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Investigating Pennsylvania Water Quality Impacts Due to Shale Gas Development

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Abstract

Unconventional drilling techniques such as hydraulic fracturing are being used to extract trapped shale gas. Specifically in Pennsylvania, the Marcellus Shale formation has been estimated to contain 13.8 trillion m^3 of extractable natural gas using hydraulic fracturing. The hydraulic fracturing process can release harmful analytes into pre-existing water supplies ruining the quality of the water. The primary fingerprint analytes associated with unconventional drilling are barium, strontium, and bromide. The Pennsylvania Environmental Protection Agency is responsible for investigating any claims of water diminution related to drilling and issues determination letters which use certified laboratories to analyze collected water samples. This study used the determination letters acquired through open records requests to extract water chemistry values and upload them to CUAHSI HIS. Similarly, industry collected pre-drill data was also uploaded to CUAHSI HIS. Pre-drill data and negative determination letter data were expected to have similar water chemistry concentrations while positive determination letter data was expected to have higher concentrations for the fingerprint analytes. Also, methane was expected to be highest for positive determination letter data. The study showed that positive determination letter data did have the highest average concentrations of barium (2.073 mg/L) and strontium (1.606 mg/L) and negative determination letter data was more similar to pre-drill data. However, average methane concentrations for negative determination letter data (25.720 mg/L) were more similar to positive determination letter data (25.985 mg/L).

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Introduction

The Marcellus Shale

Unconventional drilling methods such as horizontal drilling and hydraulic fracturing are being used to extract natural gas and oil from fractured shale layers. The extraction and subsequent usage of these fossil fuel deposits can lead to permanent environmental damage. Particularly, the unconventional drilling methods used could possibly introduce fracking fluid contaminants and allow the migration of gas into shallow groundwater through fracture passageways ruining water supplies in the vicinity of the drilling operation.

Currently, the Marcellus Shale Formation, located in the Appalachian Basin on the east coast of the United States, contains an estimated 516 trillion cubic feet of this shale gas, of which there is 50% probability that it will yield 13.8 trillion m^3 of natural gas (Penn State 2008). Similarly, the formation could contain a potential of 54 million barrels of oil (Milici 2002). Particularly in northern and western Pennsylvania, the formation and its expansive gas deposits are being extracted using unconventional drilling methods.

The Marcellus Shale formation was previously known to contain natural gas due to previous conventional oil wells drilled in Pennsylvania which penetrated the shale layer and allowed small amounts of natural gas to migrate to the surface (CRS 2009). Similarly, gamma-ray logs were used to find organic rich shales in the subsurface. Organic shales are those where natural gas and oil can be found and are distinguishable from other layers due to high levels of uranium and thorium (Harper 2008). The Marcellus lies in the Appalachian Basin Province formed in the Devonian and is a catskill clastic wedge in Pennsylvania (Milici 2002). The layer varies between 50 and 250 ft thick with the thickest layers containing the most gas.

Natural gas is formed in shale beds by deposition and burial of algae and organisms on the sea bottom. As they decay, the organism and algae release carbon which is converted into hydrocarbons, the building block of oil and natural gas (Sumi 2008). The gas and oil gets trapped in the pores of the shale and becomes trapped within the rock as the layers are deformed and pockets sealed. These pockets of gas and oil lie throughout the Marcellus and account for the bursts of natural gas seen in previous oil drilling operations(CRS 2009). The gas lies in horizontal fractures running through the shale so typical vertical drilling is not ideal for extraction of shale gas since a vertical well would only tap into one portion of the reservoir (King 2012). Instead, horizontal drilling and a process called hydraulic fracturing or fracking are employed to free and extract the trapped fossil fuels.

Hydraulic Fracturing

Fracking was developed in the 1940's as a way to expand well boreholes and to extract fossil fuels from surrounding rock fractures. Fracking uses a fluid consisting of water, proppants, and other chemicals to infiltrate and either expand the pre-existing fractures in the shale layer or induce hydraulic fracture openings. (EIA). Proppants are solid materials such as sand or ceramics used to keep a fracture so that the gas can be extracted. Some of the chemicals used in the fluid are to prevent bacteria growth and to reduce friction.

These chemicals can be harmful so the wells are designed with several safety features to prevent fracking fluid from escaping. The entire well has a telescoping steel casing which directs fluid down to the injection site and funnels the flowback fluid and gas to the surface (King 2012). The steel casing is widest at the surface and goes all the way through the water table.

Cement is then poured down the outside of the casing to ensure that the well is completely sealed. Hydrochloric acid is then poured down the well to smooth the cement borehole to decrease friction (EIA). The seal is very important to prevent the migration of any chemicals from drilling operations into shallow groundwater zones.

One well can require 4-5 million gallons of water over a 2-5 day period of drilling due to the expansive water need in hydraulic fracturing. The water is also used to make drilling mud, which not only lubricates the drill bit also suspends the drill cuttings. This mud's consistency is changed as the depth changes and barium is added to make the mud more dense (CRS 2009). Once the fracking fluid is injected into the ground and it returns to the surface, it is called flowback water and still contains gas. The flowback is contaminated water and must be disposed of according to EPA rules. On average, 60-80% of flowback is recycled and reused for more hydraulic fracturing (1), otherwise, the flowback can be taken to approved sewage facilities or more commonly injected in the ground.

Contamination Issues

However, not all of the flowback fluid used in hydraulic fracturing is fully recovered. Fracking fluids can continue to travel through the fractures in the shale and migrate into the layer outside of the recovery zone (Moinz 2011). If these fluids migrated into a water supply, they could potentially cause harm to an individual consuming the water. Although unconventional drilling provides a method to extract a large fossil fuel deposit, it has its inherent dangers.

First, with horizontal drilling comes a larger area of possible contamination compared to conventional vertical drilling. Chemicals would migrate horizontally in the fractures affecting numerous water supplies (2). However, most wells in the Marcellus formation are a mile deep whereas most residential wells are only hundreds of feet deep. But, faulty well construction such as a leaky casing or faulty concrete seal could allow flowback fluids to enter the subsurface in the same vicinity as residential wells. Along with flowback fluids, gas such as methane can seep through the faulty casing and enter groundwater (R. Vidic 2013).

The construction of the well pad also exposes underlying fractures in the lithology. A spill at the well pad could allow contamination of a shallow ground water supply as chemicals move along the fractures (Brantley 2014). At a well pad, the flowback fluids are stored in an impoundment to either be reused or disposed. Spills and leaks could occur from the impoundment damaging local water (Clark 2009). Similarly, the process of transporting flowback fluids carries a potential risk of vehicle accidents and accompanying leakage(Brantley 2014).

The injection process of flowback fluids is highly regulated and not allowed in many states. In Pennsylvania, five injection wells exist for flowback fluids. However, in Ohio there are hundreds of injection wells. These wells have been connected to minor seismic events (Clark 2009). Flowback fluids are also allowed to be disposed of at properly equipped sewage plants which remove all contaminants. However, some incidents have been reported of ill equipped sewage plants receiving flowback fluids. Also, some states such as West Virginia have very lenient waste disposal laws. In fact, some flowback fluids have been disposed of by being sprayed on land without previous treatment (Finkel 2013).

One of the main indicators of drilling impacting a water supply is an increased level of methane. Methane concentrations above 10 Mg/L can cause the methane to combust as it degasses. Also, in a well, methane can be oxidized which decreasing the overall oxygen level. In anaerobic conditions, bacteria can thrive polluting water (R. Vidic 2013).

Methane is also produced by naturally occurring thermogenic and biogenic processes. These occur within the earth and the released methane travels through hydraulic connections from deeper formations (Laughery 1998). These fugitive methane gasses are unlike those in the Marcellus because the shale traps and prevents the natural gas from leaving. Also, the natural methane and Marcellus methane can be distinguished from one another based on carbon ratios (Molofsky 2011). The elements most commonly used to identify if the degradation of water is related to Marcellus exploration are Na, Cl, Mg, Ca, Ba, Sr, and Br (Warner 2012, Hayes 2009). However; Na, Ca, and Cl are also commonly occurring in natural water so Ba, Br, and Sr are primary indicators (Brantley 2014).

Contamination Investigations

In Pennsylvania, the Pennsylvania Department of Environmental (PADEP) is in charge of processing all complaints due to shale gas drilling. The PADEP publishes all oil and gas production data every six months on their website. The PADEP will also collect a sample of water from a resident's home to test if the water has been contaminated due to drilling activities (Brantley 2014). The PADEP tests the water sample in their lab to compare concentrations of anions, cations, methane, ethane, and general water chemistry parameters of the sample to the safe water drinking standard.

Using the specific analytes mentioned above along with the timing of the impact, distance to well, and the local hydrological features, the PADEP determines if the water is contaminated due to unconventional drilling methods. Before 2012 and Act 13, the site had to be within 1000 feet of a drilling operation and reported within 6 months. The passage of Act 13 increased the distance to 2500 feet and the extended the reporting window to 12 months (Harper 2008). If unconventional drilling is found to have caused the deterioration of water, the PADEP issues a positive determination letter (PDL) and the drill operator is responsible for the restoration of the water to safe drinking water standards or provide an alternate source.

However, sometimes the PADEP establishes that the deteriorated quality of the water is not attributed to unconventional but instead pre-existing conditions such as abandoned coal mines, oil and gas wells or landfills. There is no exact location for all of these sites in Pennsylvania and in some instances, new gas wells have intersected abandoned gas wells and caused blowouts (R. Vidic 2013). These are all potential sources of shallow groundwater contamination and unfortunately affect many residents. Other possible sources of groundwater contamination that could seem like fracking pollution include salt from deicing roads and natural brines migrating from the underlying Salina formation (Rickard 1989).

In an attempt to show that unconventional drilling has not affected local water supplies, some companies are now employing water testing companies to collect pre-drill water samples from residencies near the well. The pre-drill samples serve as a baseline in case a resident files a complaint with the PADEP.

This Study

The present study used the PADEP determination letters and the industry collected pre-drill samples to identify chemical analytes which specifically show deterioration in water quality due to unconventional drilling. Specifically, negative determination letter data were compared to pre-drill and positive determination letter data to show that negative determination letter data were more similar to pre-drill data. Also, the locations of the determination letters and locations of unconventional drilling sites throughout Pennsylvania were compared to see if the number of gas wells influences the number of determination letters.

Experimental Methods

Data Acquisition

Water quality data analyzed was analyzed through certified laboratories. The majority of the data comes from 969 determination letters issued by the Pennsylvania Department of Environmental Protection (PADEP) from 2008-2012 which are accessible online due to an open records requested submitted by L. Legere (Scranton Times-Tribune). The spreadsheets were accessed through the Scranton Times-Tribune website as PDF files. Similarly, additional PADEP determination letters were acquired by an open records request for all determination letters from the North-Central, Northeast and Southwest regional offices of the PADEP. These letters were physical copies and not available online. All addresses and names were redacted to protect privacy so only the townships and counties are used as a spatial location.

In addition to the PADEP determination letters, water quality data collected by oil and gas companies was released to PADEP Office of Oil and Gas Management to be compared to potential post-drill samples. The samples were collected from groundwater wells and surface water (i.e. ponds, springs) on land owned by private entities such as homeowners and businesses before drilling in the region. These pre-drill samples serve as a baseline in case a complaint is filed about deterioration of water quality and quantity. The exact locations of the pre-drill reports were redacted so the sites were placed at the center of their respective township or borough.

Data Formatting

The water quality data and locations had to be formatted before being uploaded to the Consortium of Universities of the Advancement of Hydrologic Science Water Data Center. An Excel spreadsheet template was used as the base for formatting of all datasets. Table M1 shows all of the information required for upload.

Table M1: The layout of the spreadsheet used for data upload. Each column represents a page on the spreadsheet.

Sources Page	Sites Pages	Variables	Data Values
Organization	SiteCode	VariableCode	SiteCode
Source Description	SiteName	VariableName	Date
Source Link	Latitude	Speciation	Time
Phone	Longitude	VariableUnitsName	OffsetValue
Email	County	SampleMedium	VariableCode
Address	SiteState	ValueType	DataValue
City	LatLongDatumSRSName	IsRegular	MethodDescription
SourceState	Causality	TimeSupport	LocalDateTime
ZipCode	Comments	TimeUnitsName	UTCOffset
Citation		DataType	OffsetUnitsName
TopicCategory		GeneralCategory	OffsetDescription
Title		NoDataValue	SourceID
Abstract			QualityControlLevelID
ProfileVersion			CensorCode
MetadataLink			Comments

The sites tab contains all spatial information for each site. The site code is a unique name given to one spreadsheet. No two spreadsheets have the same site code. Next, the site name is based on the source of the data. For online PADEP reports, the site name is the local municipality and the corresponding PDF number from the Legere report so that a user could access the original water chemistry report (http://thetimes-tribune.com/). For all other PADEP reports that were not online, the site name is just the municipality name.

For all PADEP reports with a description of the collection area (i.e. sink, pond, basement), the site name also contained the collection point. Some reports had numerous collection locations and each collection point was treated as a separate site. Similarly, for all PADEP reports, the latitude and longitude on the sites page was reported as the location of the center of the municipality (i.e. township, borough) since exact addresses were redacted.

Private pre-drill water quality reports were assigned a site code based on their legal number. Site names were the municipality name followed by the corresponding test company and their collection sample identification number. The latitude and longitude for these sites were provided within the sample collection report but were redacted to 3 decimal places. All sites also had their respective states and counties uploaded as well as the datum used. For all locations, WGS 1984 was the projection used.

The sites page contained an added category, causality, which noted if the determination letters issued by the PADEP were positve, negative, or still under investigation.

The variables tab describes analytes in the reports and how they were measured. The following categories are CUAHSI controlled Vocabulary: variable name, variable units name, sample medium, value type, data type, and general category. The words used in these columns had to adhere to strict formatting rules or the data would not be uploaded. The variable code described the type of water (GW for groundwater and SW for surface water) and an abbreviation for what was measured. The variable name not only describes what was measured but also in which manor. For examples, rather than just alkalinity being the variable name, alkalinity is described as either bicarbonate or carbonate.

The units name was specified based on each report since the analysis labs did not report the same units form similar tests. The sample medium was either groundwater or surface water. The data type was sporadic for all measurements since when sample was collected it was collected at a single time not in a logger format. Also, the general category was water quality for all reports since the samples were water.

Finally, with all analytes described and identified, the sites and their respective variables were joined on the data values page. Along with the site code, the date and time of collection are on the data values page. The variable code from the variables page is then followed by the data value provided by the reports. No units are on the page since they are contained in the variables sheet. Next, the method description for each analyte was reported. These descriptions are recognized practices and allow a data user to see how the sample was analyzed. The local date and time of each laboratory test were included. Some tests such as pH and temperature are time dependent so the time between analysis and collection affects the results.

The data values page also contains two CUAHSI controlled vocabulary categories; Quality-Control-ID and Censor-Code. The Quality-Control-Level-ID describes the analysis method with 1 representing a certified laboratory. Both PADEP determination letters and pre-drill samples were designated a Quality-Control-Level-ID of 1 for this study since they were analyzed in certified labs. The Censor-Code represents whether the data value is measured or below detection limit. For analytes reported because they were below detection limit, the Censor-Code was designated 'LT' meaning less than. For analytes, which had true values reported; the censor code was reported as 'NC' for not censored. Some concentrations were reported as greater than a detection limit and were designated with a Censor-Code of 'GT'.

Analyzing the Data

From the collection of water quality reports now digitized, analysis of the data values was streamlined. The data values pages was able to be sorted based on location of collection, variable type, causality, etc in attempts to find similarities in sites which show diminution of water quality due to drilling. The data was analyzed with Microsoft Excel.

The data values were also uploaded to ArcMap 10.1 so that the spatial location of the reports could be compared to the locations of current conventional/unconventional drilling wells and known coal mines. These shapefiles were preexisting and accessible through the ArcGIS catalog. The sites were uploaded to the map so that upon clicking on a point on the map, all uploaded water quality data is accessible.

Results

In this study, we obtained data from 303 Pennsylvania DEP determination letters. Of these, 67 were positive determinations, 221 were negative determinations, and 15 were unknown (Figure 1). From these letter, 2125 water chemistry values were extracted for 38 variables from the letters and 1603 were non-censored (actual values). Table 2 summarizes the 38 parameters that were analyzed. Some data were censored because the analyzed values were below the detection limits of the analytical method. Of the non-censored values, 359 were from positive determination letters and 1244 were from negative determination letters (Figure 2). The PDLs represented 29 townships within 9 counties; likewise the NDLs represented 101 townships within 22 counties. Tables 3 and 4 summarize the counties and townships along with the relevant number of PDLs and NDLs.

The pre-drill water chemistry reports provided a total of 1166 values of analytes, 152 from surface water samples and 1014 from ground water samples. Of these, 73 of the surface water values were non-censored and 467 ground water values were non-censored (Figure 3). The pre-drill data derived entirely from Bradford County and represents 3 townships (Table 4)

A positive correlation exists between the number of positive and negative determination letters per locality with an R^2 value of 0.89 (Figure 4). The counties with the most total determination letters were Bradford and Susquehanna in northern Pennsylvania (Table 3). The county with the highest ratio of PDLs to NDLs was Lycoming county with 10 PDLs and 12 NDLs. The location of all sites is shown on map 1 (each determination letter was plotted as a point centered in the township where the samples derived). The map shows most of the determination letters were from areas in northern and western Pennsylvania with the most positive determinations in northeast Pennsylvania. A poor correlation exists between the number of shale gas wells in a county versus the number of positive determination letters, R^2 value equals 0.539 (Figure 5).

Barium and chloride concentrations from PADEP determination letters show that affected locations have the highest concentrations of barium and chloride (Figure 6a). Some negative determination sites have high barium concentrations but their respective chloride concentrations are low. Similarly, negative determination sites with high chloride concentrations have low barium concentrations. The R^2 value for positive determination letters, 0.6835, shows a stronger correlation for barium and chloride for positive determination sites than negative determination letters (R^2=0.0344)

Pre drill barium and chloride concentrations are very low for both groundwater and surface water (Figure 6b). When plotted on the same graph as NDLs and PDLs, the pre drill data is all located near the origin (Figure 6c). The NDL barium mean, 0.655 Mg/L, is more similar to the pre-drill groundwater barium mean, 0.119, than the PDL barium mean, 2.139 Mg/L. PDLs also had the highest mean chloride concentration, 91.674 Mg/L (Table 5).

A positive correlation exists between barium and total dissolved solids for positive determination sites (Figure 7a) with an R^2 value of 0.6081. Negative determination letters and pre-drill data did not show a correlation between barium and total dissolved solids (Figure 7a & 7b) . The mean barium concentration was greatest for PDLs (2.139 Mg/L). Pre-drill data and NDLs had similar mean barium concentrations, 0.128 and 0.687 Mg/L respectively (Table 6).

The positive correlation between magnesium and manganese for positive determination locations had a R^2 value of .6002 (Figure 8a). Negative determination data had the highest concentrations of both magnesium and manganese. But the data is more sporadic than and not as linear as the positive determination data. The pre drill data had higher concentrations of magnesium than either of the PADEP report types (Figure 8b). PDLs had the lowest mean manganese concentrations, 0.132 Mg/L (Table 7).

Surface and groundwater pre drill data show very small concentrations of both chloride and TDS (Figure 9a). Pre drill average TDS concentrations were more similar to average NDLs TDS concentrations, 286.083 Mg/L and 374.982 respectively, than PDL average TDS concentrations 567.5 Mg/L (Table 8). PDL data showed a positive correlation between chloride and TDS with a R^2 value of 0.9856 (Figure 9c).

Pre-drill data (Figure 10a) had the lowest mean concentrations of chloride (20.841 Mg/L) and sodium (24.526 Mg/L). These means were similar to NDL means (figure 10b); chloride (30.063 Mg/L) and sodium (41.101 Mg/L). PDLs had the highest chloride and sodium mean concentrations, 92.585 Mg/L and 74.789 Mg/L respectively (Figure 10c). Pre-drill data had the highest mean concentrations of calcium (52.44 Mg/L), magnesium (14.087 Mg/L), and sulfate (22.039 Mg/L). PDL data had the lowest average concentrations of calcium (23.042 Mg/L), magnesium (6.473 Mg/L), and sulfate (15.0 Mg/L) (Table 9).

As before, pre drill data had low chloride concentrations and high sulfate concentrations (Figure 11a). NDL data was censored for values below 15 Mg/L sulfate but some concentrations did exceed the detection limit (Figure 11b). PDL data was also censored for value below 15 Mg/L but had no locations above this detection limit (Figure 11c).

Plotting Ba/Cl concentrations vs Br concentrations for PDLs did not provide a correlation as seen in previous studies (Figure 12). Positive determination letters had the highest ratios of barium to chloride. The highest ratio of Ba/Cl also has the highest bromide concentration. Negative determination data had low Ba/Cl ratios.

Methane and ethane PADEP data (Figure 13) did not show a corresponding relationship with positive determination letters. The highest mean methane and ethane concentrations were from negative determination letters, 34.232 Mg/L and 24.490 Mg/L respectively (Table 10), and the highest values for each correspond to the same site. Pre drill sites never yielded ethane concentrations above the detection limit even when methane concentrations were measureable.

In order to compare commonly associated unconventional drilling analytes, histograms consisting of all values (censored and non-censored) for each type of reports (positive determination, negative determination, pre drill) were constructed. On the histograms, a green bar represents the EPA primary or secondary safe drinking limit (noted in the caption) with values to the right of the green bar exceeding the limit.

No safe drinking water limit exists for calcium concentrations (Figures 14a, 14b, & 14c). For all reports, the average calcium concentration was similar. Pre-drill data had the highest mean concentration, 44.425 Mg/L, and NDLs had the lowest average concentration, 35.998 Mg/L.

Pre-drill data showed the largest sulfate concentrations with a mean value of 20.077 Mg/L. (Figure 15a). Pre-drill data were the only report type to contain sulfate concentrations less than 15 Mg/L. NDL data showed most values were censored giving a high frequency at the detection limit of 15 Mg/L (Figure 15b) and had an average of 18.133 Mg/L. NDL data had sulfate concentrations greater than 15 Mg/L. PDL data was all censored, therefore only reported at 15 Mg/L (Figure 15c) with no values exceeding as seen in NDLs.

Pre-drill data had 11% and NDLs had 8%% of their strontium concentrations greater than 4 Mg/L the established safe drinking limit (Figures 16a & 16b). The highest frequency of strontium concentrations of NDLs and pre drill reports was at greater than 0.5 Mg/L but less than 1 Mg/L, 40% and 32% respectively. PDLs had the highest frequency for strontium concentrations with 31% of data values greater than or equal to 4 Mg/L (Figure 16c). PDLs had the highest mean strontium concentration, 1.606 Mg/L. Pre-drill average strontium concentration, 0.634 Mg/L, is not similar to the NDL average strontium concentration, 1.337 Mg/L.

Pre-drill data had 65% of its sodium concentrations to be greater than 20 Mg/L, the EPA safe drinking limit (Figure 17a). NDLs had 71% of its total values greater than 20 Mg/L sodium (Figure 17b). PDLs had 82% of its values greater than the safe drinking limit (Figure 17c). The average pre-drill sodium concentration, 32.43 Mg/L, was not similar to the mean NDL sodium concentration, 116.041 Mg/L. The average NDL sodium concentration was greater than the average PDL sodium concentration of 96.94 Mg/L.

The mean pre-drill manganese concentration was 0.2 Mg/L which is greater than the EPA secondary safe drinking limit of 0.05 Mg/L (Figure 18a). Pre-drill average was similar to the NDL manganese average, 0.419 Mg/L (Figure 18b), and less than the PDL mean value (Figure18c), 0.789 Mg/L.

The safe drinking limit for magnesium is 125 Mg/L and no values were greater than this limit. Pre drill data has the greatest frequency of values greater than 12 Mg/L (figure 19a) and a mean of 2.508 Mg/L. NDLs had the second highest frequency (Figure 19b) and mean (9.98 Mg/L), and PDLs had the least values greater than 12 Mg/L and the smallest mean (6.473 Mg/L) (Figure 19c).

The pre-drill average iron concentration, 1.188 Mg/L (Figure 20a), was similar to the NDL average iron concentration, 7.127 mg/L (Figure 20b). The average PDL iron concentration was 42.129 Mg/L (Figure 20c). All reports had means which were higher than the EPA secondary safe drinking limit of 0.3 Mg/L of iron.

Pre drill data had no chloride concentrations greater than the safe drinking limit of 250 Mg/L (Figure 21a). NDL data had 26% of chlorine concentrations greater than 250 Mg/L (Figure 21b) and PDLs had a 36% frequency of concentrations greater than 250 Mg/L (Figure 21c). Pre-drill data had the lowest mean chloride concentration, 14.955 Mg/L. NDL data had a higher mean chloride concentration, 99.740 Mg/L. PDL data had a mean chloride concentration of 266.782 Mg/L, so pre-drill and NDL average chloride concentrations are more similar than NDL and PDL average chloride concentrations.

The EPA safe drinking limit for methane is 28 Mg/L, but the PA DEP warns homeowners of methane concentrations greater than 7 Mg/L. The pre drill data had no methane concentrations greater than 28 Mg/L, but did have 17% of its values above 7 Mg/L (Figure 22a). The NDL data had 29% of its concentrations greater than 28 Mg/L and 72% of concentrations greater than 7 Mg/L (Figure 22b). PDLs had 27% of its methane concentration greater than 28 Mg/L and 93% of its methane concentrations greater than 7 Mg/L (Figure 22c). NDL and PDL average methane concentrations, 25.720 Mg/L and 25.985 Mg/L, did not show a substantial difference. The pre-drill average methane concentration was 2.323 Mg/L and not comparable to NDL data.

For bromide concentrations, NDL data had the greatest mean at 2.066 Mg/L (Figure 23b). The average pre-drill bromide concentration was 0.75 Mg/L (Figure 23a) and the average PDL concentration was 0.514 Mg/L (Figure 23c). The average pre-drill concentration was closer to the PDL average than the NDL, therefore, in this study, Br is not a distinct indicator of water contamination due to unconventional drilling.

Pre drill data had no barium concentrations greater than the safe drinking limit of 2 Mg/L (Figure 24a) and an average concentration of 0.335 Mg/L. The average NDL barium concentration was 1.492 Mg/L (Figure 24b) which was closer to the PDL average barium concentration, 2.073 Mg/L (Figure 24c), than the pre-drill average.

Pre drill data had 6% of its TDS concentrations above the EPA secondary safe drinking limit of 500 Mg/L (Figure 25a). NDL and PDL data had similar frequencies of TDS concentrations above the secondary safe limit at 24% and 26% respectively (Figures 25b & 25c). Both positive and negative determination letter data show over 50% of TDS concentrations less than the secondary safe limit.

Discussion

Data from positive determination letters showed the highest average concentrations of strontium (1.606 Mg/L), sodium (96.594 Mg/L), manganese (0.789 Mg/L), iron (42.129 Mg/L), total dissolved solids (527.737 Mg/L), chloride (266.782 Mg/L), and barium (2.073 Mg/L) than negative determination letter data or pre-drill data. Previous work showed the likely detection mode of fracking fluids is through the analysis of inorganic compounds such as sodium, chloride, barium, strontium, and bromide (Vidic et al. 2013). Elevated sodium and chloride concentrations are related to salts and are common; so barium, bromide, and strontium are used as Marcellus fingerprint analytes (Brantley et al 2013).

Negative determination sites did have high concentrations of sodium and chloride concentrations which can possibly be attributed to natural brines (Warner et al 2012) rather than unconventional drilling. Positive determination sites had the highest overall means of both sodium and chloride along with elevated levels of fracking related analytes (Ba, Sr, TDS) distinguishing them from negative determinations.

Positive determination data had the highest mean concentration for all of these except bromide. Positive determination letter data had the lowest mean bromide concentration (0.514 Mg/L). Negative determination sites did have examples of sites with elevated concentrations of these analytes, but NDL average concentrations were more similar to pre-drill data which was unaffected by unconventional drilling .

In this study barium and strontium are primary indicators of a drilling caused water diminution. But, Iron, manganese, and total dissolved solids had the highest means for PDL data as well and have been shown to be a possible source of diminution (Brantley et al 2013). When compared to one another, positive determination letter data showed a positive correlation for barium versus chloride, barium versus total dissolved solids, and chloride versus total dissolved solids.

Methane mean concentrations were highest for positive determination letter data (25.985 Mg/L). The mean methane concentration for negative determination letter data (25.720 Mg/L) was much greater than the pre-drill average concentration (2.323 Mg/L). A study of 60 groundwater wells in northern Pennsylvania showed that methane concentrations were higher when sampled within one kilometer of an active Marcellus well (Osburn et al. 2011).

Schon 2011 refuted this study saying elevated methane are not an inevitable effect of drilling because the samples with elevated methane had no hydraulic fracturing fluids in their samples. High methane concentrations seen in negative determination letter data could be caused by the migration of stray thermogenic and biogenically driven methane rather than fracking fluid seepage (Jackson et al 2013).

Positive determination letter data had the lowest mean concentration of sulfate with no values greater than 15 Mg/L. The mean negative determination letter sulfate concentration (18.133 Mg/L) was similar to the pre-drill average sulfate concentration (20.077 Mg/L). Sites with impacted water due to unconventional drilling have been showed to have low sulfate concentrations as it possibly combined with iron to make pyrite or interact with calcium or other alkaline earth elements (Barbot 2013).

Some believe that the PADEP has incorrectly issued negative determinations for locations which in fact were affected by unconventional drilling. In 2011, the PADEP realized there were inconsistencies in which reports were issued so after 2011, all determinations had to be approved by central adminatiraion (Brantley et al 2013). Of the 1603 uncensored determination letter concentrations, 592 were before 2011. The negative determination letter sites that have high concentrations of barium and strontium from before 2012 could have been wrongly classified.

Possible errors exist in the concentrations and accompanying means for comparison graphs. These figures were made for sites which had both of the analytes on the graph. For example, for the methane and ethane graph, if a site had a methane value but no ethane value, it was not included in the graph. The histograms however include all non-censored data for a report type unless otherwise noted. Therefore, the mean concentration for a graph might not be the same mean for a histogram.

Conclusions

Unconventional drilling fluids from hydraulic fracturing processes in the Marcellus Shale formation in northern and western Pennsylvania has been linked to diminished domestic water supplies in the vicinity of the well. These possible diminution claims are investigated by the Pennsylvania DEP (PADEP). Sites which were identified to have diminished water quality due to unconventional drilling showed the highest concentrations of barium and strontium as hypothesized, however the positive determination data did not have the highest average bromide concentration as expected.

Negative determination letter data showed mean concentrations of sulfate, strontium, manganese, magnesium, iron, and chloride which were more similar to mean values from pre-drill data rather than positive determination letters. The mean barium concentration was higher for NDL data compared to pre-drill data, but was possibly skewed due to outliers

Histograms created for each type of data source (positive/negative determination letters, pre-drill) for several analytes also show that the distribution of concentrations for negative determination data is more similar to pre-drill data then positive determination data. However, negative determination letter data did have a mean methane concentration similar to positive determination letter data but natural migration of methane could attribute for these values. The natural methane can be distinguished from fracking related methane based on the composition, but all methane concentrations were provided and not analyzed for the different weights of elements.

The Marcellus Shale formation is estimated at 50% probability to yield 13.8 trillion m^3 of natural gas (Engelder). This formation underlies ~70% of Pennsylvania and could supply the United States' current demands for decade (Brantley et al 2013). Natural gas is a relatively clean energy source and can help shift dependence from coal to a renewable energy while reducing the emissions of carbon dioxide.

The advancements in horizontal drilling make the extraction of natural gas from the shale deposit economically feasible (Vidic et al 2013) and reduce the support on foreign supplies.

Figures

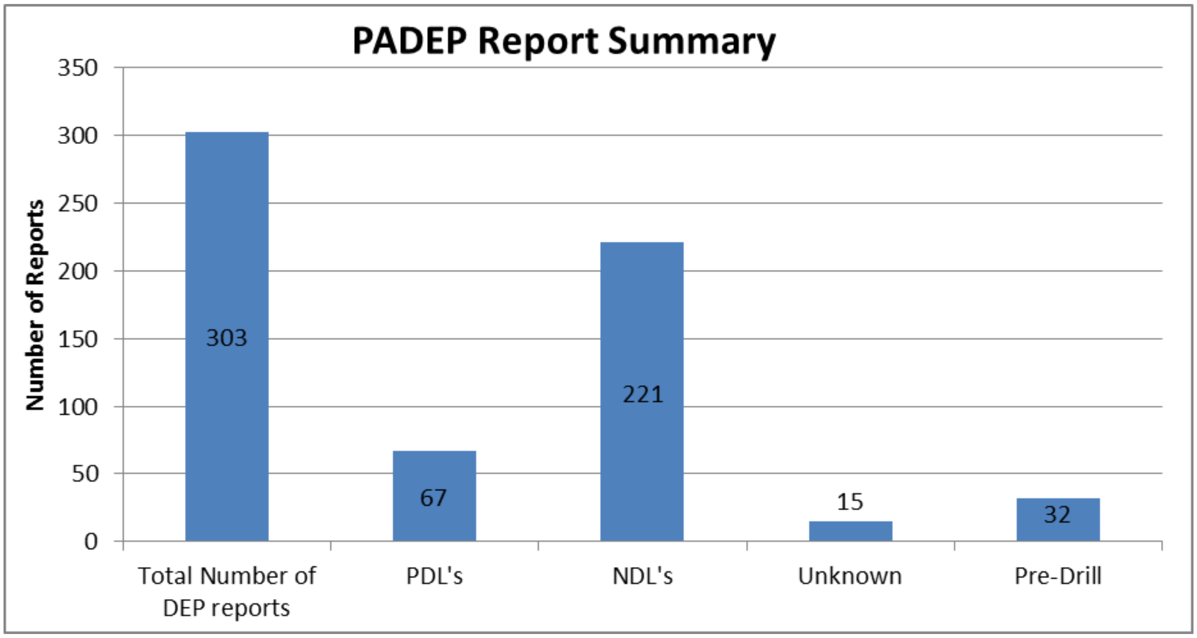


Figure 1: The number of each type of reports that were used to gather data and the type of determination (negative or positive).

Table 2: The 38 possible parameters from the determination letters and pre-dril reports used in analysis

Alkalinity, total	Propane, dissolved
Aluminum, total	Selenium, total
Arsenic, total	Sodium, total
Barium, total	Solids, total dissolved
Bromide, total	Solids, total suspended
Calcium, total	Specific conductance
Chloride, total	Strontium, total
Coliform, total	Sulfate, total
E-coli	Turbidity
Ethane, dissolved	Zinc, total
Hardness, total	Ethylene, dissolved
Iron, total	Nitrogen, nitrate (NO3)
Lithium, total	Sulfur
Magnesium, total	Phosphorus, total
Manganese, total	Osmotic pressure
Methane, dissolved	Nitrogen, NH3
Methylene blue active substances	BOD5
pH	Boron, total
Potassium, total	Nitrogen, nitrite (NO2) + nitrate (NO3)

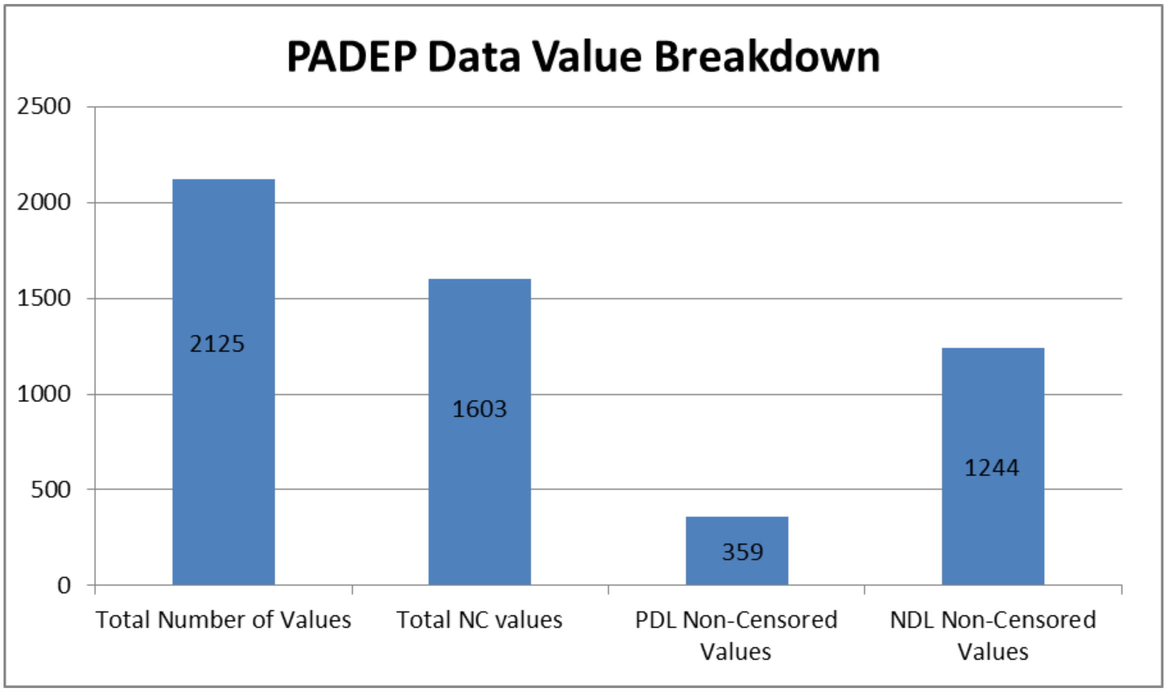


Figure 2: The number of data points acquired from the PADEP reports along with information as to whether the data were censored or uncensored.

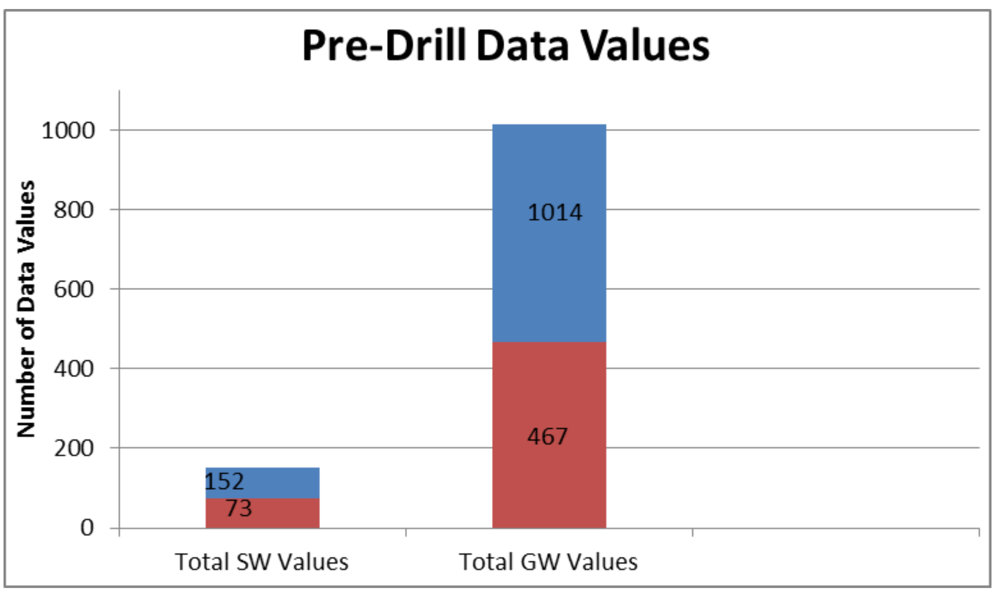


Figure 3: The number of data points acquired from pre-drill reports (blue bars) versus the number of non-censored values from the pre-drill reports (red bars).

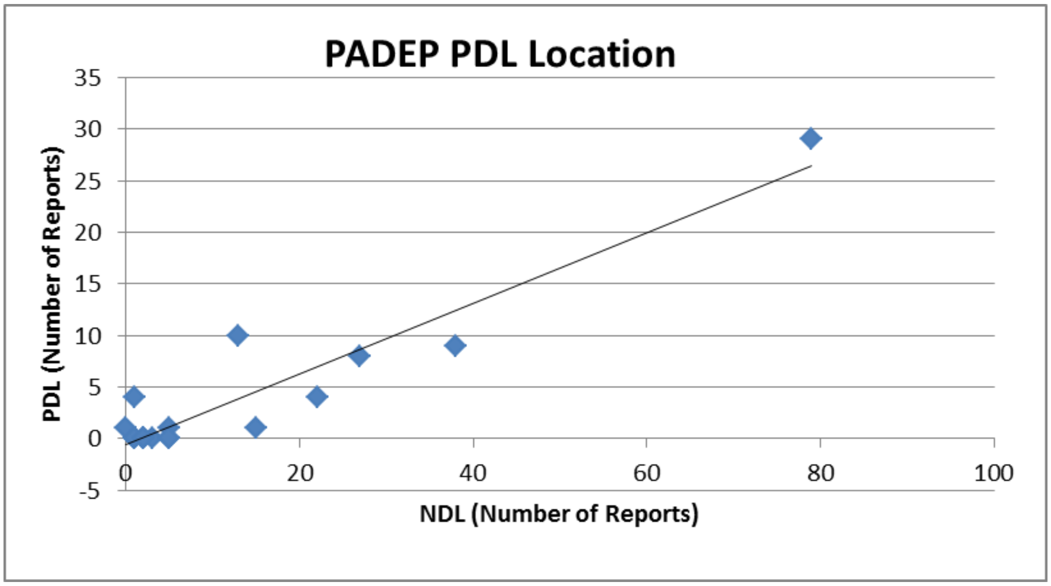


Figure 4: The number of PDL's for a given county graphed against the number of negative determinations letters for the same county. The slope equals <u>0.3413</u> and the R^2 value is <u>0.8912.</u>

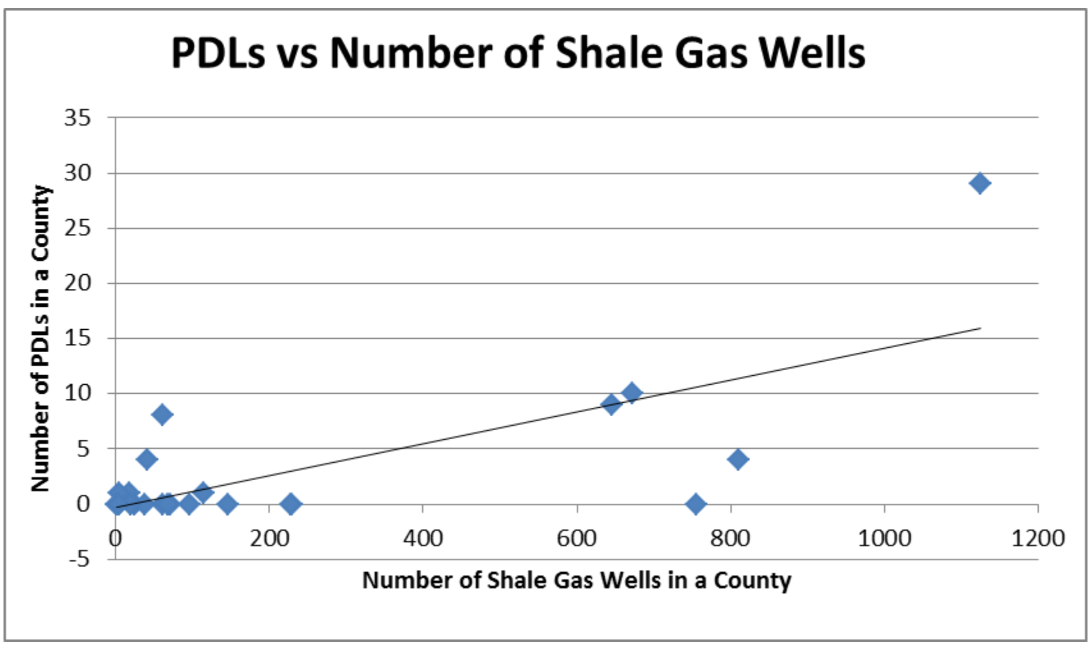


Figure 5: The number of PDLs in a county versus the number of shale gas wells in that county as of 2012. The R^2 value is <u>0.539</u> and the slope is <u>0.0145.</u>

Table 3: The number of PADEP determination letters from each county and the number of shale gas wells (2012). Where no indication was given in a letter as to whether it was a positive or negative determination, it is noted as unknown.

County	Total Numer of Sites	PDL	NDL	Unknown	Shale Gas Wells
Bradford	108	29	73	6	1125
Forest	1	1	0	0	18
Indiana	5	4	1	0	41
Lycoming	23	10	12	1	673
McKean	35	8	27	0	61
Susquehana	47	9	36	2	646
Tioga	26	4	18	4	811
Warren	6	1	5	0	4
Wyoming	16	1	13	2	114
Armstrong	1	0	1	0	146
Beaver	2	0	2	0	25
Clarion	1	0	1	0	24
Clinton	1	0	1	0	97
Crawford	5	0	5	0	2
Elk	2	0	2	0	61
Fayette	1	0	1	0	230
Jefferson	2	0	2	0	38
Lackawanna	1	0	1	0	2
Lawrence	1	0	1	0	19
Mercer	3	0	3	0	5
Potter	5	0	5	0	71
Sullivan	2	0	2	0	68
Washington	5	0	5	0	756
Wayne	2	0	2	0	4
Westmoreland	2	0	2	0	227

Table 4: Number of NDLs, PDLS, unknown, and pre-drill reports for each township and county.

County	Township	PDL	NDL	Unknown	Pre-Drill
Armstrong	Plumcreek	0	1	0	
Beaver	Hanover	0	1	0	
	New Sewickely	0	1	0	
Bradford	Alba Boro	4	2	0	
	Armenia	0	0	1	
	Asylum	1	7	0	
	Herrick	1	3	1	
	Leroy	4	1	0	
	Monroe	1	2	0	
	Burlington	0	4	1	
	Orwell	3	3	0	
	Smithfield	2	1	0	
	Granville	0	9	1	
	Terry	2	3	0	
	Albany	0	1	0	
	Columbia	0	1	0	
	Franklin	0	1	0	
	Litchfield	0	6	0	

	North Towanda	0	2	0	
	Rome	0	2	0	
	Sheshequin	0	3	0	
	Stevens	0	1	0	
	Towanda	0	2	0	4
	Ulster	0	2	0	
	Warren	0	3	0	
	Windham	0	2	0	
	Wyalusing	0	6	0	2
	Wysox	0	3	0	
	Springfield	0	0	1	
	Troy	1	0	0	4
	Tuscarora	2	2	0	
	West Burlington	6	0	0	
	Wilmot	2	1	1	
Clarion	Limestone	0	1	0	
Clinton	Leidy	0	1	0	
Crawford	East Fallowfield	0	1	0	
	Greenwood	0	1	0	

	Randolph	0	1	0	
	West Meade	0	1	0	
	Woodcock	0	1	0	
Elk	Highland	0	1	0	
	Jones	0	1	0	
Fayette	Franklin	0	1	0	
Forest	Hickory	1	0	0	
Indiana	Cherryhill	1	0	0	
	Rayne	0	1	0	
	East Wheatfield	1	0	0	
	WestMahoning	1	0	0	
	WestPikeRun	1	0	0	
Jefferson	Eldred	0	1	0	
Lackawanna	Greenfield	0	1	0	
Lawrence	Scott	0	1	0	
Lycoming	Moreland	10	3	1	
	Upper Fairfield	0	1	0	
	Wolf	0	3	0	
	Penn	0	1	0	
	Franklin	2	0	0	

	Cogan House	0	2	0	
McKean	Bradford	6	10	0	
	Westmore	0	5	0	
	Liberty	0	3	0	
	Eldred	0	1	0	
	Corydon	0	2	0	
	Foster	2	6	0	
Mercer	Delaware	0	1	0	
	South Pymatuning	0	1	0	
	West Salem	0	1	0	
Potter	Bingham	0	1	0	
	Oswayo	0	1	0	
	Sylvania	0	1	0	
	Uslysses	0	1	0	
	West Branch	0	1	0	
Sullivan	Forks	0	2	0	
Susquehana	Bridgewater	1	0	0	
	Apolacon	0	1	0	
	Rush	0	2	0	
	Silver Lake	0	1	0	
	New Milford	0	2	0	

	Franklin	0	7	0	
	Springville	0	5	1	
	Auburn	0	6	0	
	Brooklyn	0	3	0	
	Dimock	1	2	1	
	Jessup	3	0	0	
	Lenox	4	7	0	
Tioga	Charleston	2	1	0	
	Covington	0	1	1	
	Richmond	0	2	1	
	Putnam	0	1	0	
	Lawrence	0	0	1	
	Jackson	0	1	0	
	Farmington	0	1	0	
	Delmar	0	5	1	
	Clymer	0	2	0	
	Brookfield	0	1	0	
	Union	2	3	0	
Warren	Sheffield	1	0	0	
	Triumph	0	2	0	
	Columbus	0	1	0	
	Brokenstraw	0	2	0	

Wyoming	Meshoppen	1	3	0	
	Laceyville	0	1	0	
	Lemon	0	3	0	
	Mehoopany	0	2	0	
	Nicholson	0	1	2	
	Washington	0	1	0	
	Windham	0	2	0	
Washington	Amwell	0	1	0	
	Cross Creek	0	1	0	
	Mt Pleasant	0	2	0	
	West Bethlehem	0	1	0	
Wayne	Damascus	0	1	0	
	Manchester	0	1	0	
Westmoreland	Derry	0	1	0	
	South Huntingdon	0	1	0	
	Oliver	0	1	0	

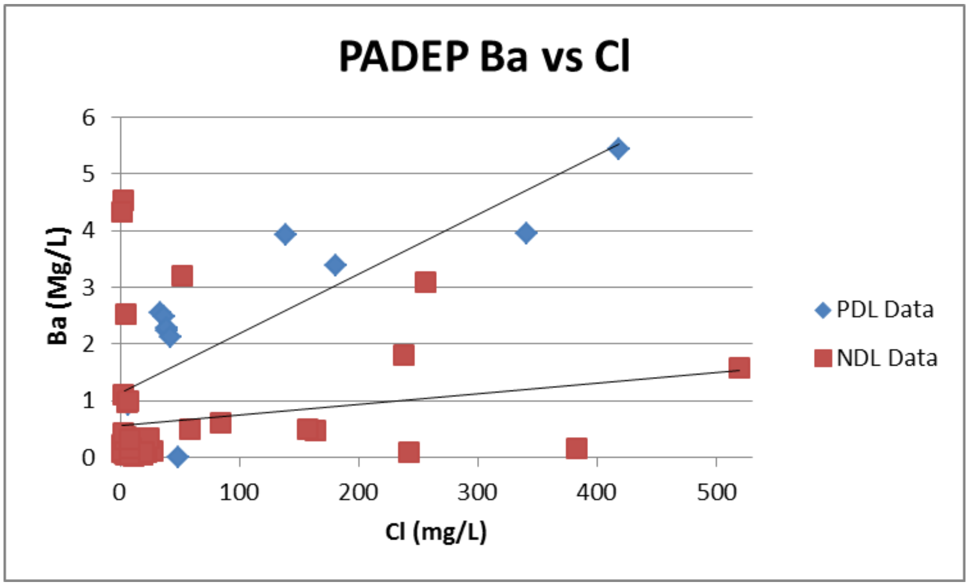


Figure 6a: Non-censored barium and chloride data from PADEP positive (blue) and negative (red) determination letters. The R^2 value for the PDLs is 0.6835 and the slope is the R^2 value for the NDLs is 0.0344.

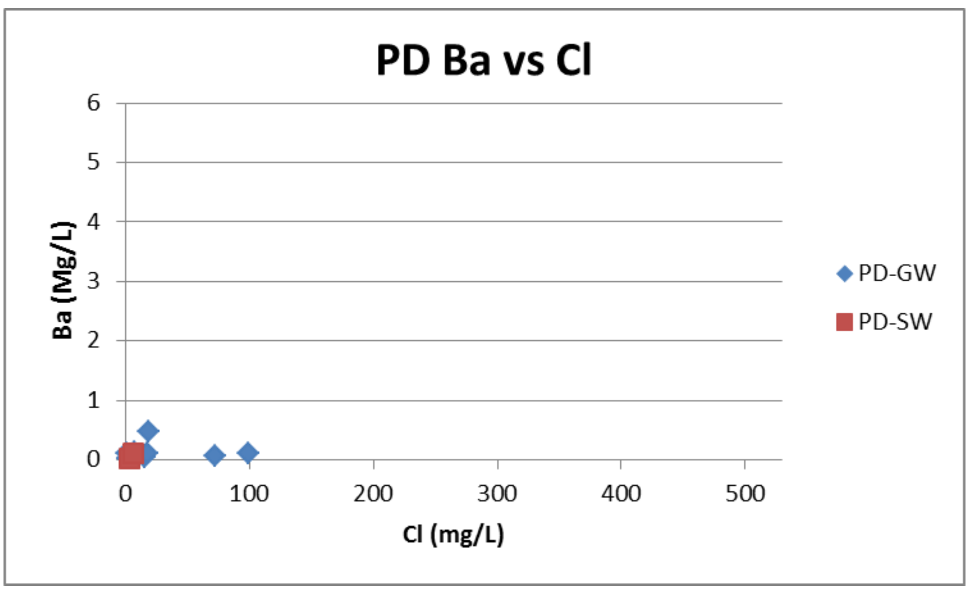


Figure 6b: Non-censored barium and chloride data from pre-drill data plotted on same scale as PADEP PDL above. Groundwater and surface water are plotted separately as shown in legend.

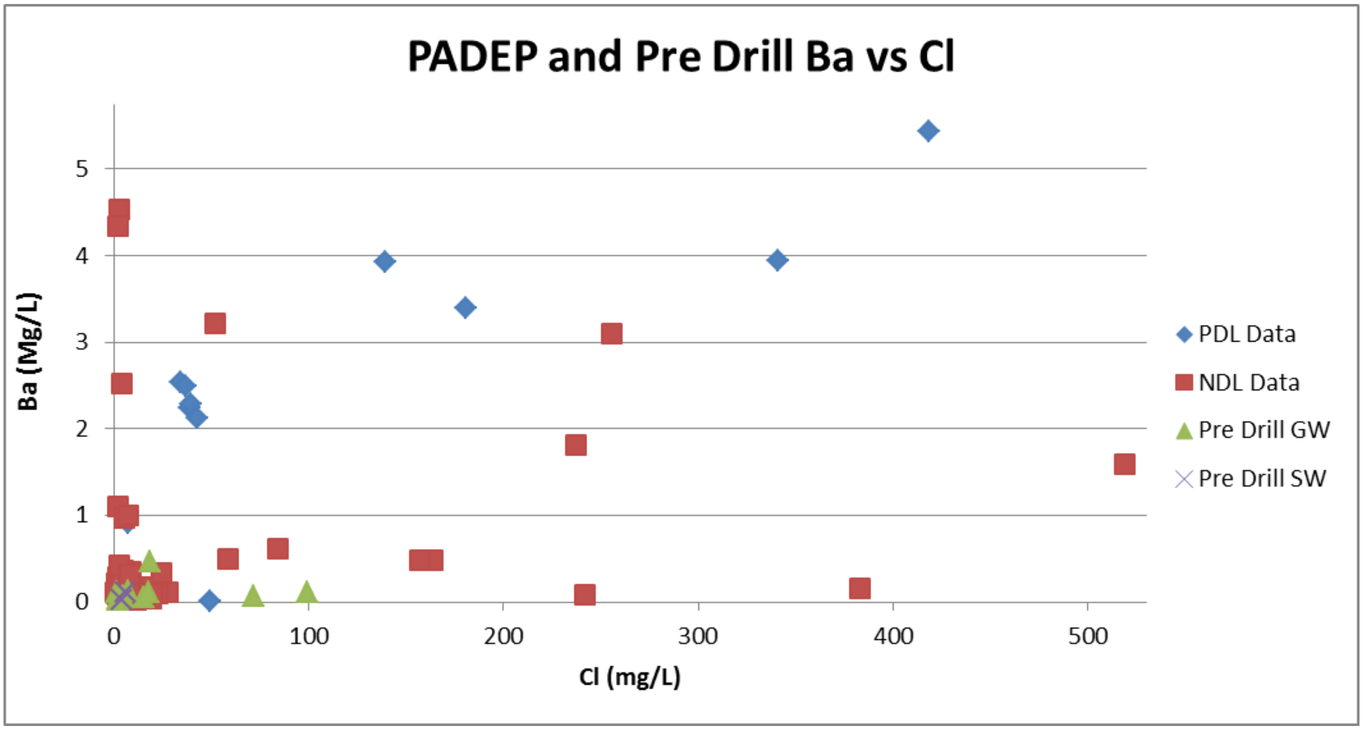


Figure 6c: The two previous plots combined to show the difference between pre-drill and post drill data spreads.

Table 5: The means and standard deviations for barium and chloride data used in correlation.

Report Type	Mean Ba (mg/L)	STD DEV	Mean Cl (mg/L)	STD DEV
PADEP PDL	2.139	1.614	91.674	126.549
PADEP NDL	0.655	1.057	48.910	104.464
Pre-Drill Groundwater	0.119	0.124	24.035	31.953

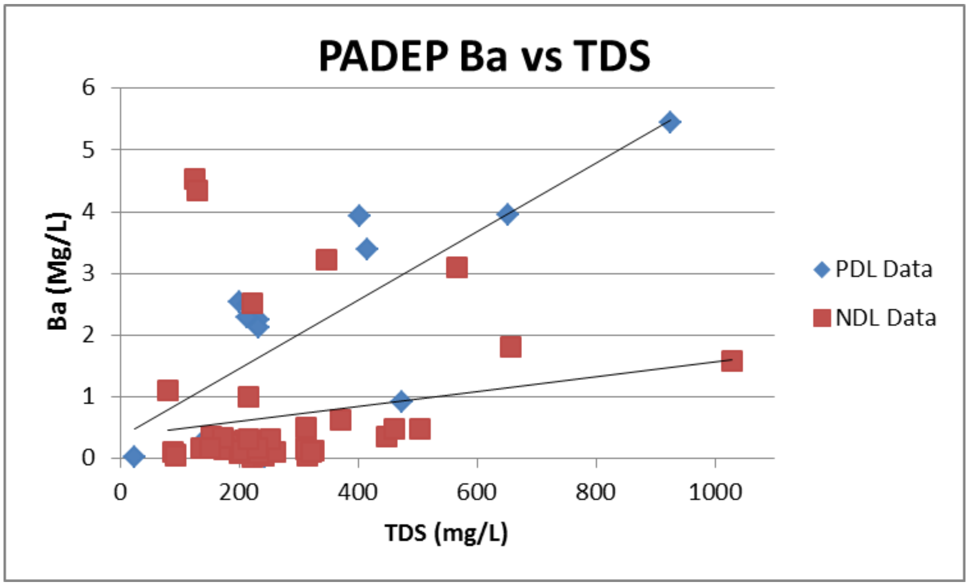


Figure 7a: Non-censored PADEP barium and total dissolved solids from positive (blue) and negative (red) determination letters. The R^2 value for PDLs was <u>0.6081</u> and the slope equals <u>0.0055.</u> The R^2 value for NDLS was <u>0.0336</u> and the slope equals <u>0.0012.</u>

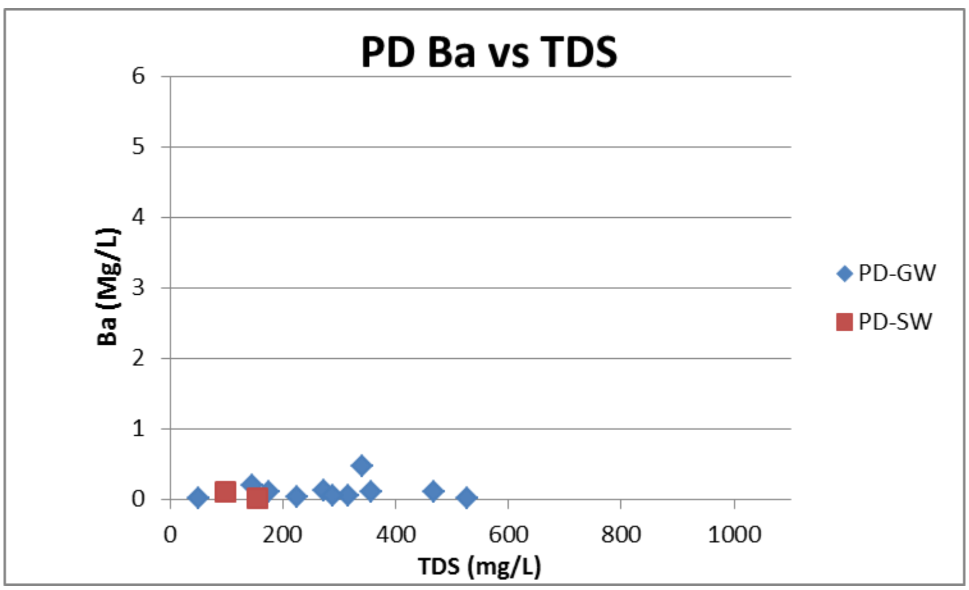


Figure 7b: Non-censored pre-drill barium and total dissolved solids for groundwater and surface water as shown in legend.

Table 6: The means and standard deviations for barium and total dissolved solids data used in correlation.

Report Type	Mean Ba (mg/L)	STD DEV	Mean TDS (mg/L)	STD DEV
PADEP PDL	2.139	1.614	323.000	227.330
PADEP NDL	0.687	1.104	267.844	167.278
Pre-Drill Groundwater	0.128	0.121	287.727	131.756
Pre-Drill Surface Water	0.064	0.046	127.500	28.500

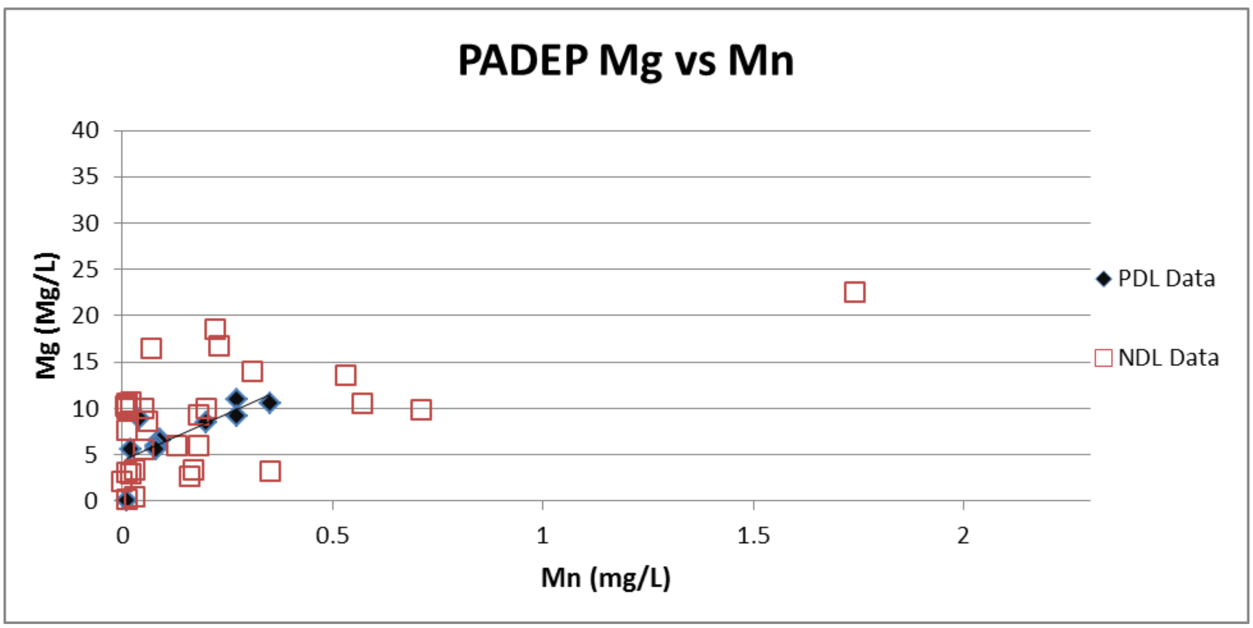


Figure 8a: Non-censored PADEP magnesium and manganese from positive (diamonds) and negative (squares) determination letters. The line applies to the PDL data. The R^2 value for PDLs is <u>0.6002</u> and the slope equals <u>20.156.</u>

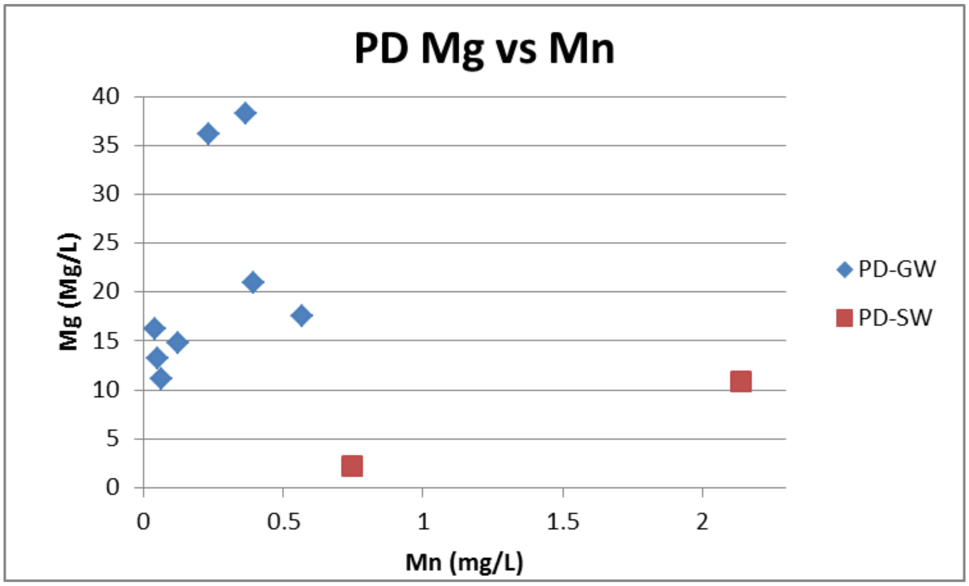


Figure 8b: Non-censored pre-drill magnesium and manganese data from surface and groundwater samples as shown in legend.

Table 7: The means and standard deviations for magnesium and manganese data used in correlation.

Report Type	Mean Mg (Mg/L)	STD DEV	Mean Mn (Mg/L)	STD DEV
PADEP PDL	7.012	2.802	0.132	0.108
PADEP NDL	8.733	5.289	5.956	28.764
Pre-Drill Groundwater	21.075	9.742	0.230	0.182
Pre-Drill Surface Water	6.575	4.325	1.444	0.696

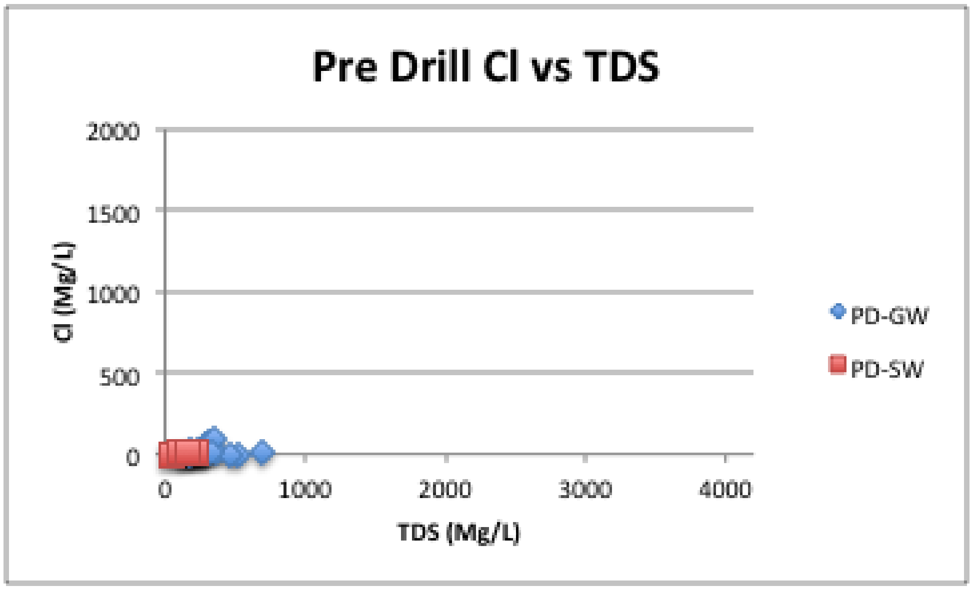


Figure 9a: Non-censored pre-drill chloride and total dissolved solids for both groundwater and surface water samples.

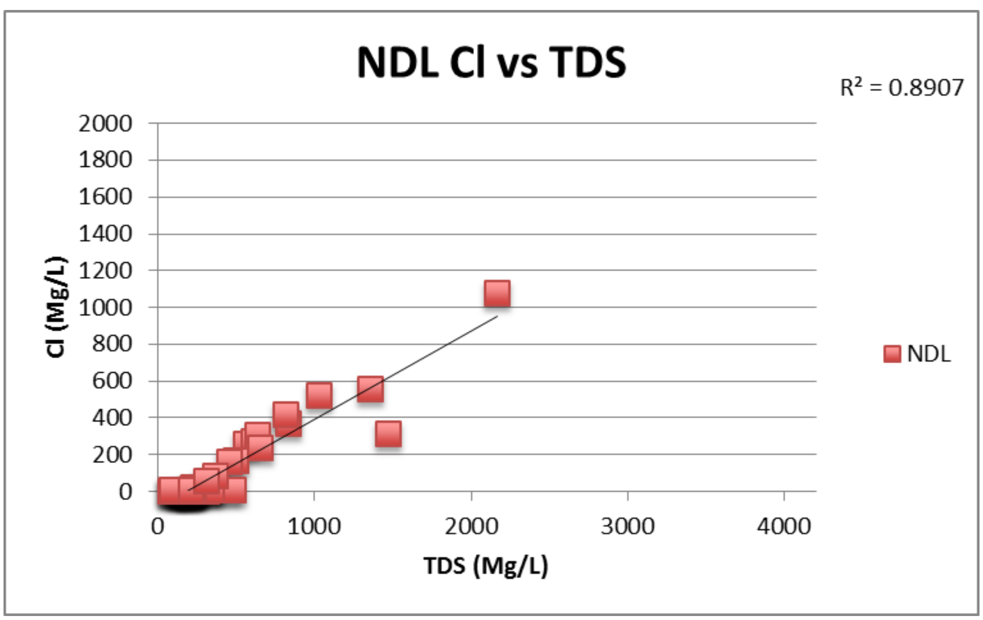


Figure 9b: Non-censored PADEP chloride and total dissolved solids from negative determination letters. The slope equals <u>0.481.</u>

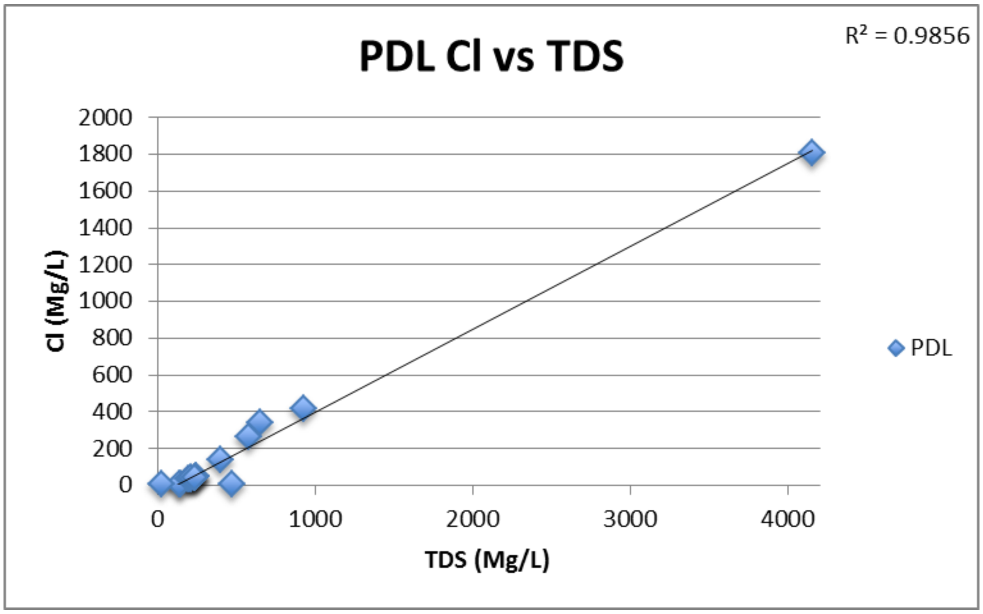


Figure 9c: Non-censored PADEP chloride and total dissolved solids from positive determination letters. The slope equals 0.4515.

Table 8: The means and standard deviations for chloride and total dissolved solids data used in correlation.

Report Type	Mean Cl (Mg/L)	STD DEV	Mean TDS (Mg/L)	STD DEV
PADEP PDL	205.375	432.521	567.500	951.105
PADEP NDL	90.827	190.514	374.982	373.780
Pre-Drill Groundwater	17.873	24.225	286.083	125.435
Pre-Drill Surface Water	8.408	67.821	132.475	67.821

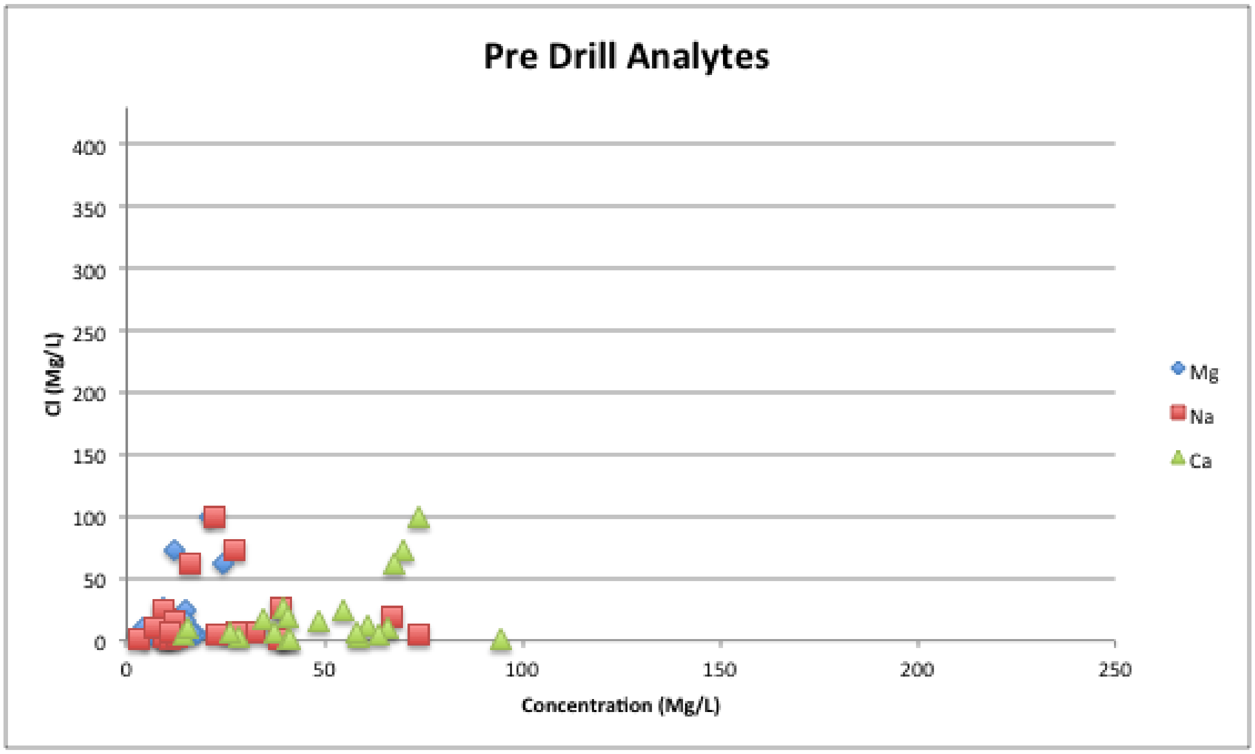


Figure 10a: Non-censored pre-drill magnesium, sodium, and calcium data plotted against chloride for groundwater samples.

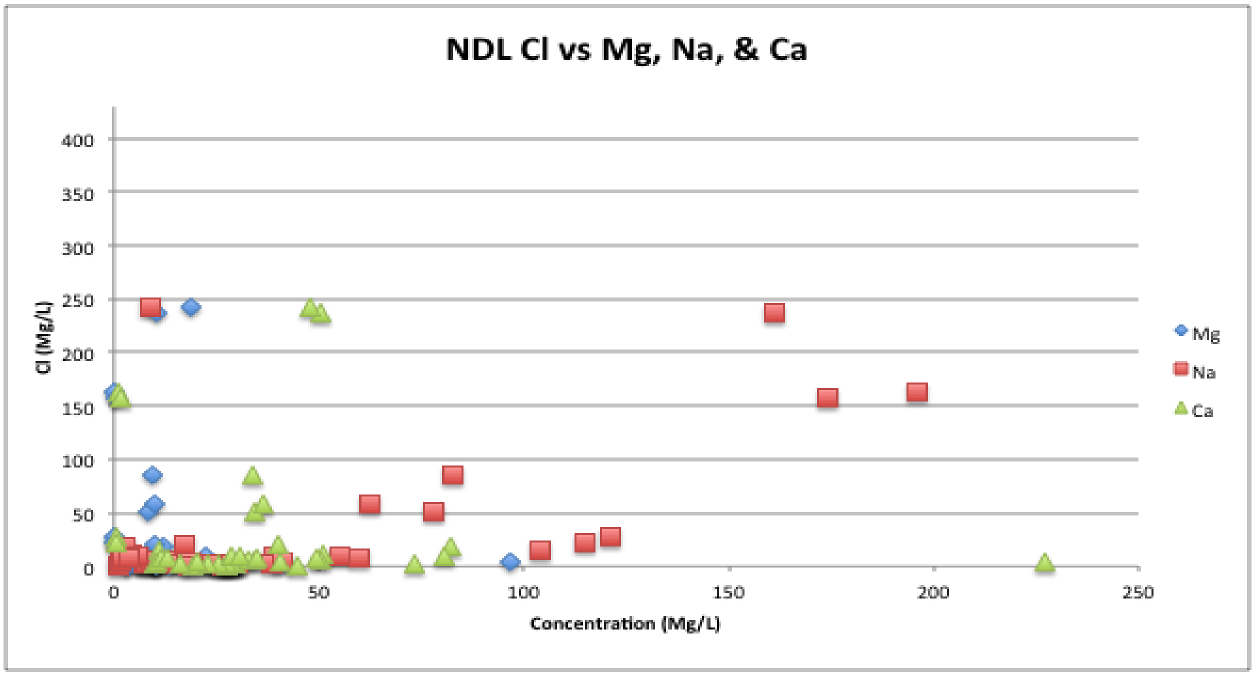


Figure 10b: Non-censored PADEP magnesium, sodium, and calcium concentrations plotted against chloride from negative determination data.

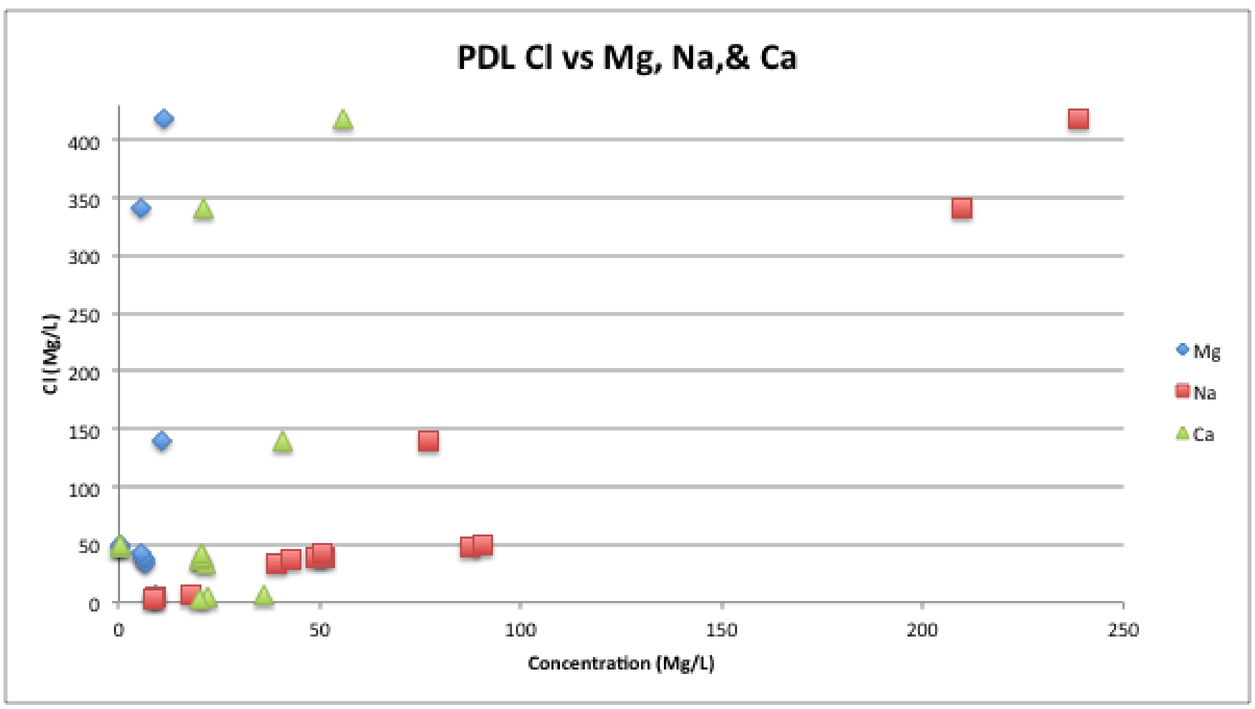


Figure 10c: Non-censored PADEP magnesium, sodium, and calcium concentrations plotted against chloride from positive determination data.

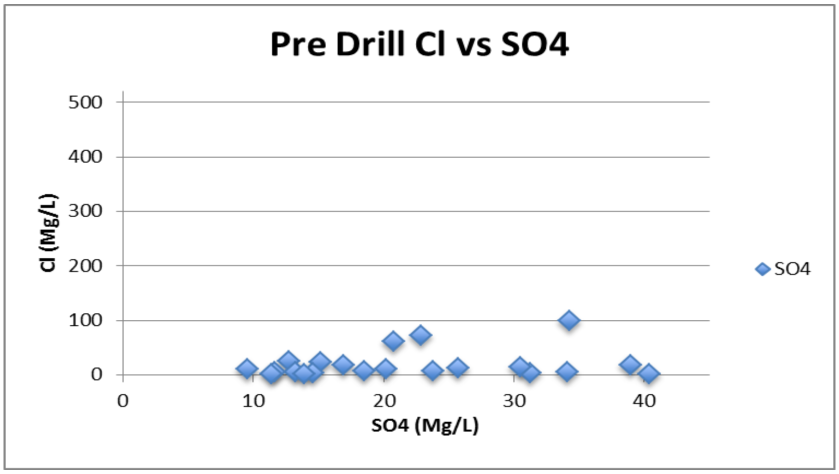


Figure 11a: Pre-drill sulfate and chloride data

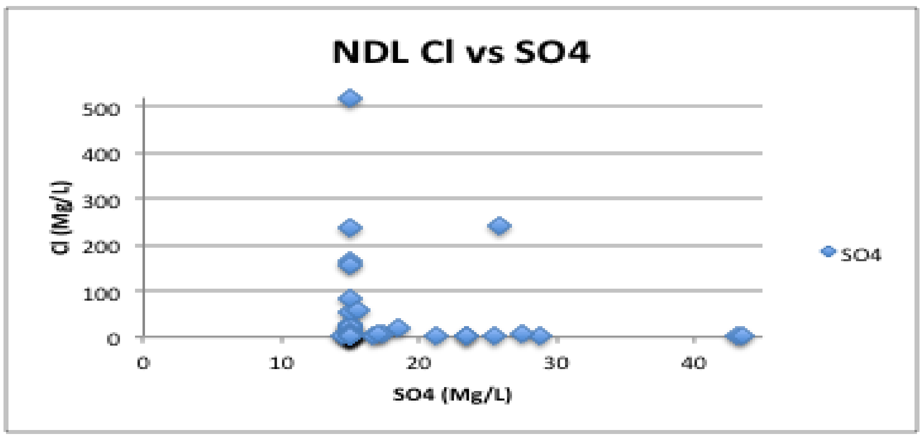


Figure 11b: Censored and non-censored PADEP sulfate and chloride concentrations from negative determination letters. Any value greater than 15 Mg/L represents a non-censored value.

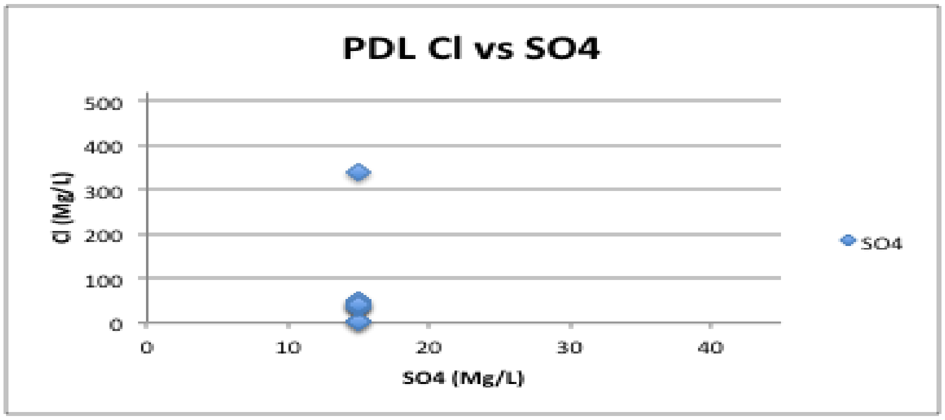


Figure 11c: Censored and non-censored PADEP sulfate and chloride concentrations from positive determination letters. Any value greater than 15 Mg/L represents a non-censored value.

Table 9: The means and standard deviations for chloride and total dissolved solids data used in correlation.

Report Type	Mean Cl (Mg/L)	STD DEV	Mean Na (Mg/L)	STD DEV	Mean Ca (Mg/L)	STD DEV	Mean Mg (Mg/L)	STD DEV	Mean SO_4 (Mg/L)	STD DEV
PADEP PDL	92.585	127.450	74.789	68.901	23.042	14.255	6.473	3.276	15.000	0.000
PADEP NDL	30.063	59.601	41.101	49.201	35.819	35.862	10.055	14.579	18.118	6.677
Pre-Drill Groundwater	20.841	27.175	24.526	19.346	52.544	18.711	14.087	7.729	22.039	9.487

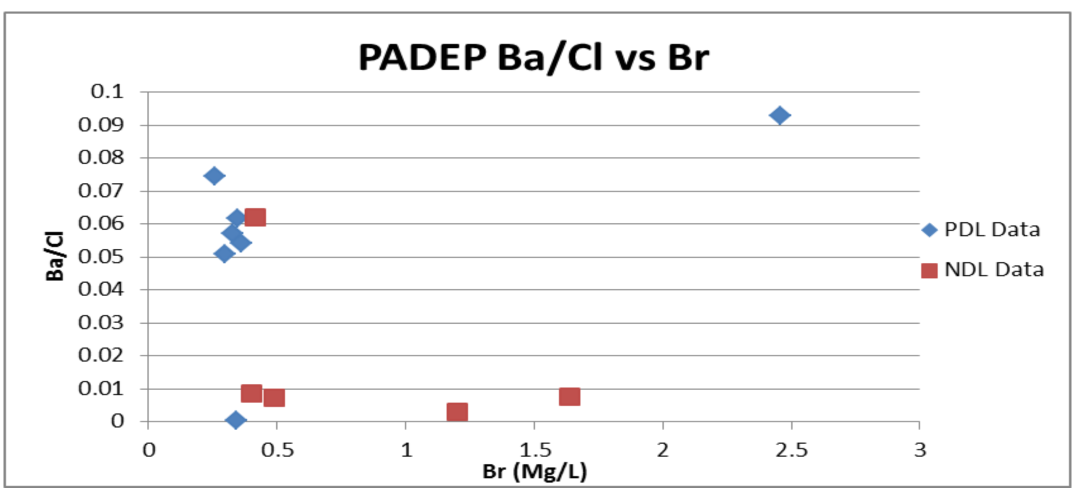


Figure 12: Non-censored PADEP barium chloride ratios and bromide concentrations for positive determination letters.

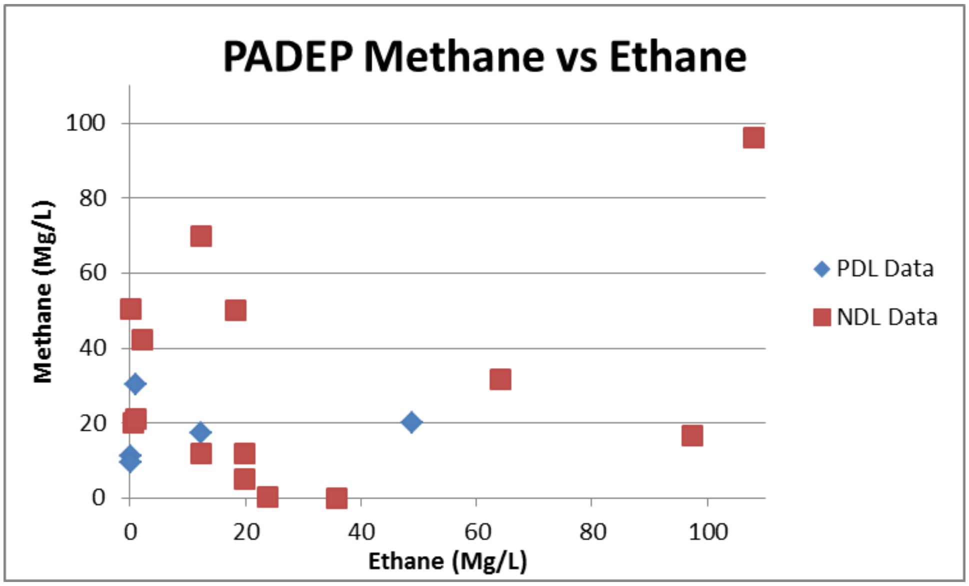


Figure 13: The relationship between methane and ethane in both negative and positive determinations.

Table 10: The means and standard deviations for methane and ethane data used in correlation.

Report Type	Mean Methane (Mg/L)	STD DEV	Mean Ethane	Std Dev
PADEP PDL	17.698	7.371	12.556	18.750
PADEP NDL	34.232	27.495	24.490	29.458

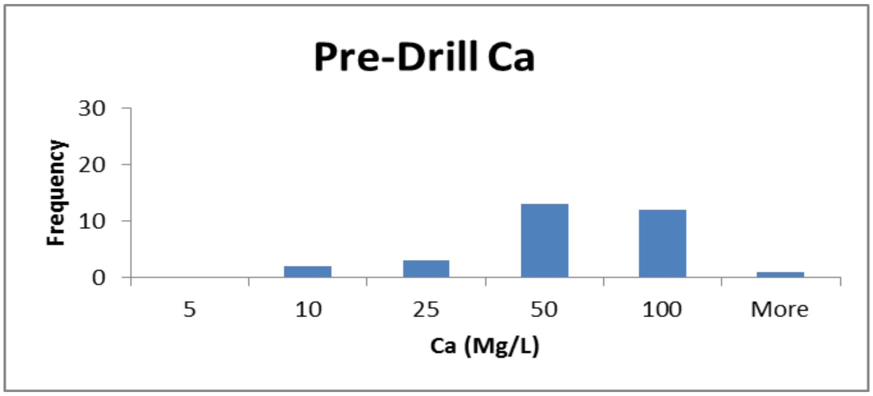


Figure 14a: The distribution of Ca concentrations from pre-drill data. The mean is 44.425 mg/L and the standard deviation is 22.789.

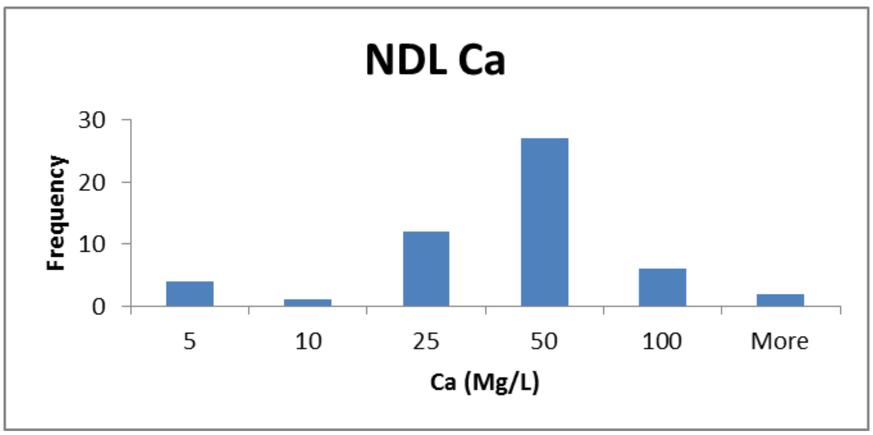


Figure 14b: The distribution of Ca concentrations from PADEP negative determination letters. The mean is 35.998 mg/L and the standard deviation is 35.526.

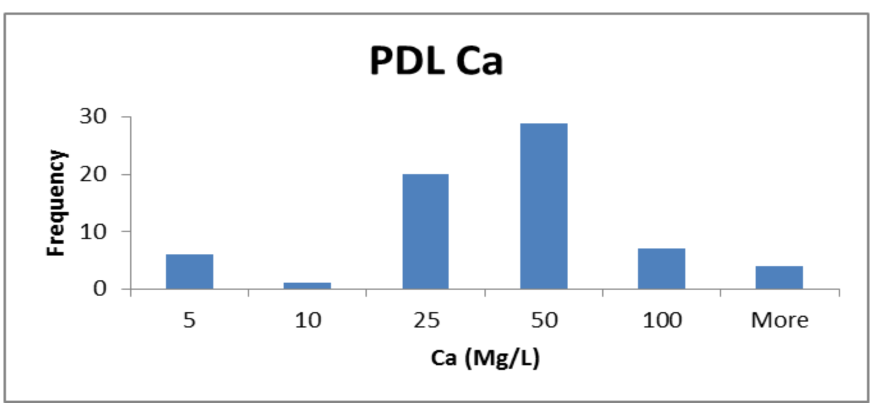


Figure 14c: The distribution of Ca concentrations from PADEP positive determination letters. The mean is 37.072 mg/L and the standard deviation is 42.403.

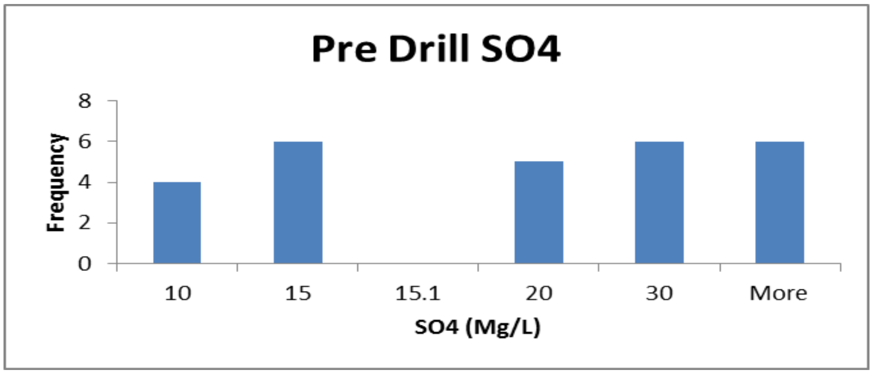


Figure 15a: The distribution of SO_4 concentrations from pre-drill data. The mean is 20.077 mg/L and the standard deviation is 9.478.

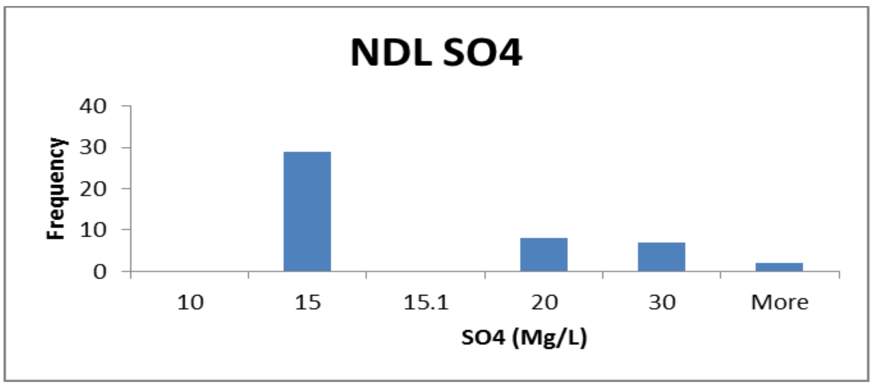


Figure 15b: The distribution of SO_4 concentrations from PADEP negative determination letters. The mean is 18.133 mg/L and the standard deviation is 6.526. This histogram includes censored data at the 15 mg/L bin.

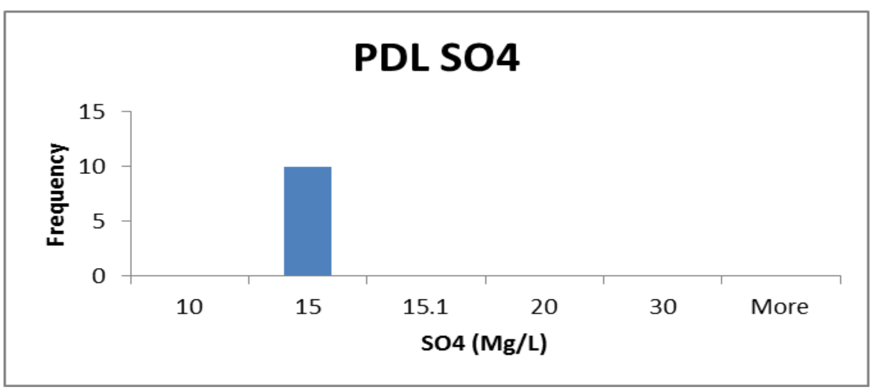


Figure 15c: The distribution of SO_4 concentrations from PADEP positive determination letters. The mean is 15 mg/L and the standard deviation is 0.

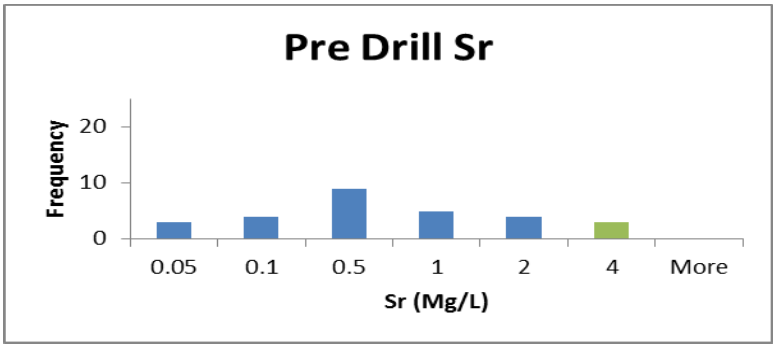


Figure 16a: The distribution of Sr concentrations from pre-drill data. The mean is 0.634 mg/L and the standard deviation is 0.698. The green bar represents the EPAdrinking Sr limt of 4 mg/L.

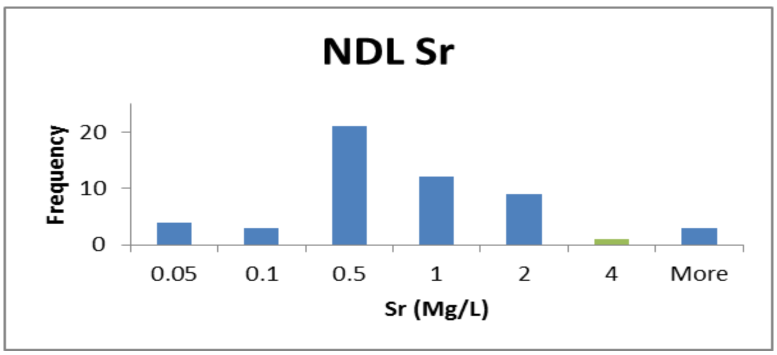


Figure 16b: The distribution of Sr concentrations from negative determination letters. The mean is 1.337 mg/L and the standard deviation is 3.184. The green bar represents the EPA safe drinking Sr limit of 4 mg/L.

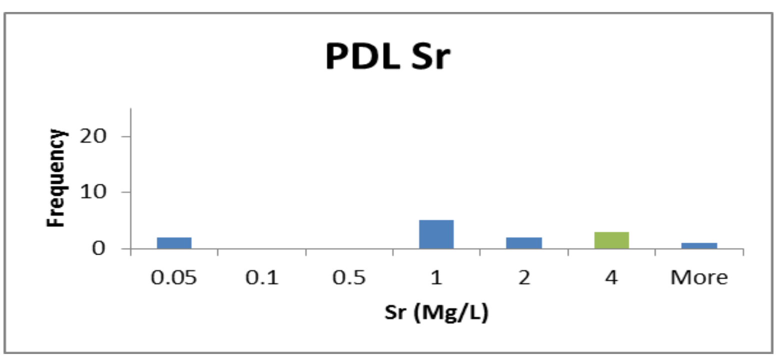


Figure 16c: The distribution of Sr concentrations from positive determination letters. The mean is 1.606 mg/L and the standard deviation is 1.516. The green bar represents the EPA safe drinking Sr limit of 4 mg/L.

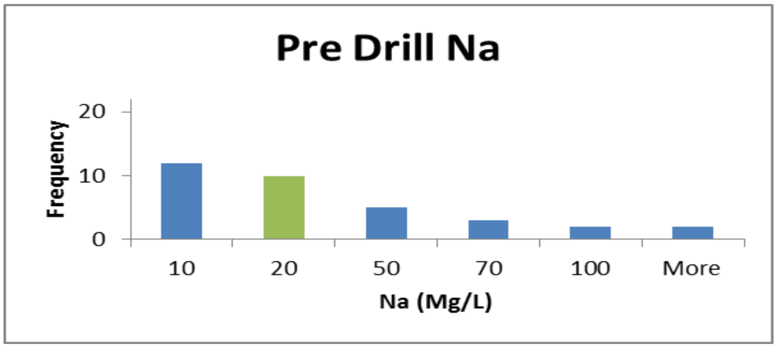


Figure 17a: The distribution of Na concentrations from pre-drill data. The mean is 32.443 mg/L with standard deviation of 36.807. The green bar represents the EPA drinking limit of 20 mg/L.

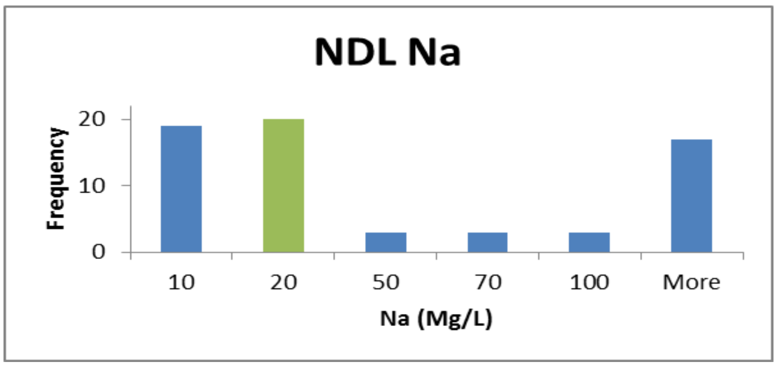


Figure 17b: The distribution of Na concentrations from negative determination letters. The mean is 75.868 mg/L with a standard deviation of 116.041. The green bar represents the EPA safe drinking Na limit of 20 mg/L.

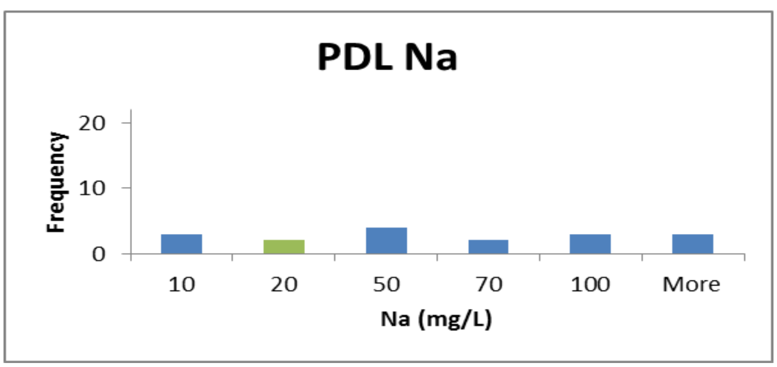


Figure 17c: The distribution of Na concentrations from positive determination letters. The mean is 96.594 mg/L and the standard deviation is 141.758. The green bar represents the EPA safe drinking Na limit of 20 mg/L.

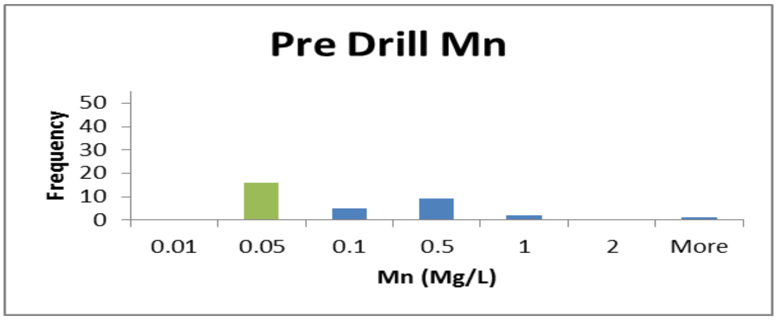


Figure 18a: The distribution of Mn concentrations from pre-drill data. The mean is 0.200 mg/L and the standard deviation is 0.390. The green bar represents the EPA secondary standard Mn limit of 0.05 mg/L.

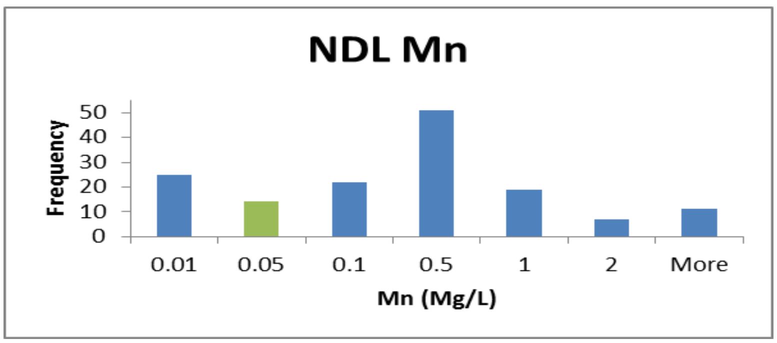


Figure 18b: The distribution of Mn concentrations from negative determination letters. The mean is 0.419 mg/L and the standard deviation is 0.824. The green bar represents the EPA secondary standard Mn limit of 0.05 mg/L.

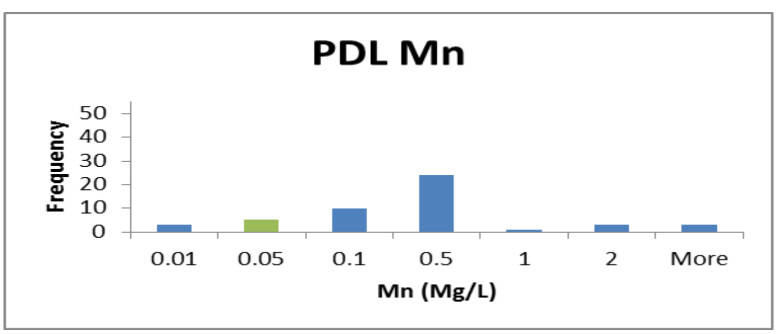


Figure 18c: The distribution of Mn concentrations from positive determination letters. The mean is 0.789 mg/L and the standard deviation is 2.133. The green bar represents the EPA secondary standard Mn limit of 0.05 mg/L.

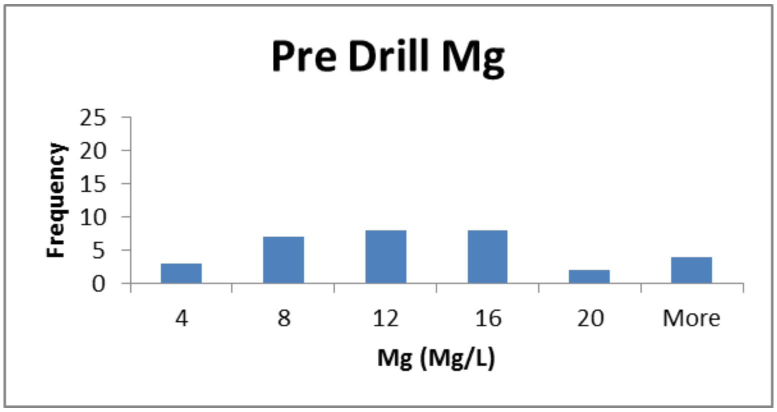


Figure 19a: The distribution of mg concentrations from pre-drill data. The mean is 12.508 mg/L and the standard deviation is 8.252.

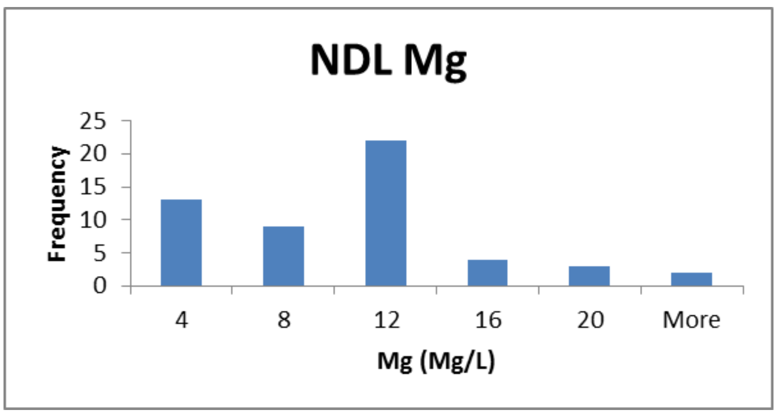


Figure 19b: The distribution of Mg concentrations from negative determination letters. The mean is 9.928 mg/L and the standard deviation is 12.964.

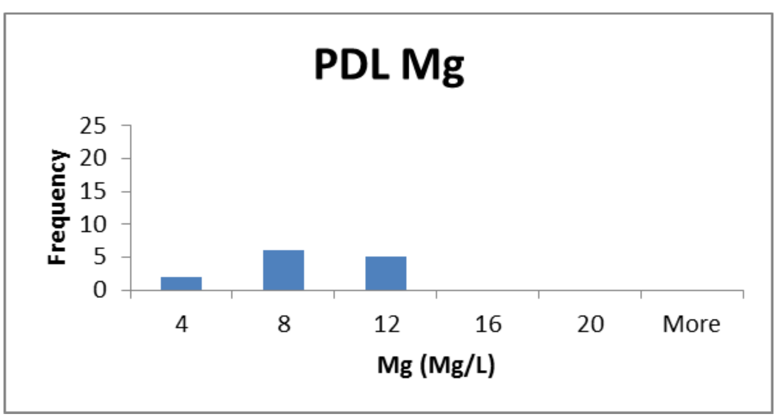


Figure 19c: The distribution of Mg concentrations from negative determination letters. The mean is 6.473 mg/L and the standard deviation is 3.276.

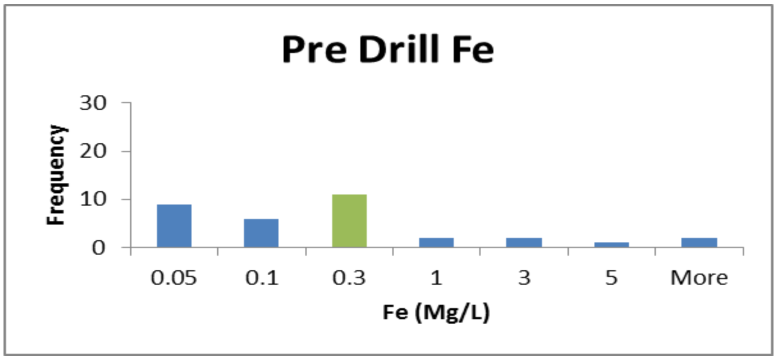


Figure 20a: The distribution of Fe concentrations from pre-drill data. The mean is 1.188 mg/L with standard deviation of 3.269. The green bar represents the EPA secondary limit of 0.3 mg/L.

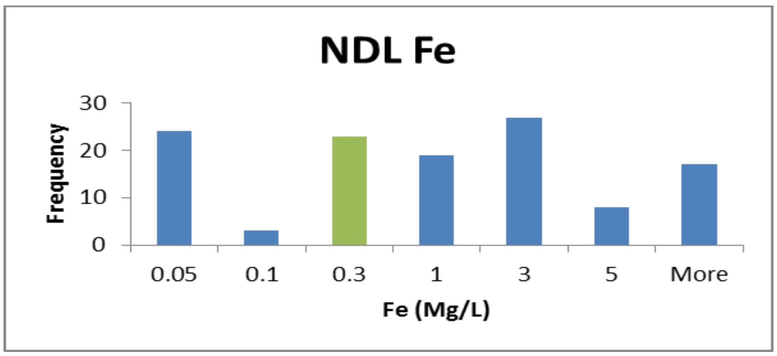


Figure 20b: The distribution of Fe concentrations from negative determination letters. The mean is 7.127 mg/L and the standard deviation is 50.336. The green bar represents the EPA secondary standard Fe limit of 0.3 mg/L.

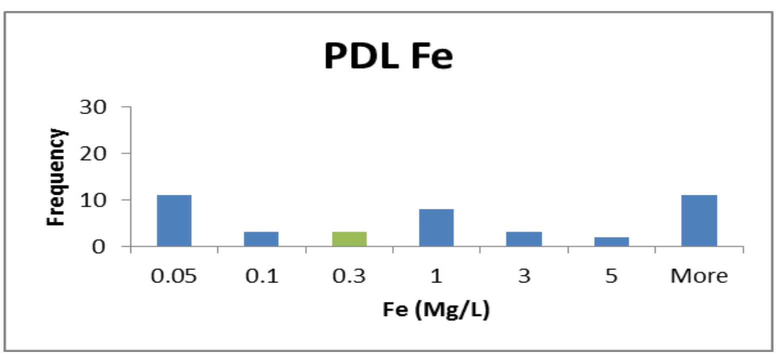


Figure 20c: The distribution of Fe concentrations from positive determination letters. The mean is 42.129 mg/L and the standard deviation is 165.903. The green bar represents the EPA secondary standard Fe limit of 0.3 mg/L.

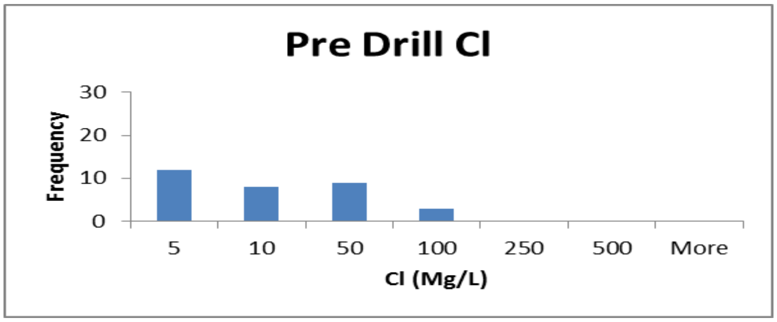


Figure 21a: The distribution of Cl concentrations from pre-drill data. The mean is 14.955 mg/L with a standard deviation of 21.691. The green bar represents the EPA secondary standard limit of 250 mg/L.

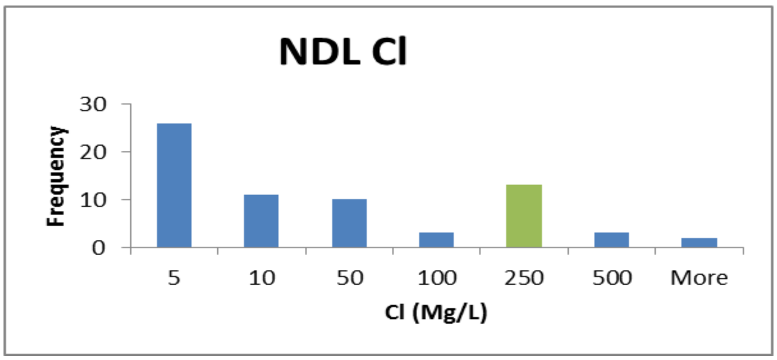


Figure 21b: The distribution of Cl concentrations from negative determination letters. The mean is 99.740 mg/L and the standard deviation is 191.641. The green bar represents the EPA secondary standard Cl limit of 250 mg/L.

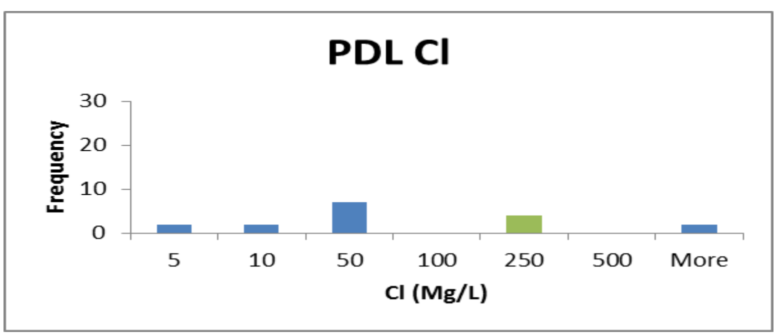


Figure 21c: The distribution of Cl concentrations from positive determination letters. The mean is 266.782 mg/L and the standard deviation is 486.214. The green bar represents the EPA secondary standard Cl limit of 250 mg/L.

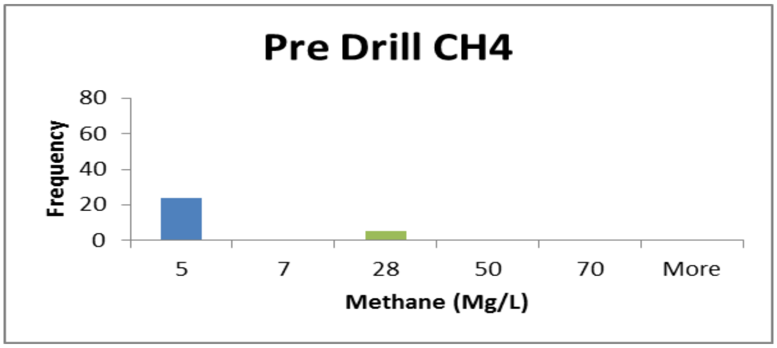


Figure 22a: The distribution of CH_4 concentrations from pre-drill data. The mean is 2.323 mg/L and the standard deviation is 4.435. The green bar represents the solubility CH_4 limit of 28 mg/L.

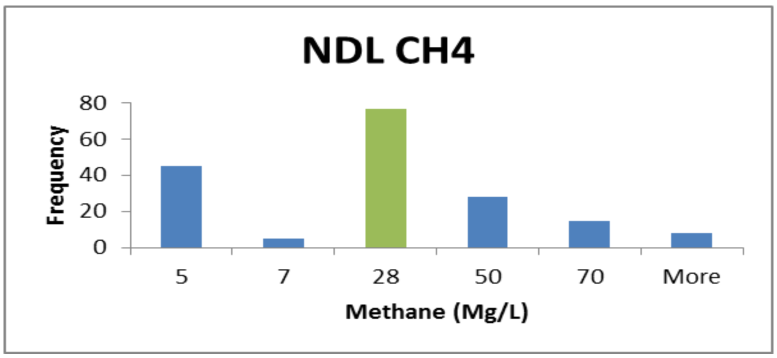


Figure 22b: The distribution of CH_4 concentrations from negative determination letters. The mean is 25.720 mg/L and the standard deviation is 71.851. The green bar represents the solubility CH_4 limit of 28 mg/L.

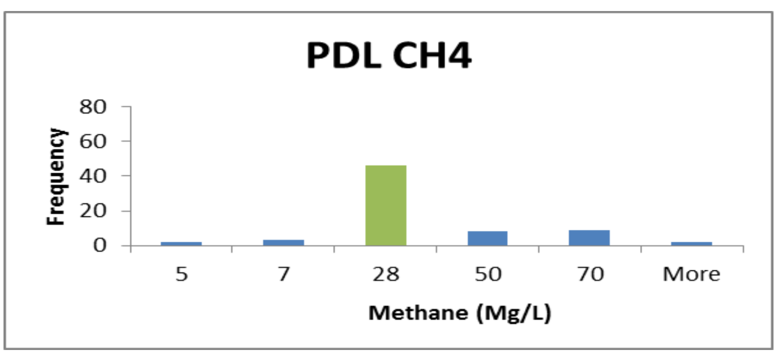


Figure 22c: The distribution of CH_4 concentrations from negative determination letters. The mean is 25.985 mg/L and the standard deviation is 18.751. The green bar represents the solubility CH_4 limit of 28 mg/L.

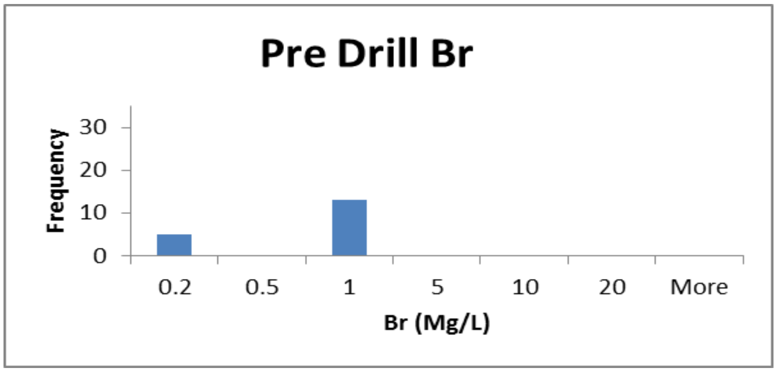


Figure 23a: The distribution of bromide concentrations from pre-drill data. The mean is 0.750 mg/L and the standard deviation is 0.403.

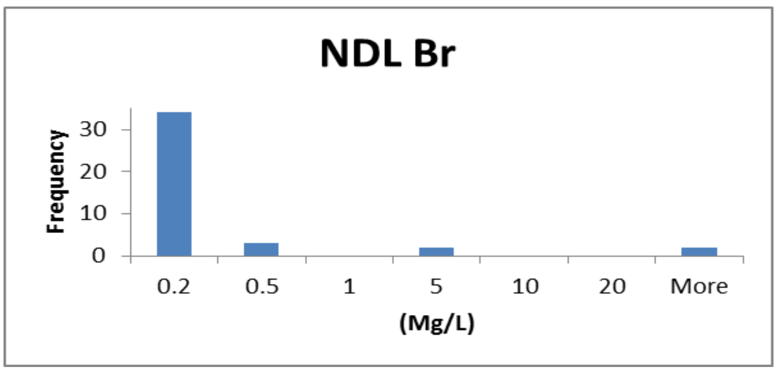


Figure 23b: The distribution of bromide concentrations from negative determination letters. The mean is 2.066 mg/L and the standard deviation is 8.153.

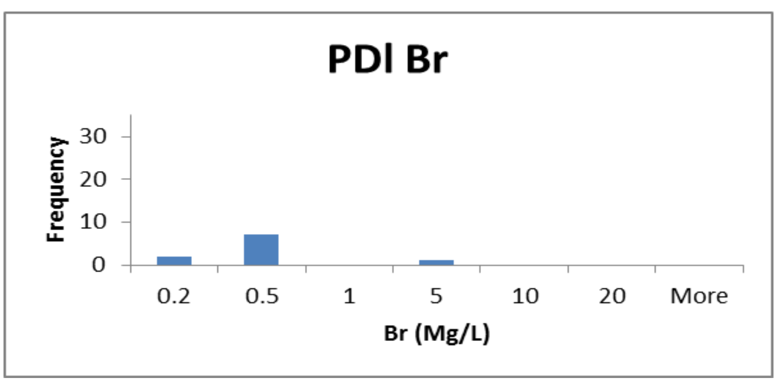


Figure 23c: The distribution of bromide concentrations from negative determination letters. The mean is 0.514 mg/L and the standard deviation is 0.650.

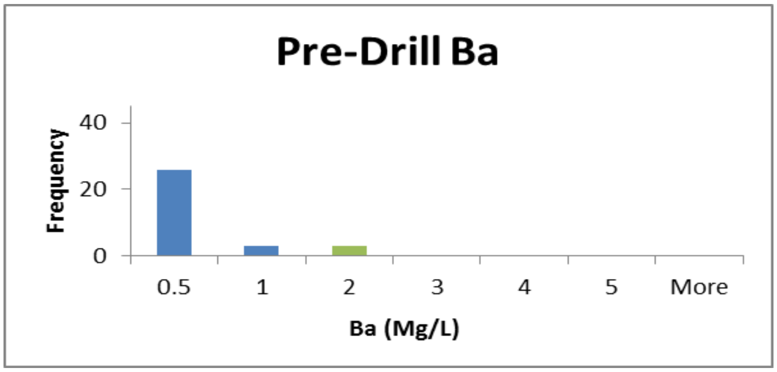


Figure 24a: The distribution of barium concentrations from pre-drill data. The mean is 0.335 mg/L and the standard deviation is 0.508. The green bar represents the EPA Ba limit of 2 mg/L.

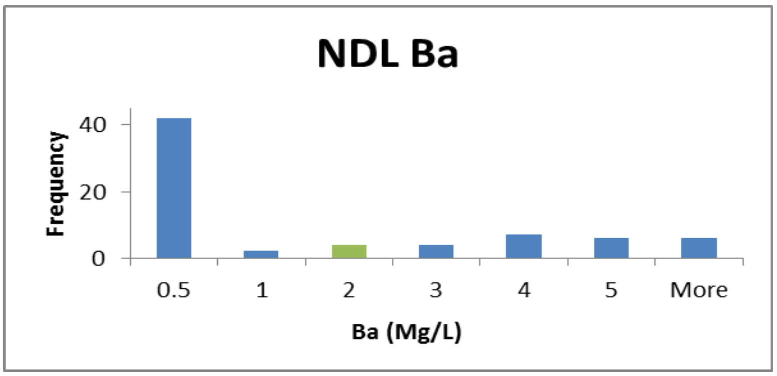


Figure 24b: Negative determination letter Barium data. The mean is 1.492 mg/L and the standard deviation is 1.945. The green bar represents the EPA Ba limit of 2 mg/L.

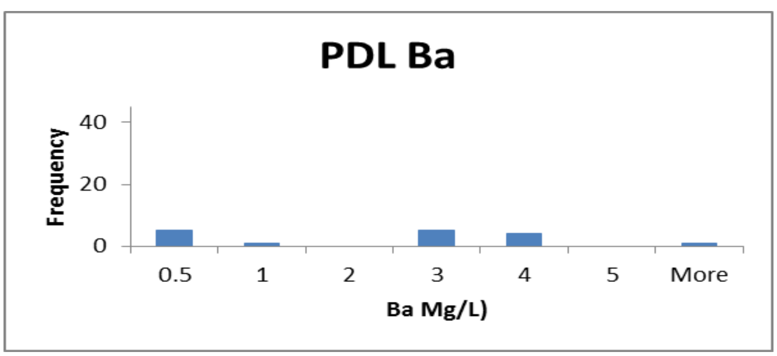


Figure 24c: The distribution of barium concentrations from positive determination letters. The mean is 2.073 mg/L and the standard deviation is 1.621. No values fell at the EPA safe drinking limit of 2 mg/L so no bar is there.

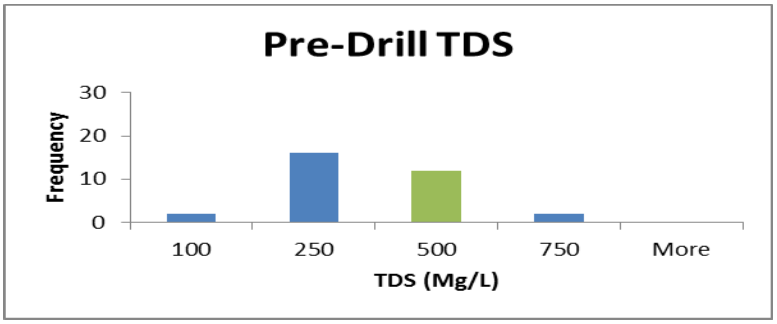


Figure 25a: The distribution of total dissolved solids concentrations from pre-drill data. The mean is 257.216 mg/L and the standard deviation is 124.525. The green bar represents the EPA secondary standard TDS limit of 500 mg/L.

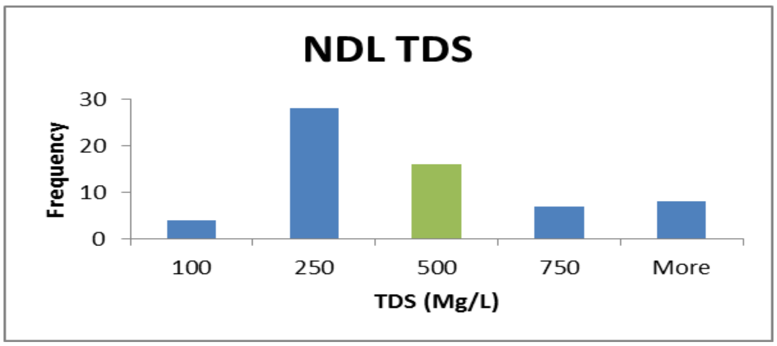


Figure 25b: The distribution of total dissolved solids concentrations from negative determination letters. The mean is 390.339 mg/L and the standard deviation is 361.510. The green bar represents the EPA secondary standard TDS limit of 500 mg/L.

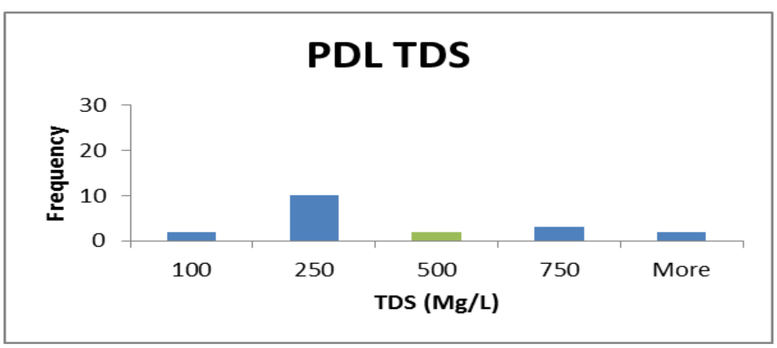
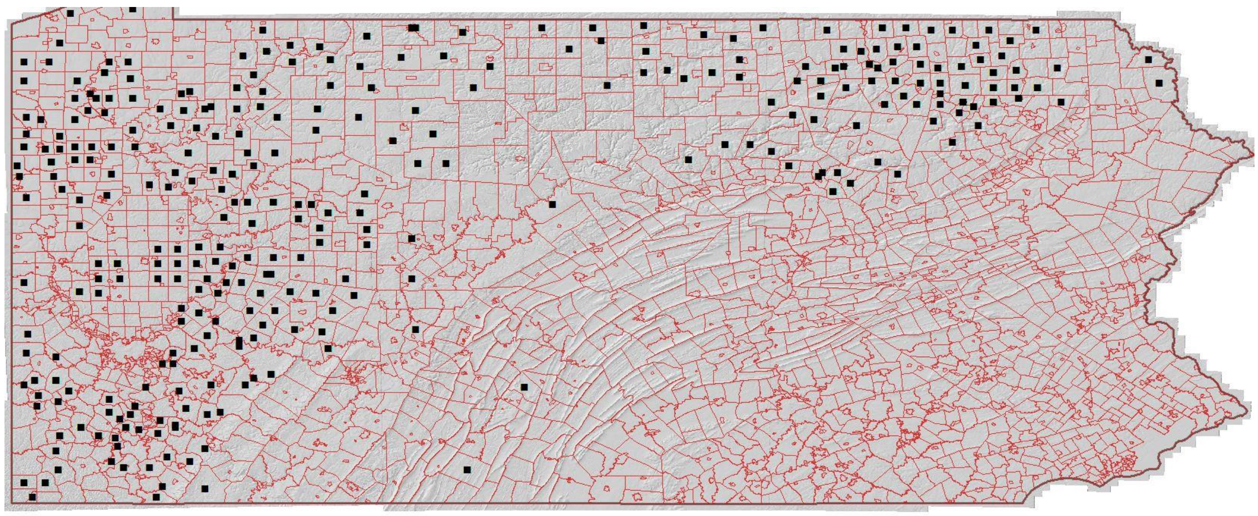


Figure 25c: The distribution of total dissolved solids concentrations from positive determination letters. The mean is 520.737 mg/L and the standard deviation is 883.466. The green bar represents the EPA secondary standard TDS limit of 500 mg/L.



Map 1: This map shows the location of every township for which we obtained at least one or more positive or negative determination letters in the state of Pennsylvania. All sites are located at the center of their township since exact locations were not provided.

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