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Determination of Trace Metals and Inorganic Contaminants in the Marcellus Shale Drilling Near Beaver Run Reservoir

Abraham Ankrah

Indiana University of Pennsylvania

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DETERMINATION OF TRACE METALS AND INORGANIC CONTAMINANTS

IN THE MARCELLUS SHALE DRILLING

NEAR BEAVER RUN RESERVOIR

A Thesis

Submitted to the School of Graduate Studies and Research

in Partial Fulfillment of the

Requirement for the Degree

Master of Science

Abraham Ankrah

Indiana University of Pennsylvania

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Indiana University of Pennsylvania
School of Graduate Studies and Research
Department of Chemistry

We hereby approve the thesis of

Abraham Ankrah

Candidate for the degree of Master of Science

Nathan McElroy, Ph.D
Associate Professor of Chemistry, Advisor

Keith Kyler, Ph.D
Assistant Professor of Chemistry

Lawrence Kupchella, Ph.D
Assistant Professor of Chemistry

Justin Fair, Ph.D
Assistant Professor of Chemistry

ACCEPTED

Timothy Mack, Ph.D
Dean
School of Graduate Studies and Research

Title: Determination of Trace Metals and Inorganic Contaminants in the Marcellus Shale Drilling Near Beaver Run Reservoir

Author: Abraham Ankrah

Thesis Chair: Dr. Nathan McElroy

Thesis Committee Members: Dr. Keith Kyler
Dr. Lawrence Kupchella
Dr. Justin Fair

The Municipal Authority of Westmoreland County contracted IUP faculty and students to carry a one year pilot around the Beaver Run Reservoir near Saltsburg, PA. In the past decade various mining companies including CONSOL Energy, drilled the shale horizontally using hydraulic fracturing approach. The study involved quarterly water sampling from the sites around the reservoir to test for total dissolved solids, some selected trace metals using atomic absorption spectrometry (AAS), inductively coupled optical emission spectroscopy (ICP-OES) and some selected inorganic salts using, Ion Chromatography.

Analyzes to date have not shown direct correlation between Marcellus drilling operation and the elevated levels of the selected chemicals.

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Chapter 1

STATEMENT OF THE PROBLEM

The research problem is to analyze water samples from the Beaver Run Reservoir in the Westmoreland County to test for Calcium, Magnesium, Iron, Manganese, Lead, Arsenic, Mercury, Chromium, Barium, Strontium, Cadmium, Bromide, Chloride, Fluoride, Iodide, Sulfate and Nitrate to help establish a baseline before the drilling and removal of gas.

Analysis will continue after establishing baseline to find out if there is any direct correlation between Marcellus and the elevated levels of substances.

Two groups of students would be working on this project. I was responsible for the determination of TDS, alkalinity and metals while the other group works on the various aspects of the project.

Chapter 2

LITERATURE REVIEW

2.1 Background of Municipal Authority of Westmoreland County (MAWC)

MAWC is the organization that supplies water to approximately 120,000 customers in Westmoreland County in Pennsylvania. The Beaver Run Reservoir was constructed in 1952 and was further enlarged in 1962. Currently, the Beaver Run Reservoir has a capacity of 11 billion gallons and produces 45 million gallons of water per day. It owns the property and oversees the operation at Beaver Run Reservoir. The land around the reservoir has been leased to various gas companies, such CONSOL Energy.¹

In May 2011, MAWC contracted Indiana University of Pennsylvania (IUP) faculties of Geography & Regional Planning (GEOG) and Chemistry (CHEM) to conduct a one year water sampling and analysis around the 1,300-acre Beaver Run Reservoir near Saltsburg, PA. As part of the contract, students from IUP's Geography department collected water samples from the reservoir, along the tributaries and streams of the property on quarterly basis and brought them to the chemistry department to be analyzed. The contaminants to be tested were proposed by MAWC on the basis of their historical occurrences and some new ones to serve as indication for possible evidence of contamination related to drilling.

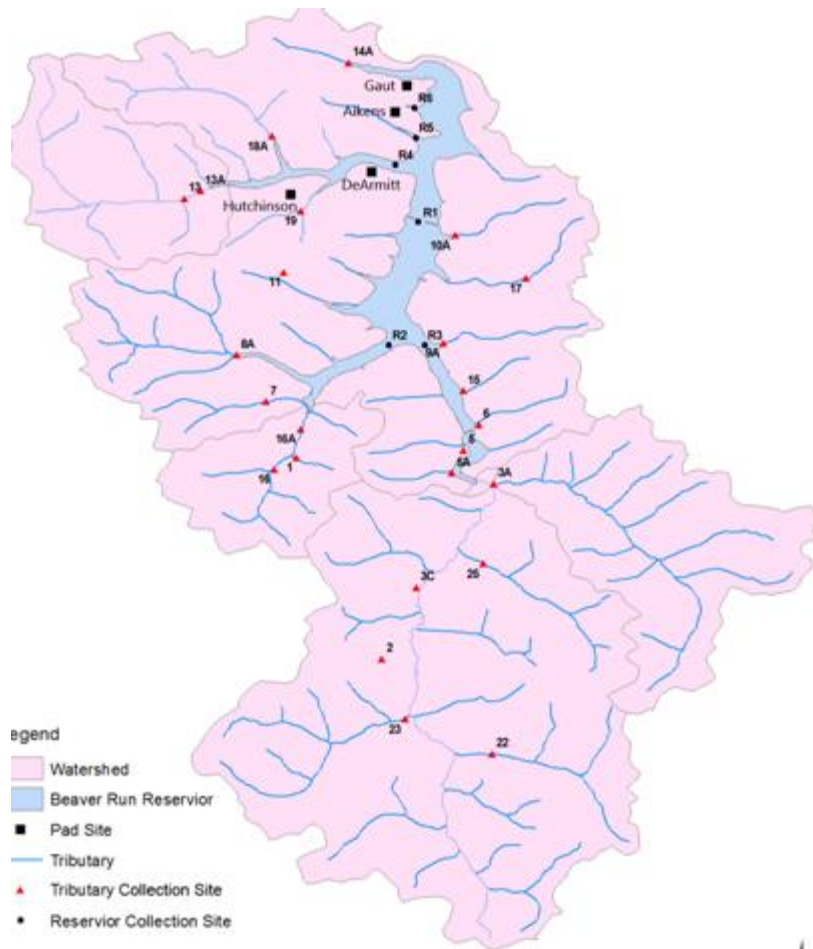


Figure 1. Collection sites for lab analysis.

© Marcellus Shale Coalition 2010

2.2 Background of Marcellus Shale

Marcellus shale is a sedimentary rock unit found in North America which was named after a village of Marcellus in New York State. In the United States, the shale can be found in New York, Pennsylvania, Delaware, New Jersey, Tennessee, Kentucky, Ohio, Maryland and Virginia. The shale is sandwiched between limestone strata with gas reserves trapped in the layers. The gas is produced by thermogenic decomposition of organic matter in the sediment under high heat and pressure. The gas is held in the pores of the rock particles.

In recent years, the shale is drilled horizontally along its seam. This method is effective and cost efficient compared to the traditional vertical way of drilling.²



Figure 2. Marcellus shale distribution in the US.

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2.2.1 How the Drilling is done

The vertical section of the well is first dug using a drilling pipe which has a drill bit connected to its end. Air is pumped into the drilling pipe to enable upward and downward movement in the well.

The next activity is to insert surface casing in the drilled hole to separate the freshwater. Cement is then pumped down the casing to prevent the contamination of the water aquifer. The drilling continues to approximately 500 feet. The vertical section stops at this point to begin the horizontal drilling. This point is called the Kick of Point (KoP).

A curved drill bit and the drilling pipe are inserted in the vertical to assist in the horizontal drilling. Once the curve is made, the drilling of the horizontal section starts and at each point, the drill is replaced. This process is called Tripping pipe.

Hydrocarbons and other fluids are prevented from getting into the well by inserted production casing. Electrical current is then introduced in the well using a perforating gun.

The shale is fractured hydraulically by pumping water, sand and lubricants into the wellbore and down the casing under high pressure. This allows gas to flow into the wellbore. Plugs are placed in the fracked section to help frack a second section of the horizontal leg. When the fracking is completed, the plugs are drilled to allow the gas to flow to the wellbore. A pipeline is built to connect the gas to the pipeline network.⁵

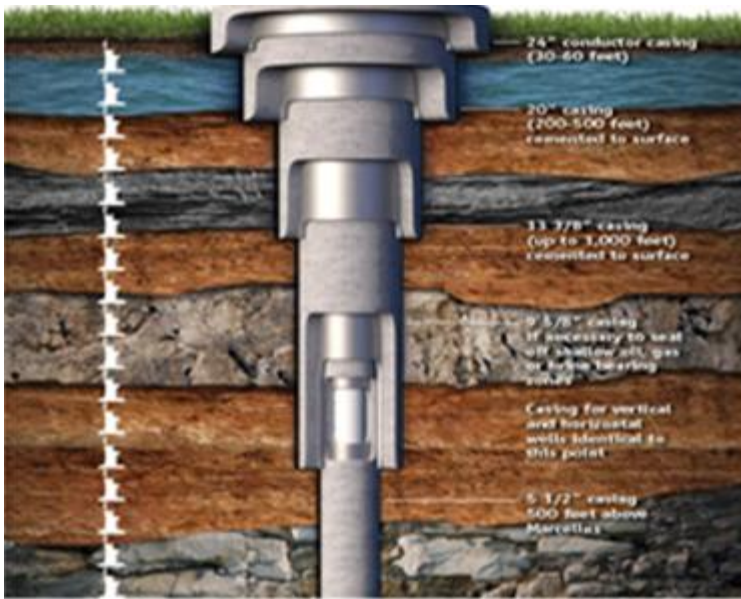


Figure 3. A diagram of production casing.

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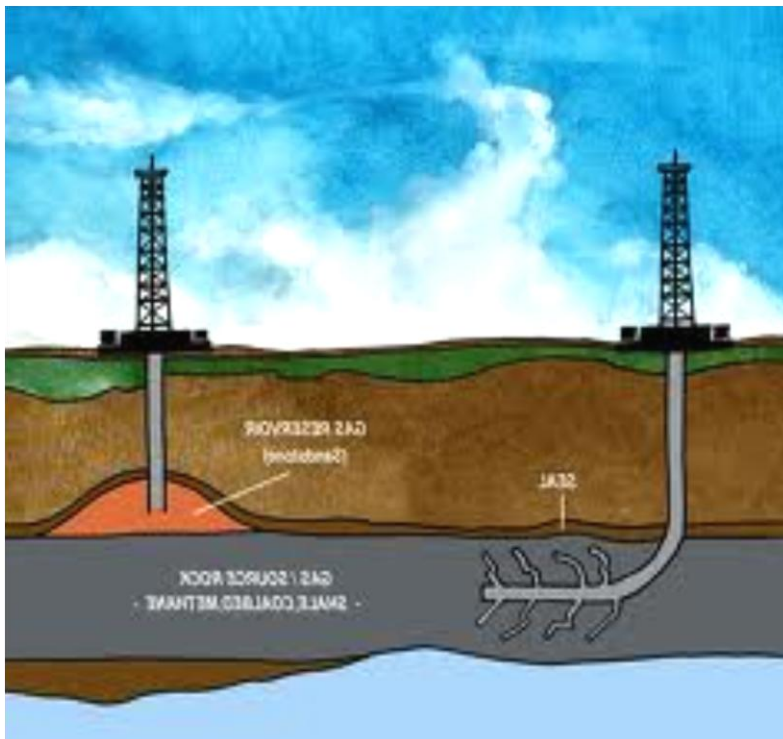


Figure 4. A diagram showing horizontal drilling and its steps.

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2.3 Water Contaminants

Water contaminants are substances found in water that have the potential to causes risk to public health at certain levels. Some contaminants occur naturally in the environment while others are present as a result of human activities such as wastes from factories, refineries, mines, mills and agriculture.³

2.3.1 Trace Metal Contaminants

Table 1. List of Selected Trace Metals and Related Health Effect

Contaminant	Health effect
Arsenic	Causes Lung Cancer ⁶⁻⁸
Barium	Causes gastrointestinal disturbance and muscular weakness ^{4,9}
Calcium	Maintains bones and teeth, helps blood to clot, transmit nerves and impulses ⁴
Chromium	Causes liver, kidney, lungs and pancreatic cancer ⁴
Cadmium	Cancers cancer ^{4,10}
Lead	Kidney damage ¹³⁻¹⁴
Iron	Helps in metabolic activities ¹⁵
Magnesium	Helps in the formation of bones ¹⁶
Manganese	Turns laundry grayish black ¹⁷⁻¹⁹
Mercury	Causes cancer and birth defect ²⁰⁻²²
Strontium	No known effect found ²³⁻²⁴

2.3.2 Anionic Contaminants

Table 2. List of Selected Inorganic Salts and Related Health Issues

Contaminant	Health effect
Bromide	Causes cancer ^{25,27}
Chloride	No health effect however, the Sodium associate with chloride can be a concern to people suffering from heart disease or kidney diseases ²⁷
Fluoride	Cause dental fluorosis ²⁸⁻²⁹
Iodide	Causes irritation to the skin, eye ³⁰⁻³¹
Nitrate	Causes diarrhea, vomiting and abdominal pains ^{4,32}
Phosphate	Unknown ³³
Sulfate	Cause diarrhea ⁴

2.4 Total Dissolved Solids (TDS)

TDS is made up of inorganic salts and small amount of organic matter dissolved in water. TDS in water comes mainly from natural sources such as sewage, run off and industrial wastewater, etc. Drinking water that contains high levels of TDS does not pose health issues. High TDS can cause drinking water to be corrosive, salty and result in scale formation. It also indicates the presence of high levels of ions above the primary and secondary standards. TDS in drinking water should be less than 500 ppm as mandated by the U.S EPA.^{34, 35}

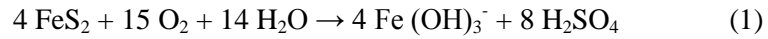
2.4.1 pH and ALKALINITY

pH is a measure of how acidic or basic a solution is. Low pH usually causes the release of toxic elements into water sources. Areas with limestone bedrock (the solid rock underlying surface soil) usually have high pH water while glaciated areas have low pH. Acid rain can also contribute to the pH of water while materials such as detergent and soap which are added to water source from domestic activities increase the alkaline nature of water.

Alkalinity is the ability of water to neutralize acid. Some water bodies contain compounds like bicarbonate, carbonates and hydroxide. Water with low alkalinity is unresistant to pH change while those with high alkalinity have the ability to resist pH change. Alkalinity in water is usually affected by change in pH, geology and soil.⁴²

2.4.2 Abandoned Mine Drainage (AMD)

AMD is the result of water getting polluted through mining activities like coal mining. It is a well known problem in Pennsylvania. AMD reaction is given as:



In the process of oxygen, water combines with pyrite to produce sulfuric acid and iron hydroxide. This lowers the pH in water and enhances the solubility of ferric ion. AMD in water is characterized by a yellow rust color. Water bodies affected by AMD usually have low pH, high acidity, and high concentration of total dissolved metals.

Metals dissolved by AMD are usually poisonous to water bodies. AMD can lead to ecological destruction and serve as a chief source of water contamination to human water.³⁶



Figure 5. A stream affected by abandoned mine drainage.

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Chapter 3

METHODOLOGY

3.1 Chemicals and standards

All reagents used in this research were purchased from Fisher Scientific without any purification.

Table 3. List of Chemicals Used

Name of chemical	Cas. No	Grade/Supplier
Hydrochloric acid	7674-01-0	Certified ACS Fisher Scientific
Nitric acid	7697-37-2	Certified ACS Fisher Scientific
Arsenic	7440-38-2	SPEX CertiPrep
Barium	7440-39-3	SPEX CertiPrep
Calcium	471-34-1	Certified ACS Fisher Scientific
Cadmium	7440-43-9	SPEX CertiPrep
Chromium	7740-47-3	SPEX CertiPrep
Iron	7782-61-8	Certified ACS Fisher Scientific
Lead	10099-94-8	Certified ACS Fisher Scientific
Magnesium	13446-18-9	Certified ACS Fisher Scientific
Manganese	17141-63-8	Certified ACS Fisher Scientific
Mercury	7439-97-6	SPEX CertiPrep
Strontium	7440-24-6	SPEX CertiPrep

3.2 Equipment used

Standard glassware was used for preparation of solutions.

Table 4. List of Equipment Used

Equipment	Brand
Atomic absorption Spectrometer	5100 PC Perkin Elmer
Inductively Coupled Plasma optical emission spectrometer	Optima 2100 DV Perkin Elmer
Ion chromatograph	761 compact Metrohm
pH meter	Accumet XL 15 Fisher Scientific
Conductivity (field) meter	Hanna Combo-pH & EC Meter (model HI 98129)

3.3 Sampling

Water samples were collected on quarterly basis by a group of Geography students from IUP. First quarter samples were collected in May 2011 with the remaining quarters collected on August 2011, December 2011, March 2012, July 2012 and November 2012 respectively. Water samples were collected from the reservoir, along the tributaries and streams of the property, stored in wide-mouth low polyethylene (LDPE) and brought to the chemistry department for analysis. A field meter was used during sample collection to determine the temperature, pH, TDS and electrical conductivity of the various water samples.

3.4 Experimental Procedure

3.4.1 Solutions used for alkalinity test

Standardized HCl solutions were prepared and used for the alkalinity titration. The concentrations of the HCl solutions for the six quarters were 0.0198 N, 0.0167 N, 0.0216 N, 0.0216 N, 0.232 N and 0.0199 N respectively.

3.4.2 Buffer solution

Buffer of pH 4.01 and 6.86 solutions were prepared by diluting the content of the commercially prepared buffer salt packets (Fisher Scientific) according to the instructions listed on the respective labels. The instruction on both packets called for diluting the pre-measured salt mixture to 1.0 L with Millipore water. This was used to calibrate the pH meter

3.5 Instrumentation

3.5.1 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

The optima 2100 DV Perkin Elmer ICP-OES owned by Geosciences department was used for the determination of the various trace metals. The instrument comprises of the ICP and the optical spectrometer. The ICP torch consists of three concentric quartz glass tubes. Argon gas creates the plasma flame at a flow rate of 0.80 L/min. Nitrogen gas and compressed air are passed through the system at flow rates of 0.5 L/min and 2.0 L/min respectively. A stable, high plasma temperature of about 7000 K is usually generated. The ICP-OES uses a charge-couple device which is a semiconductor photodetector to simultaneously analyze analytes. WinLab32 window software is used.

In using the ICP-OES, the sample is aspirated through the nebulizer which primarily charges the liquid and transports it into the plasma flame. The ICP-torch consists of three quartz crystal tubes, a radio frequency (RF) and a Tesla coil. Electromagnetic field with argon gas flowing through it is usually ignited by the Tesla coil. Argon is ignited to create the plasma flame which flows with the electromagnetic field. The aspirated samples collide with ions and electrons. The process breaks the sample into monatomic ions. The element gain energy during the collisions, so are excited and further relaxed. At particular wavelengths, the monatomic ions are spilt by optics and analyzed via a semiconductor photodetector –charged coupled device (CCD). With s a standard calibration curve, detection is possible to the lowest ppb or ppm.^{37 - 41}

Table 5. Detection Limit of Trace Metals Using the ICP-OES

Element	Signal Intensity	Concentration (ppm)	3σ	Detection Limit (ppm)
Calcium	389470.00	1.00	16693.23	0.04
Magnesium	54483.20	1.00	656.70	0.01
Iron	602722.50	1.00	22768.23	0.04
Manganese	451939.50	0.10	7621.02	0.002
Lead	1611.90	0.01	124.38	0.0008
Arsenic	91.70	0.01	75.27	0.008
Mercury	195.50	0.01	132.45	0.002
Chromium	6001.30	0.01	144.54	0.0002
Barium	23990.50	0.01	226.95	0.0001
Strontium	1033095.80	0.01	46923.72	0.0005
Cadmium	6540.40	0.01	118.98	0.0002

3.5.2 pH Meter

All instrumental pH measurement in this study was carried out using Accumet XL by 15 Fisher Scientific with a combination of a glass electrode. The pH meter is temperature dependent and all measurements were taken at room temperature.

3.6 Analysis

3.6.1 Trace metals

It must be noted that the method adopted for the determination of the metals were not any of the EPA methods but rather that which was agreed upon by MAWC and the chemistry department. The 1 L clean plastic was first shaken and 200 ml of the water sample was transferred into a small container. The solution was then acidified with a 1:1 HNO₃ solution, filtered with a help of a syringe and a 0.45 μ m filter. The ICP-OES was calibrated with standards to obtain a linear curve with a correlation coefficient in the range 0.99998 – 1.00000.

Table 6. ICP-OES Standards

Element	Standard A	Standard B	Standard C	Standard D
Arsenic	0.01	0.1	1.0	5.0
Barium	0.01	0.1	1.0	5.0
Calcium	1.0	25.0	50.0	75
Cadmium	0.01	0.1	1.0	5.0
Chromium	0.01	0.1	1.0	5.0
Iron	1.0	5.0	10.0	20.0
Mercury	0.01	0.10	1.0	5.0
Magnesium	1.0	7.5	15.0	25.0
Manganese	0.1	1.0	5.0	10.0
Lead	0.01	0.10	1.0	5.0
Strontium	0.01	0.10	1.0	5.0

3.6.2 Total Dissolved Solids

Empty evaporating dishes were washed, dried in an oven, allowed to cool and then stored in desiccators. The mass of each empty evaporating dish was first determined. The water samples were filtered with a 0.45 µm filter and 100 ml of it transferred into the dish and dried in an oven at 110 °C. The drying time was between 4 to 6 hours. After drying, the dish was allowed to cool, put in desiccators and reweighed.

$$\text{TDS} = (\text{B}-\text{A}) * 1000 / \text{Vml} \quad (2)$$

Where B is sum of the mass of residue and mass of dish, A is the mass of empty dish and V is the volume in ml of the samples used.

3.6.3 pH and Alkalinity

The pH meter was calibrated with pH buffer solution of 4.01 and 6.86. The water sample was analyzed at a temperature of 25 °C for all the samples. A 100 ml aliquot was placed in a 250 ml beaker with a stirrer.

The initial pH was first recorded and the sample titrated against a standardized HCl solution. Upon addition of ~0.5 ml of the HCl, a small pH (<0.2 pH units) change was expected during titration. The titration continued until a pH < 4 was reached. The equivalence point was calculated with Excel and the amount of total compounds that neutralize acid was counted as the alkalinity value. In using Excel, we plotted a change in volume against the change in pH to get the steepest slope.

$$\text{Alkalinity (ppm CaCO}_3\text{)} = V_{\text{eq}} * C * 50,000 / V_{\text{sample}} \quad (3)$$

Where V_{eq} is the equivalence point; C is the concentration of acid used and V_{sample} is the volume of the sample used.

RESULTS AND DISCUSSION

4.1 Total Dissolved Solid

Our interest was to find dissolved solids and not sediment or suspended matter. Most natural waters give residual on evaporation²³ with any heat source which when weighed show a fair agreement between the dissolved solids and the sum of the determined constituents.

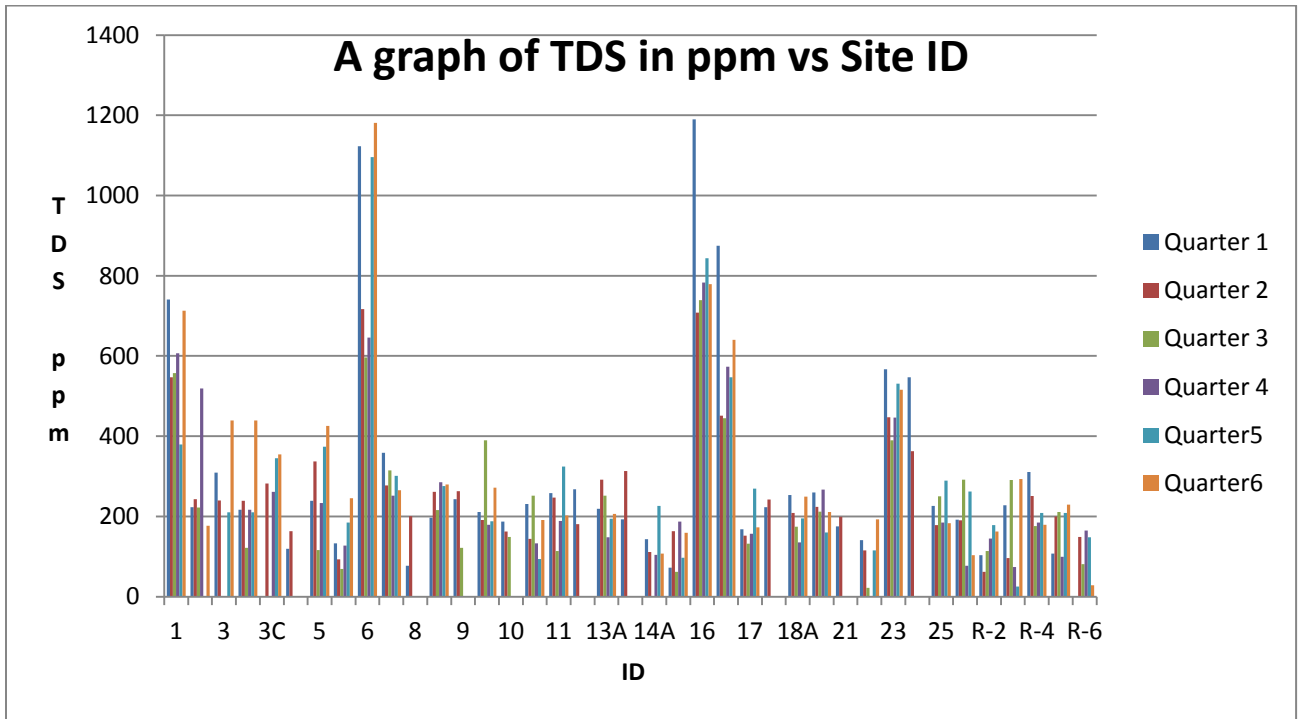


Figure 6. Summary TDS for six quarters.

The gravimetric method was used for the TDS determination. TDS often results from weathering and dissolution of rocks and soil. Fig 6 shows a graph of the TDS of the six quarters against the various sampling sites. Samples for the various quarters were dried at an oven temperature of 110⁰ C for four to six hours.

Quarter one TDS sampling was done in the month of May 2011. Thirty-seven (37) samples were analyzed and an average TDS of 306 ppm was recorded. Significant TDS values were recorded in all the samples which could be due to weathering of rock, soil formation and snowy climate which was observed in early January through April. However, sampling sites 1, 6, 16, 16A 23 and 24 recorded values above 500 ppm which is mainly due to low pH values recorded at those sites.

Quarter two samples were collected in the month August 2011. It must be noted that the drilling of the well started around this time. Thirty-nine (39) samples were analyzed and an average of 245 ppm was recorded. The drop in TDS values compared to the first quarter can be as a result of high temperature observed during the summer. Although the general trend for quarter two was low, the previous acidic site recorded the highest values. Though drilling of the well was ongoing, the TDS values recorded were lower compared to the established baseline.

Quarter three samples were analyzed in December 2011. Generally, quarter three recorded higher values as compared to quarter two but lower than quarter one. This may be due to the presence of snow experienced in the month of December. Twenty-eight (28) samples were analyzed and an average of 240.71 ppm was recorded.

In March 2012, quarter four samples were collected and analyzed. There was a general rise in the TDS values for most of the sampling sites. Notably among them was sampling site 2 which recorded a value of 519 ppm. The general increase may be due to the severe rainfall and snow experienced during the period. Although the values were high, they were not higher than the

established baseline. Twenty-eight (28) samples were analyzed and an average of 259.48 ppm was recorded.

A total of twenty-nine (29) samples were collected in July 2012 to constitute quarter five samples with an average of 293.96 ppm. Quarter five recorded very low values for the entire duration. This once again can be attributed to high temperature recorded in the month of July.

Quarter six sample showed higher TDS concentration from the various sites as compared to the other quarters which is a result of high amount of rains and snowy climate which was observed in the month of November, when the samples were collected. Twenty-nine (29) samples were analyzed and an average of 315.72 ppm was recorded.

Table 7. Quarterly TDS Results in ppm

Site	ID	1Q	2Q	3Q	4Q	5Q	6Q
1	01	741	547	557	607	379	713
2	02	223	243	222	519	255	177
3	03	309	240				
3A	03A	217	239	122	217	210	439
3C	03C		282		261	345	355
4	04	119	163				
5	05	239	337	116	233	374	426
5A	05A	133	93	69	127	185	245
6	06	1123	717	596	646	1096	1181
7	07	359	277	315	252	301	265
8	08	77	201				
8A	08A	197	261	216	285	276	280
9	09	243	263				
9A	09A	211	191	122	179	188	272
10	10	187	162				
10A	10A	231	144	390	133	94	191
11	11	258	247	149	189	324	202
13	13	268	181				
13A	13A	219	292	252	148	194	206
14	14	193	313	114			
14A	14A	143	111		104	226	107
15	15	72	163	62	187	97	159
16	16	1190	708	739	783	844	779
16A	16A	875	451	445	573	547	640
17	17	168	152	132	157	269	173
18	18	223	242				
18A	18A	253	209	174	135	195	249
19	19	260	224	212	267	160	211
21	21	175	199				
22	22	141	115	22	147	115	193
23	23	567	447	390	446	531	516
24	24	547	363				
25	25	226	178	292	185	289	183
R-1	R1	192	190	292	77	262	103
R-2	R2	103	62	114	145	178	162
R-3	R3	228	96	291	74	25	293
R-4	R4	311	251	176	185	209	179
R-5	R5	107	200	211	99	209	229
R-6	R6		149	81	165	148	28

1Q= first quarter, 2Q=second quarter, 3Q=third quarter, 4Q= fourth quarter, 5Q= fifth quarter, 6Q=sixth quarter

4.2 pH and Alkalinity

Alkalinity of the various sample sites were determined to measure the the capacity of the water to neutralize acid. This is important, because its helps to determine the sampling site's ability to neutralize acidic pollution from rainfall or wastewater. The titration method was used to determine the alkalinity and the time for each titration was one hour. pH and alkalinity were determined under room temperature. The Accumet XL 15 pH meter and Accumet combination pH electrode produced by Fisher Scientific were used for the pH readings. Buffer solutions with pH standard of 4.01 and 6.86 were used for the calibration of the pH meter. A 100 ml aliquot of each sample was titrated against standardized HCl solutions. Upon addition of 0.5 ml of the acid, a change of pH <0.2 was expected until the pH < 4.0 . At pH <4 , the alkaline compounds in the samples were used up and the results reported as ppm of CaCO_3 .

A graph of first derivative (dpH/dv) against change in volume (dv) is plotted with the help of excel and the equivalence point was determined at the steepest point of the curve. Alkalinity was calculated as the concentration of CaCO_3 in ppm using equation (3).

Samples which were found to be acidic did not have titration test performed on them due to the fact that alkaline compounds in the samples were either not present or very low to neutralize any additional acid. Sampling sites with high pH values recorded high alkalinity values.

Table 8. Titration Results for Quarter Two Sample Site 11

titrant volume (mL)	pH	dv	dpH/dv
0.00	7.66	0.255	-0.33333
0.51	7.49	0.76	-0.3
1.01	7.34	1.26	-0.2
1.51	7.24	1.76	-0.14
2.01	7.17	2.26	-0.22
2.51	7.06	2.76	-0.18
3.01	6.97	3.26	-0.08
3.51	6.93	3.76	-0.08
4.01	6.89	4.26	-0.06
4.51	6.86	4.76	-0.3
5.01	6.71	5.26	-0.22
5.51	6.60	5.76	-0.08
6.01	6.56	6.26	-0.16
6.51	6.48	6.76	-0.04
7.01	6.46	7.26	-0.06
7.51	6.43	7.76	-0.02
8.01	6.42	8.26	-0.08
8.51	6.38	8.76	-0.08
9.01	6.34	9.26	-0.34
9.51	6.17	9.76	-0.42
10.01	5.96	10.26	-0.22
10.51	5.85	10.76	-0.46
11.01	5.62	11.26	-0.52
11.51	5.36	11.76	-1.42
12.01	4.65	12.26	-1.14
12.51	4.08	12.76	-0.42
13.01	3.87		

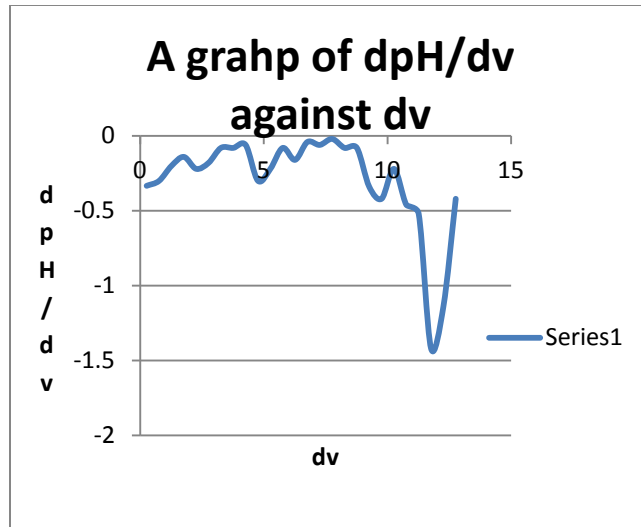


Figure 7. Titration curve for quarter two site 11

Table 9. Alkalinity Results for the first Six Quarters

Site	ID	1Q	2Q	3Q	4Q	5Q	6Q
1	1	acidic	10.52	acidic	acidic	26.22	27.46
2	2	68.69	64.8	6.76	67.61	90.12	67.26
3	3	93.05	73.15		56.81		
3A	03A	73.01	81.5	67.61		72.62	92.14
3C	03C		43.92		51.41	136.42	
4	4	34.96	60.62				
5	5	78.41	81.5	67.31		107.42	102.09
5A	05A	94.61	85.67	89.21	67.61	113.22	107.06
6	6	acidic	acidic	acidic	Acidic	acidic	acidic
7	7	79.71	94.02	67.61	56.81	124.82	112.04
8	8	108.71	102.37				
8A	08A	105.21	102.37	51.41	56.81	153.82	141.89
9	9	72.87	81.5				
9A	09A	61.74	73.15	56.81	51.41	137.59	107.06
10	10	46.01	56.45				
10A	10A	73.01	64.8	40.61	51.41	108.34	92.14
11	11	112.86	98.2	89.21	67.61	149.29	151.84
13	13	67.45	64.8		51.41		92.14
13A	13A	62.21	60.62	29.80		61.54	
14	14	51.41	43.92	40.10			
14A	14A	56.81	60.62		40.61	67.39	121.99
15	15	62.21	60.62	56.81	56.81	84.94	77.21
16	16	acidic	acidic	acidic	acidic	acidic	acidic
16A	16A	acidic	6.35	acidic	acidic	acidic	acidic
17	17	73.91	48.1	51.41	51.41	90.79	67.26
18	18	39.81	68.97				97.11
18A	18A	72.30	77.32	56.81	51.41	84.94	136.91
19	19	100.01	94.02	67.61	62.21	125.89	136.91
21	21	67.61	68.97				
22	22	81.89	81.5	56.81	56.81	125.89	112.04
23	23	55.96	135.78	83.81	83.81	172.69	117.01
24	24	116.21	85.67				
25	25	51.41	62.71	67.61	67.61	114.19	102.09
R-1	R1	32.68	35.15	78.41	78.41	36.21	62.29
R-2	R2	56.81	39.75	56.81	56.81	36.21	62.29
R-3	R3	62.51	52.27	56.81	56.81	40.46	57.31
R-4	R4	49.02	43.92	48.71	48.81	31.96	52.34
R-5	R5	62.21	35.57	56.81	56.81	36.21	52.34
R-6	R6		43.92	56.81	56.81	40.46	62.39

Note. Sites that were blank under particular quarters were not analyzed.

Titration of quarter one samples was done using standardized 0.0198N HCl solution. Samples 1, 6, 16 and 16A recorded initial pH in the acidic region. Sites with low alkalinity are very susceptible in pH whereas those with high alkalinity resist change in pH. Alkaline compounds like carbonate or bicarbonate which measure the alkalinity of water may be result from rocks or soil contained in carbonate mineral.

For quarter two, standardized 0.0167 N HCl solution used for the titration. The values obtained were in the range 10.52 -135.78 ppm. The average value for quarter two was 66.08 ppm. Sampling site 1 recorded the lowest value of 10.52 ppm while 23 recorded the highest value of 135.78 ppm.

A standardized 0.0216 N HCl solution was used for the titration for quarter three samples. The alkalinity values obtained for the remaining were in the range 6.76 - 89.21 ppm with an average of 58.40 ppm.

A standardized 0.0216 N HCl solution was used for the titration. Sample sites 1, 6, 16 and 16A were found to be acidic with pH of 5.78, 6.66, 4.48 and 4.59 respectively. The remaining sites gave values in the range of 35.21 -89.21 ppm. The average alkalinity was 56.10 ppm.

A standardized 0.0232 N HCl solution was used for the titration of quarter five samples. Sampling sites 6, 16 and 16A had initial pH <5. The alkalinity results for the remaining sampling sites were in the range 26.22 - 172.69 ppm and an of average 91.14 ppm.

A standardized 0.0199 N HCl solution was used for the titration of quarter six samples. Alkalinity results were in the range of 27.46 - 151.84 ppm with an average alkalinity value of 90.99 ppm. Sampling sites 6 , 16 and 16A recorded pH < 5.

4.3 Trace Metal Determination

A 5100 PC Perkin Elmer atomic absorption spectrometer was initially used in the determination of the trace metals. There were problems with several of the lamps so the inductively coupled plasma optical emission spectrometer (ICP-OES) owned by the Department of Geosciences was used. The limit of detection (LOD), 3σ , where σ is the standard deviation of the blank is listed in Table 17. The signal intensities obtained for the blank solution of each standard curve was averaged and used in the calculation of the LOD.

An Optima 2100 DV ICP from Perkin Elmer was used in the determination of the trace metals. 200ml of each sample was acidified with 5ml 1:1 HNO₃ solution. The acidified solution was then filtered using a 0.45- μ m filter with the help of a syringe. A linear calibration curve and correlation coefficients of 0.99998 -1.0000 was obtained in all cases.

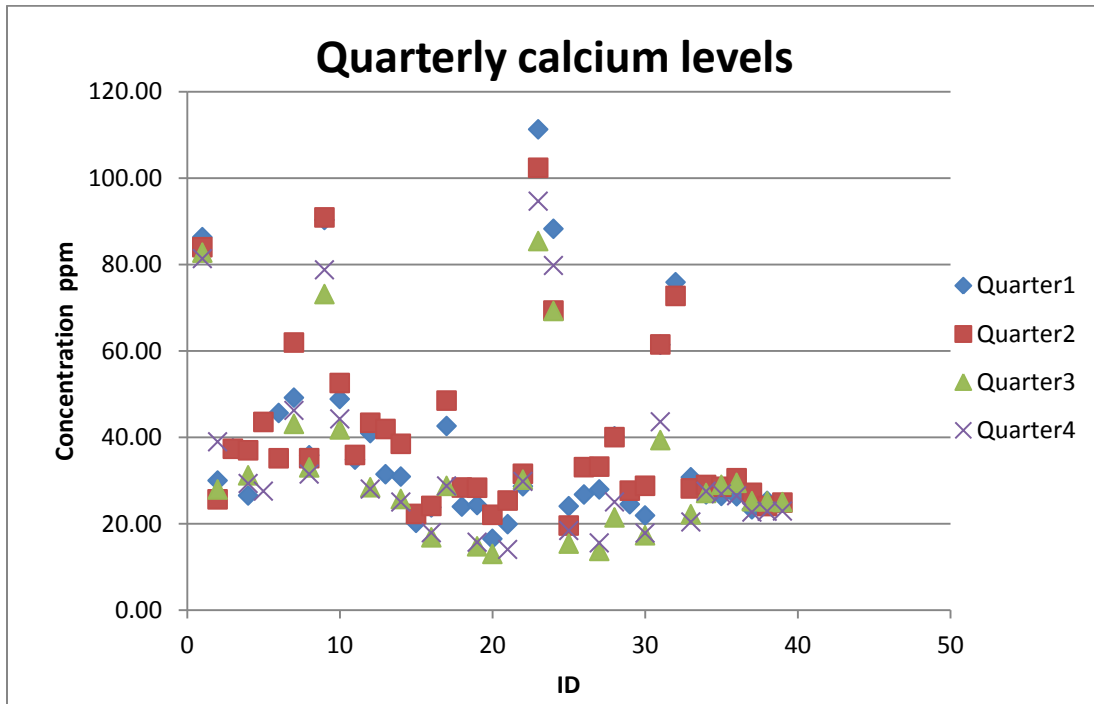


Figure 8. Quarterly calcium levels.

Absorbance of Calcium using the ICP-OES was done at 317.933 nm. Higher levels of calcium were record for sample ID's 01, 06, 16 and 16A in all quarters. Quarter one recorded the highest calcium level with sample ID 16 recording 111.30 ppm as the highest calcium level over the quarters. Since the remaining quarters barely recorded extremely values of calcium, the calcium present could be attributed to natural process like rock weathering and soil formation, rainfall and snowy climate.

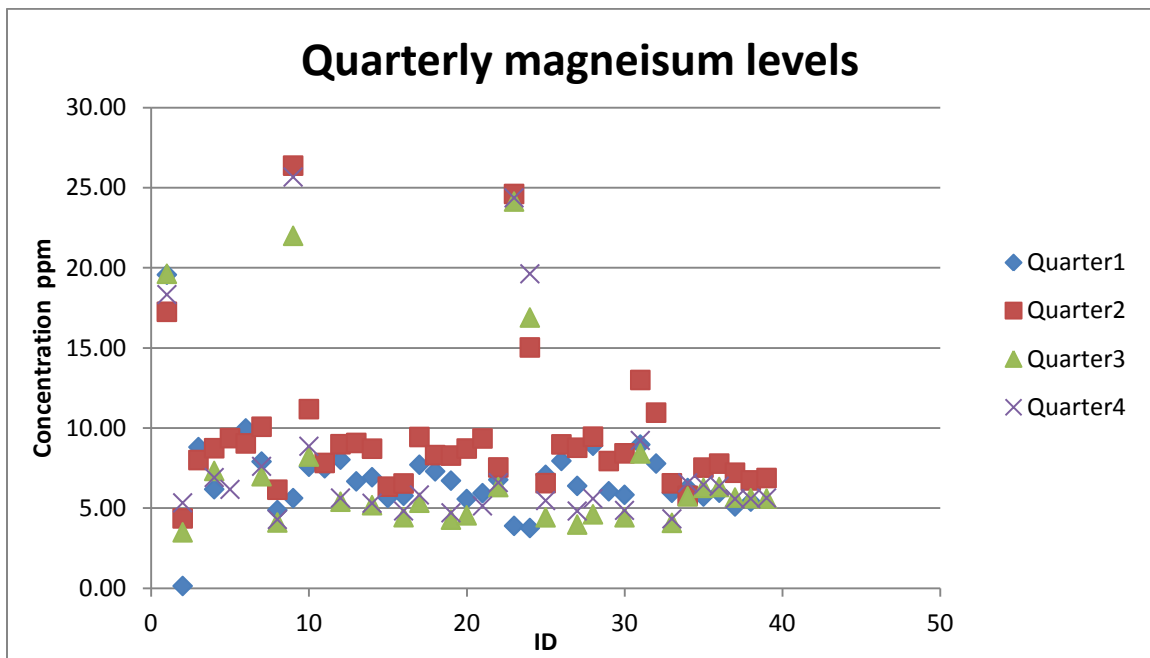


Figure 9. Quarterly magnesium levels.

Absorbance of Magnesium using the ICP-OES was at a wavelength of 279.077nm. Magnesium concentration on the average was not as high as compared to calcium. Quarter two samples recorded the highest levels of magnesium. Although quarter two samples recorded higher values than the baseline established, the result did not show a direct correlation with drilling of the well. The higher values recorded in quarter two may be as a result of rain fall recorded in the month of July. Sample ID 6 recorded 26.38 ppm which was the highest magnesium recorded so far.

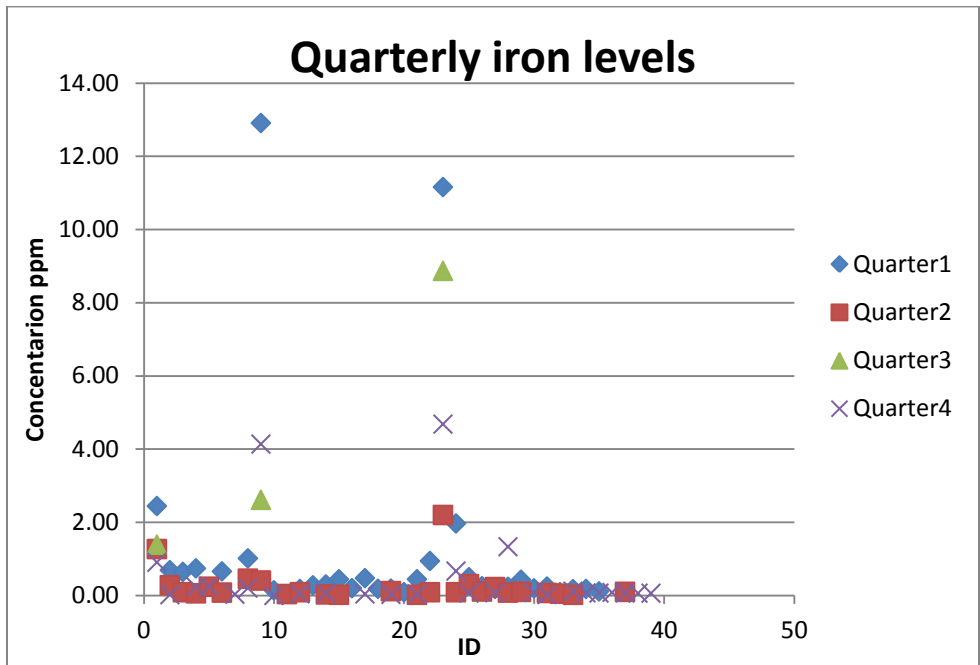


Figure 10. Quarterly iron levels.

Absorbance of iron was done at wavelength 259.393nm. From the fig 10, it is clear that most of the sites recorded extremely low values of iron over the period while some readings were below the estimated limits of detection.

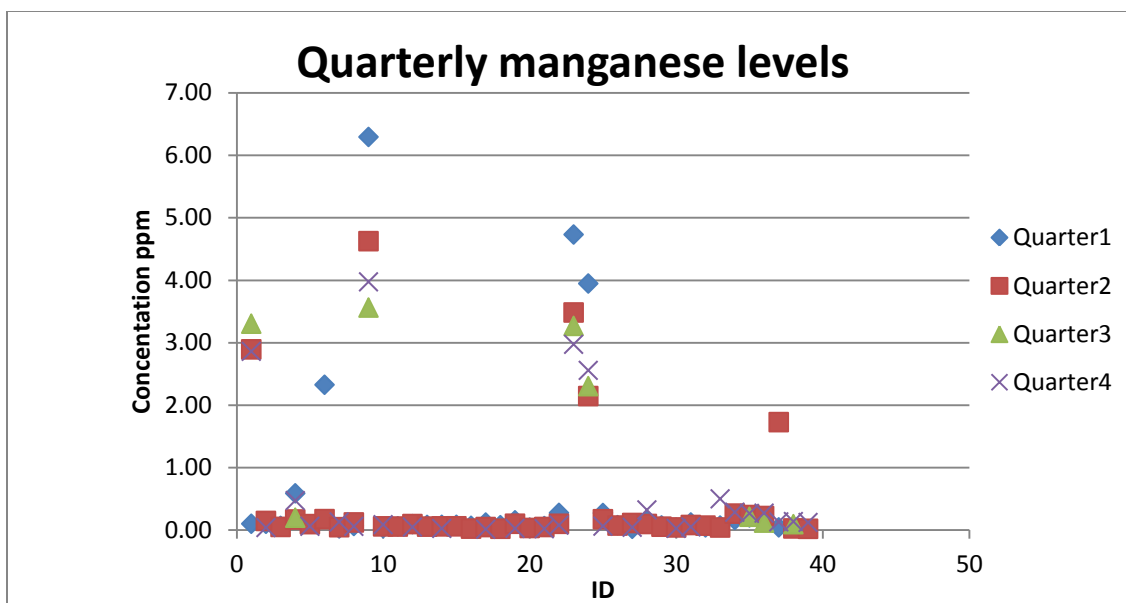


Figure 11. Quarterly manganese levels.

Absorbance of Manganese was done at a wavelength of 257.610 nm. Quarter three and four had some ID's below the detection limit of Manganese. Manganese level in general was very low in all quarters. Sample ID 6 and 16 recorded significant values in all quarters.

Absorbance of lead was done at wavelength of 220.353nm. Lead was detected below its detection limit. Arsenic absorbance was at a wavelength of 193.696 nm. Although arsenic is naturally occurring in rock minerals, they were not detected by the ICP-OES in any quarter of the research. Mercury absorbance was at wavelength 302.150 nm. Mercury was detected below the detection limit. A wavelength of 267.716 nm was expected for the absorbance of chromium but no trace of chromium has been detected so far. Cadmium absorbance was at a wavelength 228.802 nm and like chromium; it has not been detected at this point of the research.

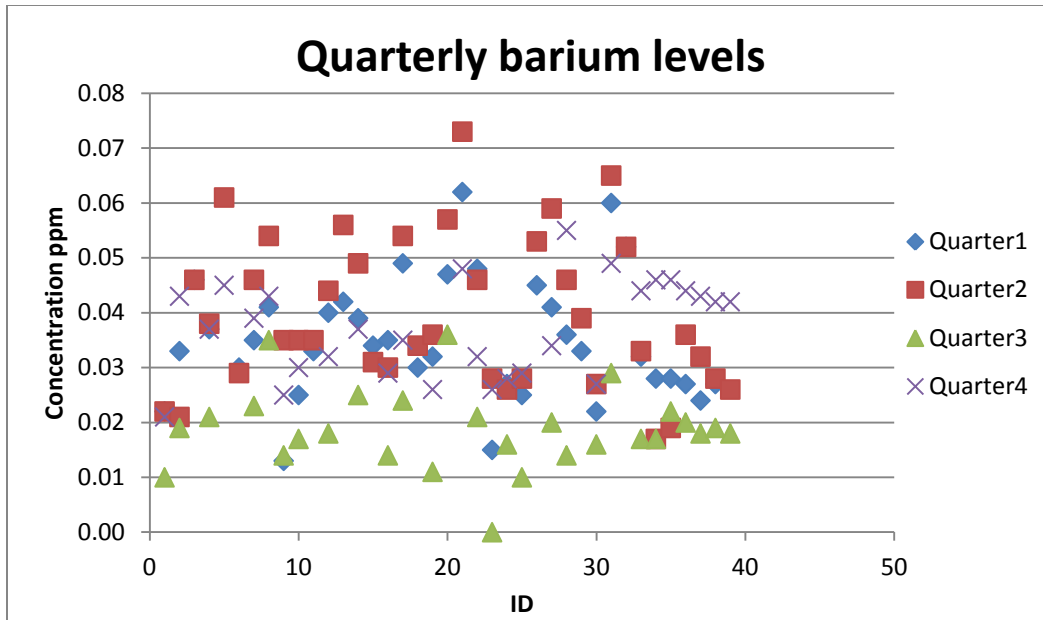


Figure 14. Quarterly barium levels.

Barium absorbance was at a wavelength 233.527 nm. The level of barium recorded over the quarters could be as a result of its presence naturally in the environment. The barium concentrations recorded were low and cannot pose a health issue to mankind. Quarter two recorded the highest barium level.

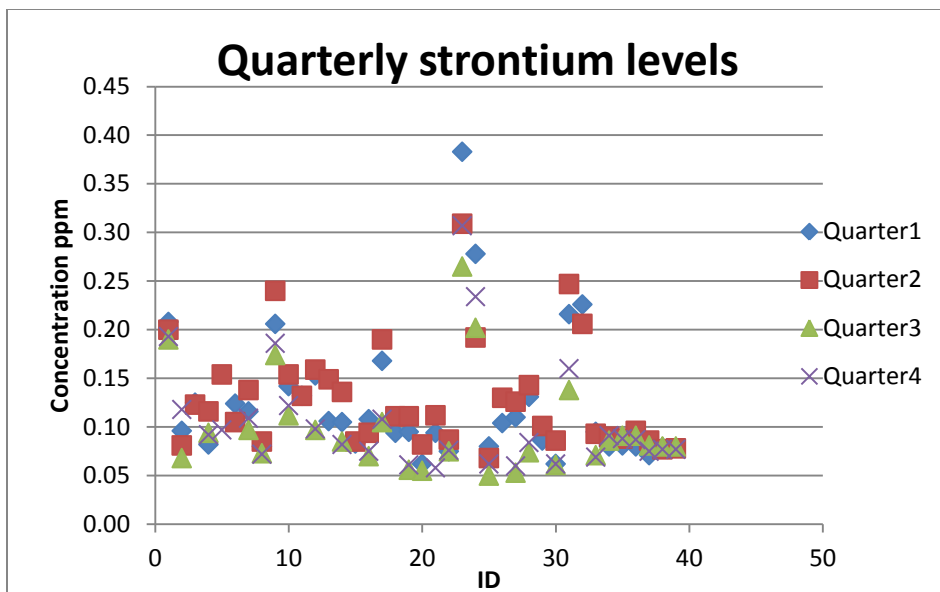


Figure 13. Quarterly strontium levels.

Strontium absorbance was at wavelength 407.771 nm. Detection was in a range of 0.05 – 0.31 ppm over the quarters with the acidic site recording the highest values.

Chapter 5

SUMMARY/CONCLUSION

Two groups of students have been working on the entire project until now. I worked on the determination of metals with the ICP-OES, TDS and alkalinity determination.

Samples were collected from the drilling site on quarterly basis to be analyzed. The idea was to prove whether there was a direct correlation of the drilling of the well.

First quarter samples were used to establish a baseline before the drilling and gas removal. Samples ID which has low pH values recorded the high amount of metals throughout the study.

The gravimetric method was used to determine the TDS in ppm. Sample ID with low pH values recorded high TDS values throughout the study.

The drilling of the well involves the use of highly concentrated solutions. The results available show a consistent pattern in the levels of these metals. The metals present are usually through natural processes like weathering of the rock and soil formation.

In conclusion, the result available to us does not show a direct correlation of the drilling of the well on the samples analyzed.

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Appendix A

List of abbreviations

AMD	Abandoned mine drainage
KOF	Kick of point
MAWC	Municipal Authority of Westmoreland County
IUP	Indiana University of Pennsylvania
US	United States
EPA	Environmental Protection Agency
MCL	Maximum Contaminants Level
SMCL	Secondary Maximum Contaminants level
ppm	part per million
ppb	part per billion
TDS	Total Dissolved Solid
DL	Detection Limit

Appendix B

LOD of Inorganic Contaminants by Ion Chromatography

Anion	concentration (ppm)	3σ	Signal intensity	Detection limits (ppm)
Fluoride	0.01	0.133544535	14.796	0.00009
Chloride	1.0	0.153847791	14.808	0.01
Bromide	0.1	0.008660253	14.696	0.0001
Nitrate	0.1	0.008997616	14.694	0.0001
Phosphate	0.1	0.008254869	14.694	0.0001
Sulfate	1.0	0.016405575	14.701	0.001

Appendix C

First quarter anions results

Site	F (ppm)	Cl ⁻ (ppm)	Br ⁻ (ppm)	NO ₃ ⁻ (ppm)	PO ₄ ²⁻ (ppm)	SO ₄ ²⁻ (ppm)
1	0.14	67.74	0.70	10.10	0.41	431.44
2	0.14	60.35	3.80	4.18	0.42	19.62
3	0.18	72.39	0.43	4.70	<DL	33.36
3A	0.07	27.08	0.93	2.09	<DL	34.50
4	0.08	17.46	0.48	3.11	0.31	149.07
5	0.10	42.35	0.47	4.28	<DL	93.38
5A	0.13	3.03	0.83	1.64	<DL	25.44
6	0.22	0.72	0.25	0.46	0.31	56.55
7	0.08	46.36	0.42	1.78	0.28	96.69
8	0.11	26.48	0.48	3.02	0.33	20.95
8A	0.10	49.25	0.42	4.55	0.29	21.69
9	0.08	6.55	0.60	11.66	0.36	36.71
9A	0.10	6.84	0.55	8.93	0.31	33.15
10	0.08	36.86	0.51	3.40	0.30	19.29
10A	0.01	33.55	0.66	4.74	<DL	20.11
11	0.05	41.82	0.47	2.83	0.32	18.75
13	0.06	50.41	0.65	2.81	<DL	93.58
13A	0.17	50.77	0.68	2.85	<DL	21.19
14	0.26	1.08	0.24	0.50	<DL	1.95
14A	0.11	30.57	0.45	2.29	0.26	25.40
15	0.13	2.30	0.62	2.42	0.29	55.09
16	0.32	75.89	0.38	1.97	<DL	709.48
16A	0.27	57.07	0.38	3.86	<DL	508.48
17	0.11	33.64	0.47	4.77	<DL	21.35
18	0.10	42.88	0.58	2.67	<DL	45.50
18A	0.14	36.10	0.55	4.17	<DL	38.89
19	0.13	65.14	0.89	4.46	0.29	20.41
21	0.05	25.17	0.52	5.58	<DL	22.59
22	0.14	9.36	0.64	8.75	<DL	25.29
23	0.18	206.64	0.94	5.34	0.30	41.27
24	0.13	67.02	0.46	4.81	0.33	125.13
25	0.19	41.61	0.50	2.63	0.27	25.77
R-1	0.14	35.79	0.49	5.52	<DL	56.43
R-2	0.17	58.86	0.36	3.36	0.31	54.29
R-3	0.03	27.03	0.38	2.56	<DL	45.87
R-4	0.18	40.19	0.70	3.84	0.29	46.25
R-5	0.11	40.39	0.54	4.43	<DL	48.97

Appendix D

Second quarter anions results

Site	F ⁻ (ppm)	Cl ⁻ (ppm)	Br ⁻ (ppm)	NO ₃ ⁻ (ppm)	PO ₄ ²⁻ (ppm)	SO ₄ ²⁻ (ppm)
1	0.04	74.24	0.46	17.58	0.40	310.66
2	0.16	65.01	3.16	11.79	0.87	13.96
3	0.10	66.66	0.33	4.27	<DL	34.27
3A	0.09	48.53	0.31	4.50	0.28	43.98
3C	0.14	101.06	0.34	4.44	0.32	25.57
4	0.06	23.95	0.32	5.69	0.29	61.61
5	0.11	69.34	0.32	6.82	0.35	101.17
5A	0.10	3.31	0.31	4.30	0.28	20.06
6	0.08	66.31	0.30	1.96	0.47	409.36
7	0.08	57.83	0.30	1.37	0.29	76.85
8	0.11	28.01	0.33	5.76	0.44	16.89
8A	0.09	59.06	0.31	4.79	<DL	20.75
9	0.08	45.90	0.30	10.13	0.42	35.61
9A	0.12	36.37	0.32	8.51	0.43	29.92
10	0.14	33.90	0.31	4.21	0.33	18.40
10A	0.07	34.81	0.32	4.23	0.32	18.68
11	0.14	45.98	0.33	3.49	0.34	19.67
13	0.06	62.65	0.35	3.95	0.31	20.73
13A	0.12	60.87	0.34	3.53	0.31	27.08
14	0.14	51.41	0.44	4.47	0.29	32.03
14A	0.06	49.41	0.30	4.96	0.29	31.36
15	0.06	2.40	0.32	3.45	0.30	42.34
16	0.08	81.60	0.29	4.55	0.47	397.26
16A	0.05	57.47	0.31	3.43	0.39	230.86
17	0.08	42.71	0.31	2.67	0.29	10.60
18	0.15	64.80	0.34	3.54	0.29	30.25
18A	0.14	57.58	0.30	3.81	0.29	27.37
19	0.13	71.91	0.37	3.93	0.30	21.63
21	0.10	31.29	0.29	6.26	0.29	18.34
22	0.13	19.39	0.31	4.99	0.35	20.25
23	0.12	204.59	0.31	5.30	<DL	33.20
24	0.09	35.09	0.30	3.39	0.34	135.49
25	0.15	31.55	0.32	3.82	0.31	20.39
R-1	0.10	47.60	0.33	2.45	0.32	53.84
R-2	0.15	43.88	0.30	2.90	0.31	54.17
R-3	0.04	44.38	0.46	2.82	0.31	49.83
R-4	0.11	49.91	0.57	3.17	0.28	47.12
R-5	0.17	42.99	0.62	2.42	0.28	42.88
R-6	0.09	38.44	0.31	1.97	0.29	47.76

Appendix E

Third quarter anions results

Site	F (ppm)	Cl ⁻ (ppm)	Br ⁻ (ppm)	NO ₃ ⁻ (ppm)	PO ₄ ²⁻ (ppm)	SO ₄ ²⁻ (ppm)
1	0.02	62.47	0.37	10.20	0.45	336.10
2	0.16	39.53	1.59	5.27	0.43	24.72
3A	0.13	28.86	0.25	5.27	0.28	52.53
5	0.02	30.53	0.25	5.90	0.31	88.26
5A	0.13	2.76	0.23	5.21	0.30	24.17
6	0.05	24.93	0.26	3.32	0.51	360.50
7	0.05	30.21	0.24	1.62	0.29	79.92
8A	0.11	22.87	0.25	3.68	<DL	24.01
9A	0.05	4.98	0.21	11.34	0.33	36.18
10A	0.20	17.00	0.24	7.70	0.28	20.45
11	0.09	22.54	0.24	3.84	0.30	22.05
13A	0.17	21.16	0.24	3.10	<DL	23.41
14	0.12	14.69	0.24	7.13	0.29	30.42
15	0.08	2.10	0.22	4.09	0.31	65.43
16	0.16	57.86	0.23	3.52	0.60	456.65
16A	0.17	47.16	0.26	4.91	0.44	289.62
17	0.13	22.48	0.25	6.47	0.28	28.20
18A	0.16	19.12	0.23	5.02	<DL	26.17
19	0.13	27.39	0.26	4.65	0.30	22.73
22	0.15	13.60	0.24	8.75	0.29	21.25
23	0.18	91.81	0.31	7.83	<DL	37.98
25	0.14	13.86	0.32	3.42	0.29	22.04
R-1	0.01	42.85	0.25	1.65	0.28	52.77
R-2	0.13	39.61	0.25	3.47	0.30	53.17
R-3	0.01	39.96	0.24	2.81	0.30	53.92
R-4	0.14	38.87	0.28	2.76	0.29	45.73
R-5	0.14	38.83	0.26	1.88	0.29	45.77
R-6	0.04	39.07	0.25	2.32	0.29	45.91

Appendix F

Four quarter anions results

Site	F ⁻ (ppm)	Cl ⁻ (ppm)	Br ⁻ (ppm)	NO ₃ ⁻ (ppm)	PO ₄ ²⁻ (ppm)	SO ₄ ²⁻ (ppm)
1	0.10	62.28	0.35	11.37	0.41	290.89
2	0.20	258.82	1.76	2.77	0.29	22.89
3A	0.18	57.33	0.25	4.88	0.32	44.07
3C	0.19	93.86	0.24	5.96	0.31	28.93
5	0.14	45.46	0.24	5.03	0.29	90.49
5A	0.21	2.70	0.23	4.68	0.30	23.50
6	0.08	33.56	0.24	1.74	0.55	401.72
7	0.15	46.80	0.23	2.35	0.29	70.06
8A	0.22	40.71	0.23	3.75	0.28	21.27
9A	0.13	13.64	0.22	8.21	307.00	50.87
10A	0.20	38.78	0.24	6.02	0.28	20.65
11	0.20	42.84	0.22	3.59	0.27	19.21
13A	0.19	33.68	0.24	4.41	0.29	22.40
14A	0.21	22.52	0.23	7.15	0.28	25.90
15	0.14	1.77	0.23	3.19	0.30	70.93
16	0.08	90.93	0.25	3.90	0.40	391.34
16A	0.17	83.81	0.27	5.82	0.36	311.88
17	0.11	35.48	0.24	6.38	0.28	30.73
18A	0.14	30.25	0.23	3.66	0.28	24.13
19	0.17	44.09	0.25	4.67	0.29	20.42
22	0.13	16.04	0.21	8.09	0.28	21.41
23	0.03	207.47	0.25	7.61	0.30	34.90
25	0.17	21.37	0.22	3.54	0.28	23.52
R-1	0.02	41.62	0.24	3.63	0.28	56.64
R-2	0.08	41.39	0.24	3.88	0.28	58.55
R-3	0.16	41.39	0.23	3.95	0.28	57.34
R-4	0.14	35.17	0.25	3.64	0.27	45.38
R-5	0.16	35.69	0.24	4.00	0.28	45.48
R-6	0.17	34.97	0.23	3.24	0.28	45.45