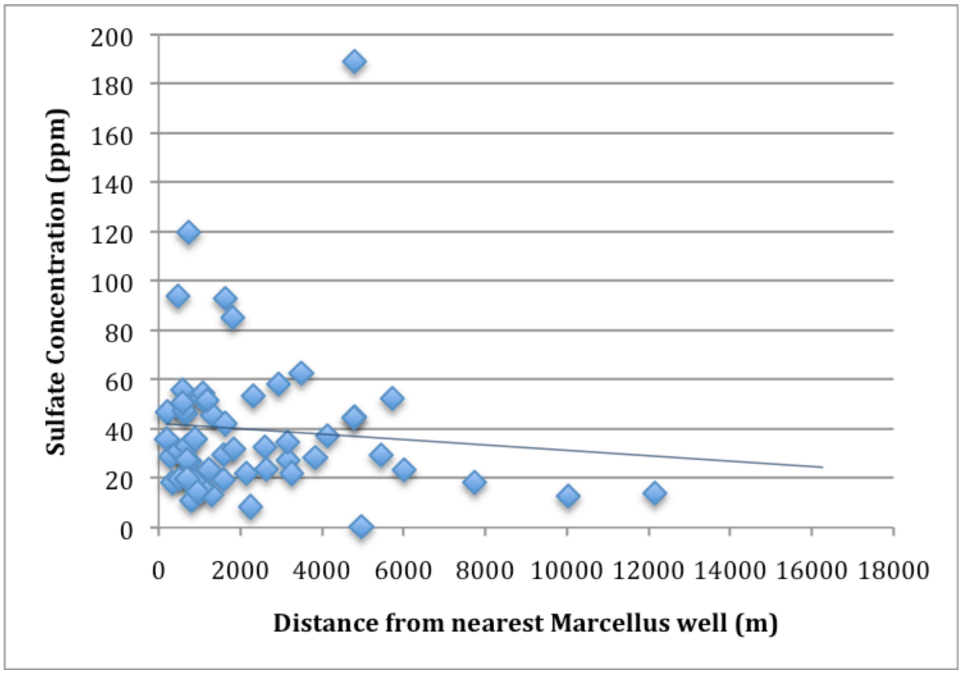

**Tin Concentration (ppb) by Distance to Gas Well (R-Square = 0.023)**




**Zinc Concentration (ppb) by Distance to Gas Well (R-Square = 0.006)**




**Nitrate as Nitrogen Concentration (ppm) by Distance to Gas Well (R-Square = 0.003)**




**Sulfate Concentration (ppm) by Distance to Gas Well (R-Square = 0.008)**