THE PENNSYLVANIA STATE UNIVERSITY
COLLEGE OF EARTH AND MINERAL SCIENCES

DEPARTMENT OF GEOSCIENCES

Impact of Oil and Gas Industry Wastewater on Water and Sediment Chemistry In One Stream In West-Central Pennsylvania

A Senior Thesis in Geosciences

by

Daniel Snyder

Submitted in partial fulfillment
of the requirements
for the degree of

Bachelor of Science

Summer 2014

Reviewed and approved by:

Susan Brantley, Distinguished Professor of Geosciences

5-2-14
Date

Peter J. Heaney, Professor of Geosciences
Associate Head for Undergraduate Programs

5/2/14
Date

Impact of Oil and Gas Industry Wastewater on Water and Sediment Chemistry In One Stream In West-Central Pennsylvania

Daniel Snyder

ABSTRACT

Hydraulic fracturing fluid is composed of large volumes of water that contain roughly 1% chemical additives, and proppant. Fracking fluid is injected during shale gas development and returns to the land surface mixed with formation waters produced during gas extraction. These waters are treated several ways, including processing at centralized waste treatment (CWT) facilities. Treated wastewater from conventional oil and gas wells are discharged at Blacklick Creek, PA, according to recommended PA water standards. However, the treatment plant has been subject to fines from the EPA. Water and sediment chemistry near the discharge point were tested in several ways: direct measurement of electrical conductivity (EC), UV/visible spectrometry of in-stream water, and laboratory analysis. Laboratory analysis included dissolved organic carbon (DOC), major anions, and cations, and metals. Preliminary results indicated very high salt concentrations downstream from the treatment discharge. Water analyses were be compared to chemical analyses of the sediments of the creek.

ACKNOWLEDGEMENTS

I would like to express my gratitude to Dr. Andrew Neal for his integral role in this project. He provided his expertise and helped me with a wide variety of field and analytical methods. I would also like to thank Dr. Susan Brantley, my thesis advisor. She provided me with excellent guidance and encouragement with the project. I would also like to thank Laura Liermann, Henry Gong, Dr. Ephraim Govere for help with my IC, ICP-AES and DOC lab work. Also, thanks to my family, and friends for support, and encouragement through the entire thesis process. This research was made possible by the Geosciences Department at Pennsylvania State University. Financial Support was provided by National Science Foundation Grant EAR – 1239285 (S. Brantley) for the Susquehanna Shale Hills Critical Zone Observatory.

Introduction

During initiation and production of gas from shale gas wells, waste fluids and produced fluids are returned to the land surface after drilling and fracking (Robart 2012). The waste fluids are known as flowback fluid soon after initiation, but production waters after the first two weeks. Flowback fluids are typically held at the surface for subsequent disposal, treatment, or reuse (Kargbo et al 2010).In PA, before 2011, Centralized Waste Treatment plants (CWT) were legally allowed to discharge these treated wastewaters from both conventional and unconventional oil and gas wells into streams in Pennsylvania. After 2011, such wastes can only be discharged legally by CWTs for waste from conventional oil/gas wells.

Flowback fluids can contain total dissolved solids (TDS) and salt concentrations exceeding 100,000 mg/L (Haluszczak et al 2013). In PA unconventional gas wells, these salts come from the brines in the subsurface, including from the Marcellus Shale formation. This formation is the second saltiest and one of the most radiogenic sedimentary basins in the United States (Vidic et al 2013). This creates a major problem in remediating, or recycling the flowback fluid for industry and society. The large water volumes, large concentrations of TDS, and complex chemical compositions of the flowback fluid have generated concern with the public about the remediation and management of the fluid.

Salts are an important factor to look at because they can damage water quality. When a CWT discharges brine, it is common to see large concentrations of different salts. A large problem that is experienced with municipal waste treatment plants is downstream concentrations of Br. Br is a major anion that is found in the salt beds surrounding oil and natural gas deposits in Pennsylvania. Disinfection of Br compounds produces brominated-DBP (disinfection by-products) which are highly toxic (Hladik et al 2014). Before 2011, in PA, several researchers pointed out that bromine was present at unacceptably high concentrations in the Allegheny river watershed and concern was expressed about the possibility of formation of brominated DBP in drinking water for Pittsburgh. For that reason, in 2011discharge was no longer allowed into PA stream from unconventional oil/gas wells.

Nonetheless, CWTs can still discharge brine from conventional oil/gas wells. For example, the Josephine brine plant releases brine into Blacklick creek in the Allegheny river watershed. In addition to the CWT, there is a large amount of abandoned coal mines that are found along the Blacklick Creek watershed. Acid Mine Drainage (AMD) generates SO_4 which then gets discharged into the creek. The organic compounds that are being released from the effluents discharge could create a potential interaction. Also, the effluents discharged from the CWT have contained material that generates radioactivity. These particles have had an effect on the radioactivity of varying sections found in Blacklick Creek, particularly around the discharge pipe. The radioactivity levels that were seen (^{226}Ra and ^{228}Ra) were at values exceeding the range of EPA regulations, and in the range of technologically enhanced naturally occurring radioactive material (TENORM) (Warner et al 2013).

Commonly CWTs have a problem with maintaining an acceptable effluent discharge which falls within the EPA (Environmental Protection Agency) standards. Under the Clean Water Act, Josephine Brine remediation plant has had several violations for elevated levels of Br and radioactivity greater than the EPA (Environmental Protection Agency) standard (USEPA 2011). In 2011, the Pennsylvania Department of Environmental Protection (PADEP) requested that unconventional natural gas development (UNGD) flowback waters stopped being disposed through CWTs (Agency 2012, Ferrar et al 2013). Other remediation techniques have existed prior, but have become more relevant recently. There are very few Class II injection wells that are found in Pennsylvania. As a result, wastewater has to be transported to Ohio in order to discharge the fluids safely (Ferrar et al 2013, Lutz et al 2013, Soeder & Kappel 2009). However, a problem that arises with injection wells is the seismic activity associated with them (Ellsworth 2013). Another favored remediation technique is the reuse of the fracking fluid. This has been known to help production in the fracking wells (Folger et al 2009). However, precipitation of minerals can occur due to the over saturation of the fluid from concentrations getting too large.

The interest with Blacklick Creek has come from its large amount of contamination. The contamination that is being discharged into Blacklick Creek from the Josephine Brine Treatment plant includes organic compounds, salts, and radioactivity from particles. Also, Blacklick Creek lies within the Pittsburgh watershed, which the contamination eventually makes its way to municipal waste treatment plants (Cyprych et al 2013). The Josephine Brine Treatment plant has broken EPA regulations for concentrations seen in their discharge (USEPA 2011).

Salts are important because unconventional wells and conventional wells generate large concentrations of salts with their waste fluids- produced and flowback. CWTs are not effective at removing large concentrations of salts from the flowback fluids they receive.

In this study, the discharged effluents from the Josephine Brine Treatment Facility were analyzed and evaluated. Upstream and downstream, from the point of effluents discharge, sediment and stream water were collected and analyzed The collection sites for sediment and stream water can be identified by the green dots in Figure 1.

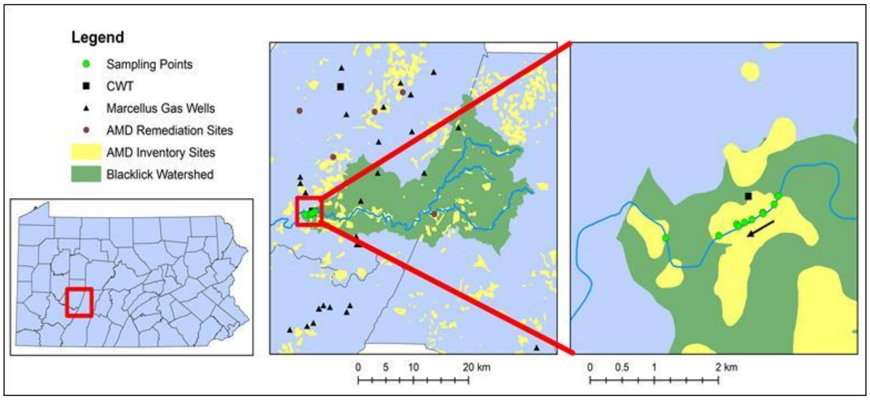


Figure **1**: Figure created by Andrew Neal of the study site on Blacklick Creek showing oil/gas and AMD inventory sties surrounding the Blacklick Creek watershed per USEPA records.

There were three different sampling dates to the creek in order to get samples of varying streamflow. The different streamflow in the creek, allowed for the impact of dilution to be observed on the effluents. We hypothesize that within the 2,067 m sampling window, the concentration of anions and cations will not return to background levels. Also, we hypothesize that the effluent particles are interacting with the Fe rich soils found on the creek bed.

Methods

The major concentrations of Br, SO_4, Cl, Ca, Na, and Sr were analyzed from the effluents of the Josephine Brine Treatment plant by analyzing stream water and sediments found in Blacklick Creek. The stream water and sediments were taken upstream and downstream from the effluent discharge location. Samples from Blacklick Creek were collected on three separate dates throughout a three month time period that started in October 2013 and ended in December 2013. Sixteen water samples, and eight sediment samples were collected ~357 m upstream to ~2,067m downstream along the river channel from the effluents discharge point. On the three different sampling dates, water samples were collected using acid washed high density polyethylene (HDPE) plastic bottles. Dissolved organic carbon (DOC) samples were also collected and filtered using a 0.45 µm filter-top into combusted glass containers. Sediment grab samples were collected on the first two sampling dates, but not the third because streamflow was too great. Sediment samples were not taken at every location because of the lack of sediment that was present. Sediment samples were collected at the sites: upstream, site #2, CWT/stream, midstream, site #1, site #3, and downstream. After transportation back to Pennsylvania State University, samples were stored in a refrigerator until analysis

The dates for the DOC samples were analyzed 2-3 weeks after collection (Table 7) in order to prevent degeneration of DOC. The samples were analyzed for DOC at Pennsylvania State University in the Soil Research Cluster Laboratory. The samples were analyzed on a Shimadzu Total Organic Carbon Analyzer TOC-5000A equipped with an infrared detector in order to measure parts per million (ppm) of DOC. The machine was calibrated using a 1000 ppm stock solution that was diluted by Laura Liermann and Daniel Snyder to four different standards of 5, 10, 15, and 30 ppm of DOC. The repeated analyses of standard solutions for TOC-5000A are reliable to within 2-5%. The percentage of error for the calculations were done using the 5% value in order to show the least accurate case possible.

Each site's water samples were split in order to analyze them for both cations and anions. The water samples that were run for cations were filtered using a 0.45 µm filter in the laboratory, within 528 hours (10/7), 96 hours (10/25) and 840 hours (12/6) of sampling. They were then acidified using 15 µL of high purity HCl. The samples were analyzed using a Perkin-Elmer Otima 5300 using Inductively Coupled Plasma Spectrometry (ICP-AES). The elements that were analyzed from the samples were Al, Ca, Fe, K, Mg, Mn, Na, P, Si, and Sr. The repeated analyses of standard solutions for the ICP-AES are reliable to within 2-5%. The percentage depends on the concentration level and the particular element that is being analyzed for. The percentage of error for the calculations were done using the 3% value.

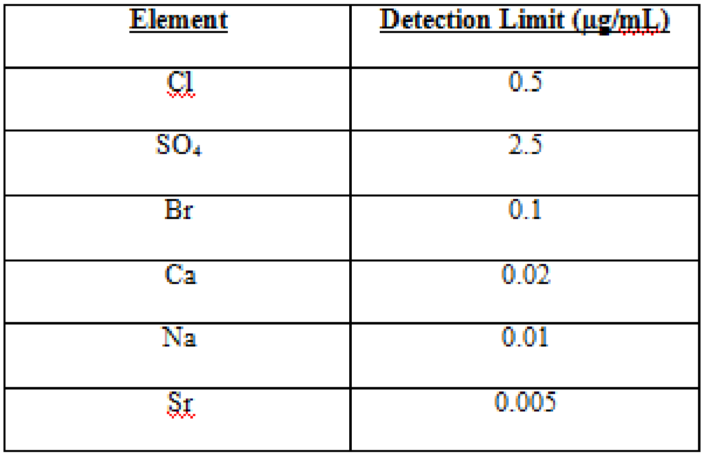
The water samples collected for anion analysis were filtered in the laboratory within 528 hours (10/7), 96 hours (10/25) and 840 hours (12/6) of sampling using a 0.45 µm filter. They were then run several times at different dilution factors on a Dionex ICS2500 ion chromatography system. This system is equipped with a IonPac AS18 4x250 mm anion exchange column, and IonPac AG18 4x50 mm guard column. The samples were diluted in order to allow for the concentrations to fall within the calibration curve, and get a more accurate result. The run conditions for F, Cl, SO_4, Br and NO_3 included a 39 mM, KOH eluent, and each isocratic run was ~12 minutes per sample. The percentage of error for the calculations were done using the 5% value in order to show the least accurate case possible.

The sediment grab samples were analyzed with sequential extractions. Samples of the sediment were scooped out of the grab bag, and placed inside a covered Petri dish. They were then placed in an oven for a span of 3 to 4 days at roughly a constant temperature of 50˚C in order to evaporate off the moisture. The samples were then weighed out into 0.5 g samples. To extract the exchangeable fraction, 10 mL of 0.1 M ammonium acetate was added to the 0.5g sample and shaken in an end-over-end shaker at room temperature for 1 hour. The samples were then allowed to settle overnight. The samples were centrifuged at 3000 rpm for 5 minutes and decanted through a 0.45 µm filter into a clean 15 ml tube. The decanted solution was then saved and analyzed for exchangeable fractions. The leftover sediment pellets were then washed with 5 ml of deionized (dI) water in order to remove residual ammonium acetate and were centrifuged again. The DI water was decanted and discarded, 10 mL of 0.5 M HCl was then added to the sediment pellets and placed in an end-over-end shaker at room temperature for 17 hours. The samples were centrifuged, decanted and filtered as above. The decanted solutions were analyzed for the amorphous fractions. The pellets were washed with dI water and the water was discarded as described above. In the third extraction to remove the organic-bound fraction, 5 ml of high-purity H_2O_2 was added to the pellets from the previous extraction steps. The samples were heated to 20˚C for 1 hour to allow for the reaction to occur. The samples were then heated to 85˚C for 1 hour with the cap loose in order to alleviate pressure build up. An additional 5 ml of H_2O_2 was added to the samples and was allowed another hour at 85˚C in order to completely react. 25 ml of 1 M ammonium acetate, at pH 2, was added to the samples and then placed in an end-over-end shaker for 16 hours at room temperature. The samples were then centrifuged and filtered as above. The decanted solution was analyzed for the organic-bound fraction. The three different fractions were analyzed using an ICP-AES.

When all of the sediment samples were dried and taken out of the oven, the sample collected from the CWT's effluent discharge point on October 25th developed a white crystalline precipitate. These crystals were collected and ground to 150 microns. The sample was analyzed using a PANalytical Empryean X-Ray Diffractometer. The scan was performed in a zero background holder, with a K-Cu source.

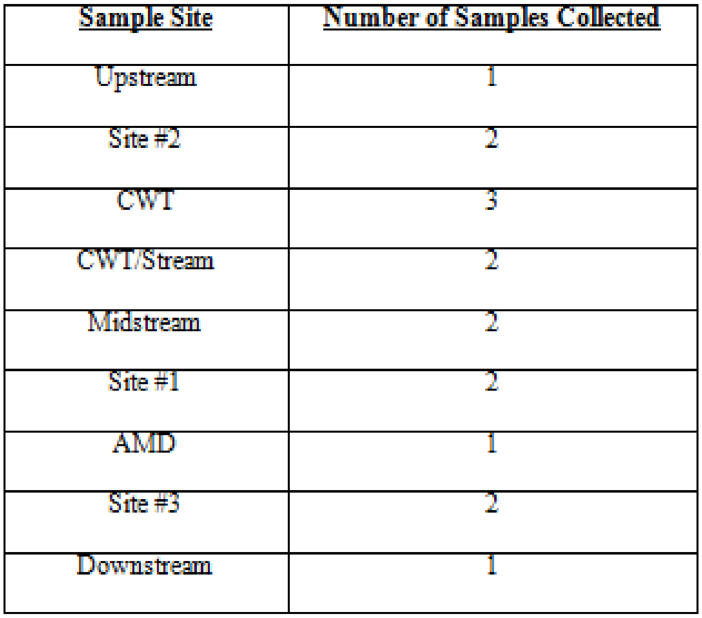
Results

The results from the water samples collected on October 7th, October 25th, and December 6th are displayed in Tables 1 and 2. The tables are composed of major anions (Cl^-, Br^-, SO_4^{2-}) and cations (Ca^{2+} Na^+, Sr^{2+}). All other cations and anions data can be found in Appendix A. The concentration measurements for each location along the river for 10/7 and 10/25 were overall similar, but varied slightly. The streamflow was low on these two dates. The streamflow was higher on 12/6 and gave lower concentrations for each sampling site compared to the other two field sampling dates. The detection limits for each analyte used can be seen in Table 3. The number of samples collected and analyzed from each site can be seen in Table 4.



Element	Detection Limit (µg/mL)
Cl	0.5
SO_4	2.5
Br	0.1
Ca	0.02
Na	0.01
Sr	0.005

Table 3: The detection limits of each analyte during Blacklick Creek Study



Sample Site	Number of Samples Collected
Upstream	1
Site #2	2
CWT	3
CWT/Stream	2
Midstream	2
Site #1	2
AMD	1
Site #3	2
Downstream	1

Table 4: Total number of samples that were collected and analyzed for Cations and Anions at each site

Table 1: Concentrations of major anions Cl, SO_4, and Br (µg/mL) from water samples collected at Blacklick Creek.

Locations	**Cl (µg/mL)**			**SO_4 (µg/mL)**			**Br (µg/mL)**		
	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Upstream	26.9 ± 1.4	-	-	214.4 ± 10.7	-	-	0.195 ± 0.0098	-	-
Site #2	-	19.9 ± 1.00	17.9 ± 0.90	-	156 ± 7.8	33.9 ± 1.7	-	BD	BD
CWT	83,410 ± 4,170	91,130 ± 4,550	15,960 ± 790	918 ± 46	976 ± 49	269 ± 13	441 ± 22	497 ± 25	57.2 ± 2.9
CWT/Stream	40,140 ± 2,010	76,140 ± 3,810	-	349 ± 17	1,191 ± 59.6	-	79.7 ± 3.9	386 ± 19	-
Midstream	4,770 ± 240	2,450 ± 122	-	339 ± 17	203 ± 10	-	21.1 ± 1.1	11.6 ± 0.58	-
Site #1	-	1,100 ± 55	84.1 ± 4.2	-	158 ± 7.9	32.0 ± 1.6	-	4.76 ± 0.24	0.650 ± 0.033
AMD	21.4 ± 1.1	-	-	363 ± 18	-	-	0.220 ± 0.011	-	-
Site #3	-	450 ± 23	70.1 ± 3.5	-	156 ± 7.8	42.6 ± 2.1	-	2.20 ± 0.11	0.251 ± 0.013
Downstream	29.8 ± 1.5	-	-	209 ± 11	-	-	0.107 ± 0.054	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 2: Concentrations of major cations Ca, Na, and Sr (µg/mL) from water samples collected at Blacklick Creek.

Locations	**Ca (µg/mL)**			**Na (µg/mL)**			**Sr (µg/mL)**		
	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Upstream	59.9 ± 1.8	-	-	27.7 ± 1.39	-	-	BD	-	-
Site #2	-	49.4 ± 1.5	15.5 ± 0.464	-	21.5 ± 1.07	10.6 ± 0.53	-	BD	0.084 ± 0.00420
CWT	12,847 ± 385.4	13,652 ± 409.6	2,240 ± 67.2	32,300 ± 1,620	33,100 ± 1,650	6,790 ± 340	1,190 ± 59.7	1,450 ± 72.4	178 ± 8.91
CWT/Stream	2,520 ± 75.5	11,790 ± 353.84	-	6,660 ± 333	30,500 ± 1,520	-	219 ± 10.9	1,190 ± 59.6	-
Midstream	817.9 ± 24.5	439.2 ± 13.12	-	2,100 ± 105	1,020 ± 51.1	-	60.6 ± 3.03	37.9 ± 1.89	-
Site #1	-	210.1 ± 6.30	25.0 ± 0.75	-	433 ± 21.7	40.0 ± 2.00	-	16.8 ± 0.84	0.852 ± 0.04
AMD	110.9 ± 3.33	-	-	16.1 ± 0.807	-	-	BD	-	-
Site #3	-	125.2 ± 3.76	22.6 ± 0.68	-	215 ± 10.8	31.4 ± 1.57	-	7.21 ± 0.36	0.634 ± 0.03
Downstream	58.6 ± 1.8	-	-	26.8 ± 1.34	-	-	BD	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

For each anions and cations examined, there was a general trend that occurred. The upstream samples that were collected exhibited lower concentrations, i.e. background levels. For some of the ions, the concentration upstream was minute enough to be below the detection limit. The discharge point of effluents had elevated concentrations of each ion (Table 1-2). The concentrations located at the discharge point were ~300-3000 times greater than background levels. Every point downstream from the effluents discharge was composed of a more dilute ion concentration relative to the last sample location upstream. Plotting concentration vs. distance from the point of effluent discharge documents the dilution effect in Blacklick Creek (Figures 1-6). The values for location AMD were left out since this point is a tributary into Blacklick Creek. Figures showing graphs of all the other anions and cations plotted vs. distance can be observed in Appendix A.

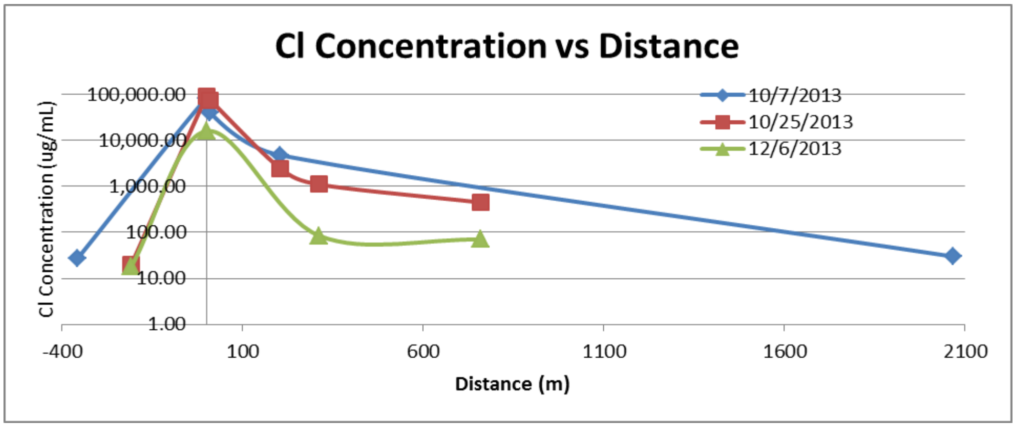


Figure 1: Concentrations of Cl (µg/mL) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

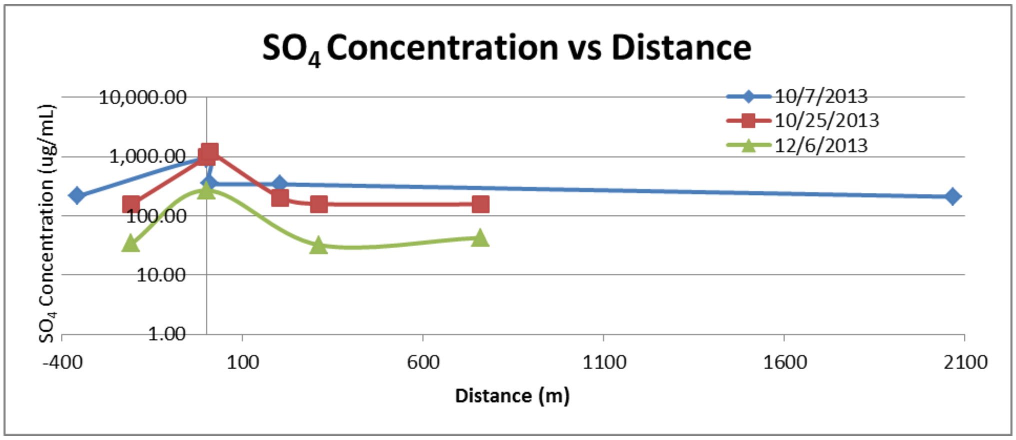


Figure 2: Concentrations of SO_4 (µg/mL) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

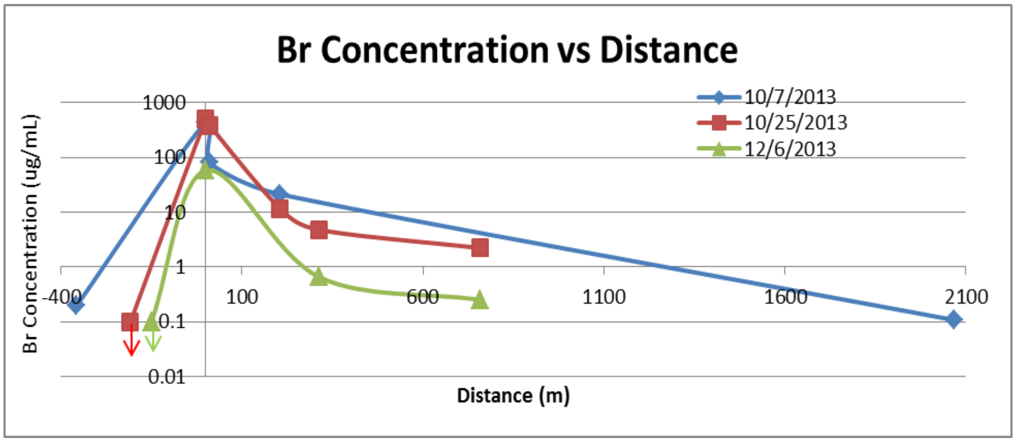


Figure 3: Concentration of Br (µg/mL) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

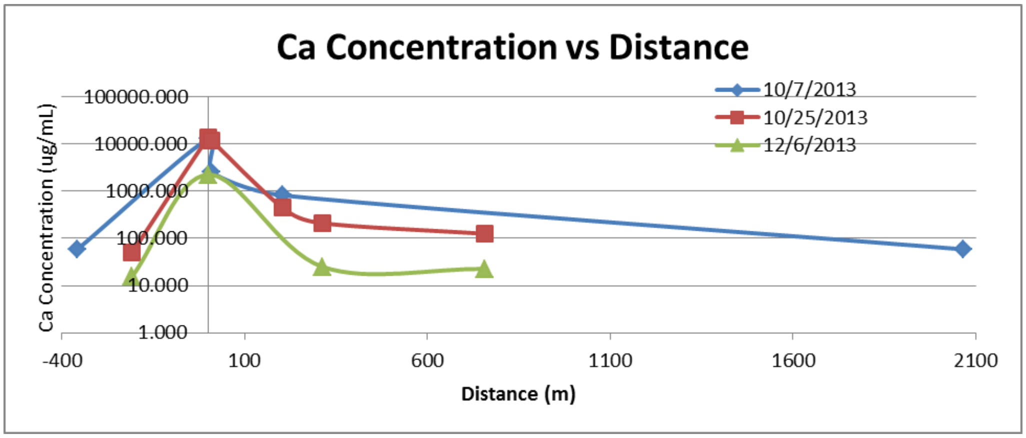


Figure 4: Concentration of Ca (µg/mL) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

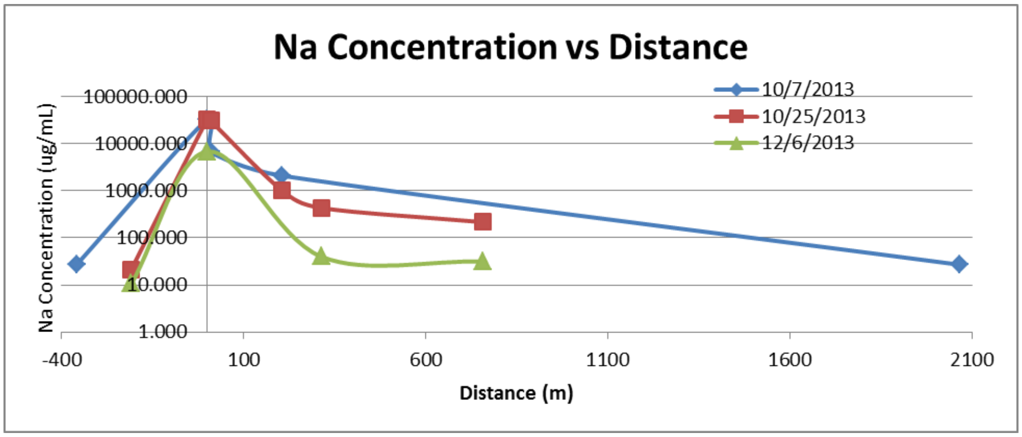


Figure 5: Concentration of Na (µg/mL) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

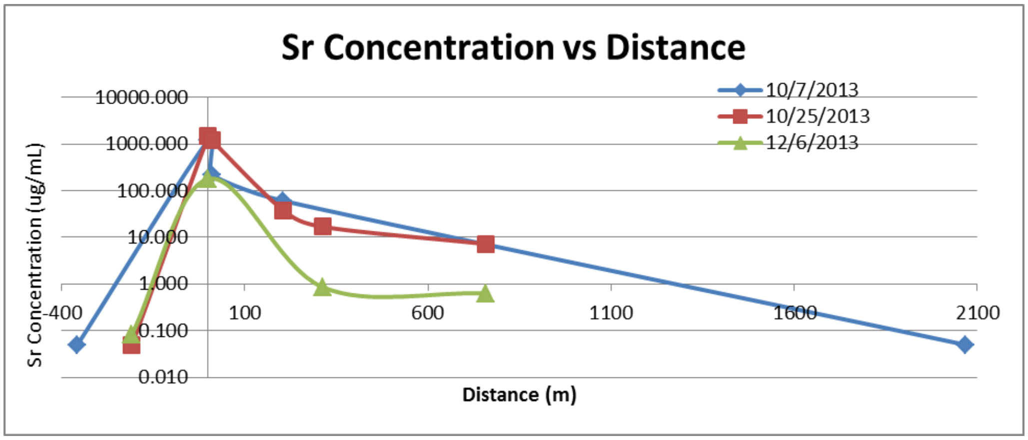


Figure 6: Concentration of Sr (µg/mL) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

Major anions and cations in Table 1-2 were also plotted against a Warner et al paper. The Warner et al . data were collected and compared to the data for the three different sampling dates on Blacklick Creek. Warner et al reported average concentrations for major anions and cations over a 2-year period that began in August 2010 to November 2012. The average concentrations for their 2-year sampling period can be seen in Table 5. Warner et al. samples were collected at several distances downstream, but varied slightly from our collection locations. The concentrations from our three sampling events encompassed sections of their data, or were very similar. The major anions and cations data correlation were plotted on Figures 7 - 12.

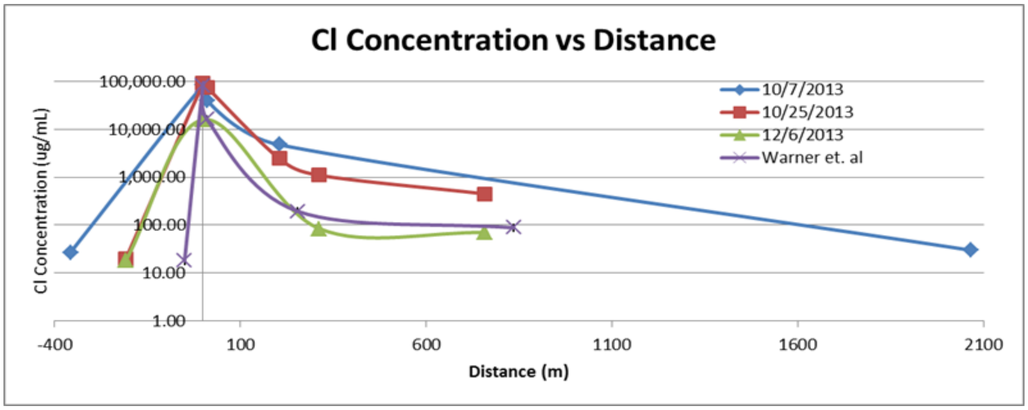
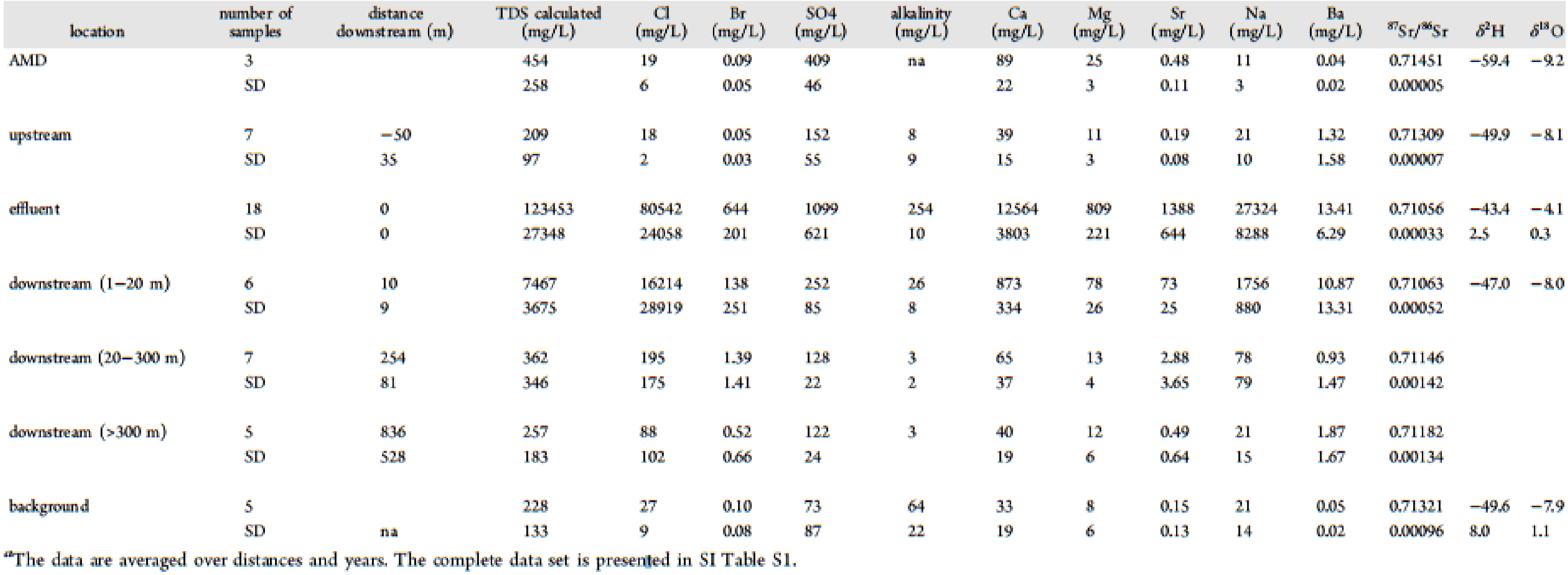


Figure 7: Concentrations of Cl vs. Blacklick Creek from data collected on 10/7, 10/25, 12/6. Data of average concentrations found in Blacklick Creek from Warner et al paper plotted vs. distance

Table 5: Summary of Means and Standard Deviation (SD) values of chemical and isotopic from upstream and downstream on Blacklick Creek near the CWT discharge from Warner et al.



location	number of samples	distance downstream (m)	TDS calculated (mg/L)	Cl (mg/L)	Br (mg/L)	SO4 (mg/L)	alkalinity (mg/L)	Ca (mg/L)	Mg (mg/L)	Sr (mg/L)	Na (mg/L)	Ba (mg/L)	$^{87}Sr/^{86}Sr$	δ^2H	$\delta^{18}O$
AMD	3		454	19	0.09	409	na	89	25	0.48	11	0.04	0.71451	−59.4	−9.2
	SD		258	6	0.05	46		22	3	0.11	3	0.02	0.00005		
upstream	7	−50	209	18	0.05	152	8	39	11	0.19	21	1.32	0.71309	−49.9	−8.1
	SD	35	97	2	0.03	55	9	15	3	0.08	10	1.58	0.00007		
effluent	18	0	123453	80542	644	1099	254	12564	809	1388	27324	13.41	0.71056	−43.4	−4.1
	SD	0	27348	24058	201	621	10	3803	221	644	8288	6.29	0.00033	2.5	0.3
downstream (1−20 m)	6	10	7467	16214	138	252	26	873	78	73	1756	10.87	0.71063	−47.0	−8.0
	SD	9	3675	28919	251	85	8	334	26	25	880	13.31	0.00052		
downstream (20−300 m)	7	254	362	195	1.39	128	3	65	13	2.88	78	0.93	0.71146		
	SD	81	346	175	1.41	22	2	37	4	3.65	79	1.47	0.00142		
downstream (>300 m)	5	836	257	88	0.52	122	3	40	12	0.49	21	1.87	0.71182		
	SD	528	183	102	0.66	24		19	6	0.64	15	1.67	0.00134		
background	5		228	27	0.10	73	64	33	8	0.15	21	0.05	0.71321	−49.6	−7.9
	SD	na	133	9	0.08	87	22	19	6	0.13	14	0.02	0.00096	8.0	1.1

[a] The data are averaged over distances and years. The complete data set is presented in SI Table S1.

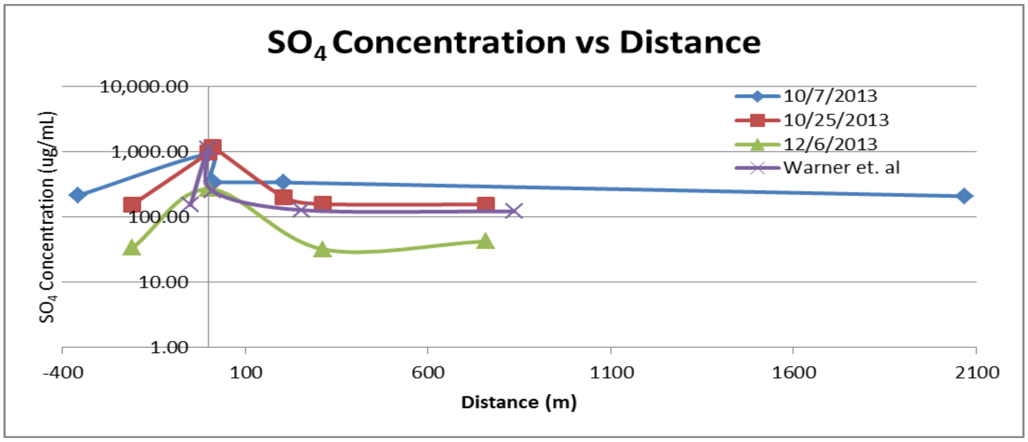


Figure 8: Concentrations of SO_4 vs. Blacklick Creek from data collected on 10/7, 10/25, 12/6. Data of average concentrations found in Blacklick Creek from Warner et al paper plotted vs. distance

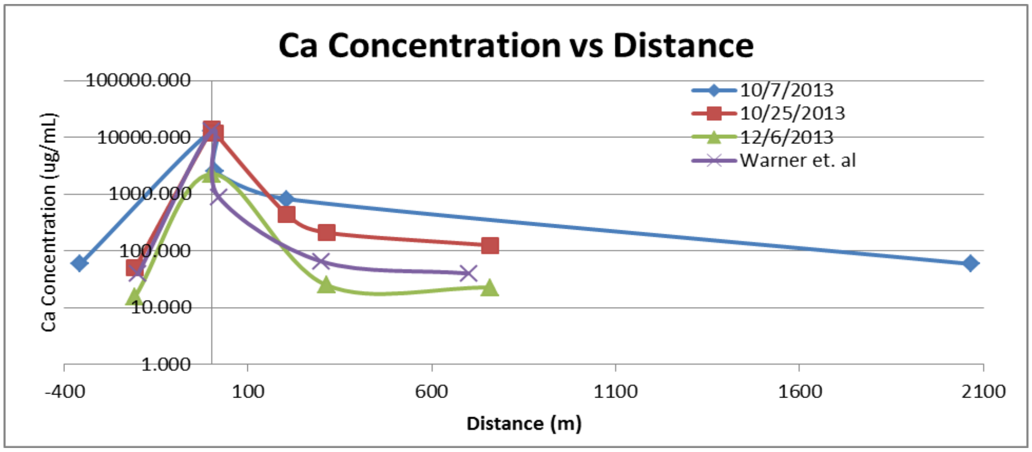


Figure 9: Concentrations of Ca vs. Blacklick Creek from data collected on 10/7, 10/25, 12/6. Data of average concentrations found in Blacklick Creek from Warner et al paper plotted vs. distance

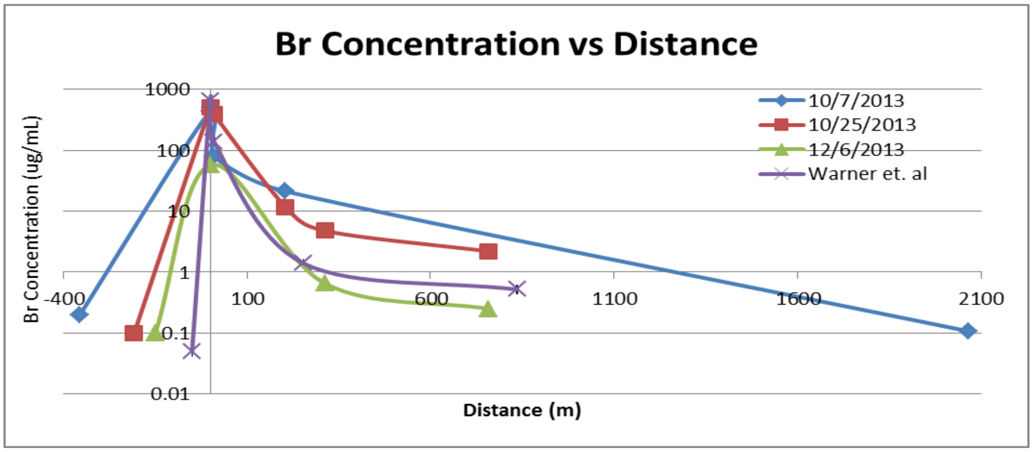


Figure 10: Concentrations of Br vs. Blacklick Creek from data collected on 10/7, 10/25, 12/6. Data of average concentrations found in Blacklick Creek from Warner et al paper plotted vs. distance

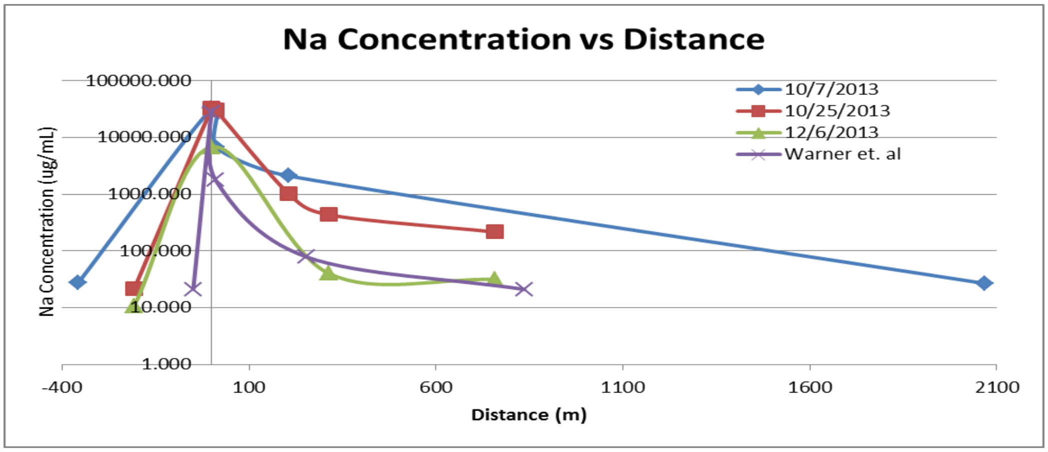


Figure 11: Concentrations of Ca vs. Blacklick Creek from data collected on 10/7, 10/25, 12/6. Data of average concentrations found in Blacklick Creek from Warner et al paper plotted vs. distance

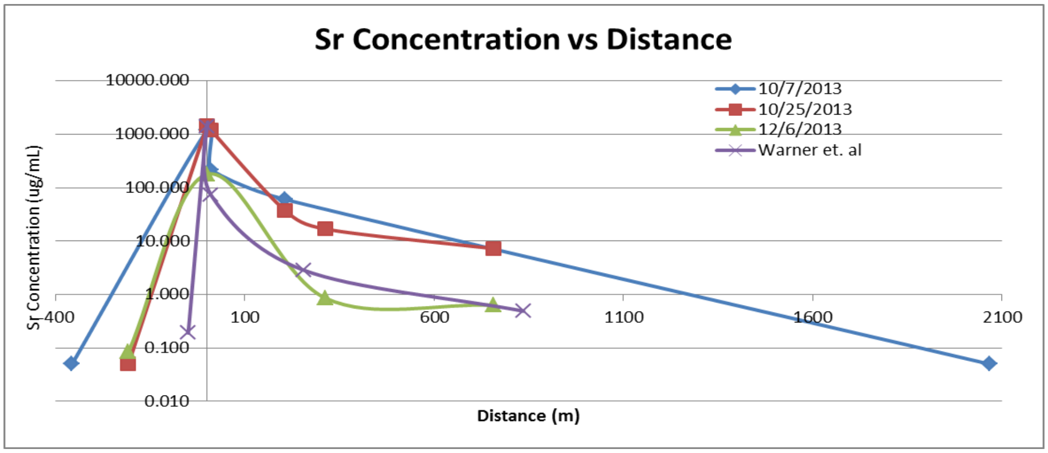


Figure 12: Concentrations of Sr vs. Blacklick Creek from data collected on 10/7, 10/25, 12/6. Data of average concentrations found in Blacklick Creek from Warner et al paper plotted vs. distance

A technique from Llewellyn 2014, allowed for Cl/Br weight ratios to be cross plotted with Cl concentrations, in order allow geochemical ratios to identify the origins of the different effluents or stream waters. On Figure 13, the lower mixing curve area is the allotted range for Appalachian Brines. Although they varied in concentration, the CWT samples exhibited concentrations that were plotted within the lower mixing curve. This concluded that the effluent discharge had orientated from within the Appalachian Basin.

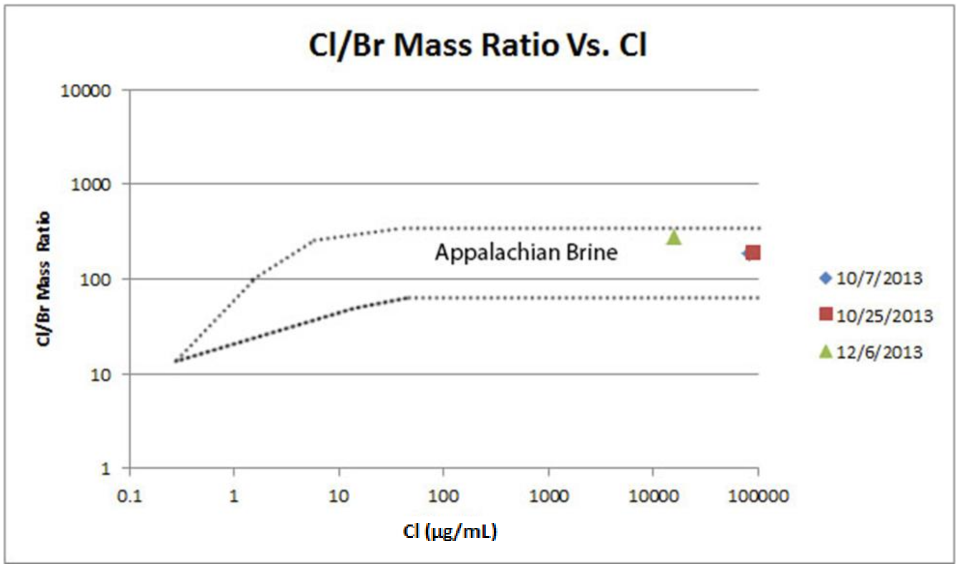


Figure 13: Cl/Br Mass Ratio (µg/mL Cl/ µg/mL Br) Vs. Cl Concentration (µg/mL) from data collected 10/7, 10/25, 12/6

The results for DOC of sampling dates October 7th, October 25th, and December 6th are displayed in Table 7. Measurements along the stream showed similar concentrations from the three different sampling dates. Concentrations near the point of effluent discharge were elevated to a range of 211 – 423 µg/L. The concentration of DOC vs. distance can be seen in Figure 14.

The dilution factors for Cl, SO_4, Br, Na, and DOC were analyzed in Table 6 and 7. The ratio of each point downstream from the point of effluent discharge was divided by the effluent concentration on each day of sampling. The AMD point was not compared since that sampling location is from a tributary feeding into Blacklick Creek. The ratios seen are not all the same throughout the different sampling dates. Downstream from the point of effluent discharge, DOC mimics the dilution of Cl. These concentrations reach background levels further downstream than the major anions and cations. All of the other elements show a drastic amount of variation at each sampling site throughout the three different sampling dates.

Table 6: Dilution ratios downstream from point of effluents discharge. Dilution ratio was generated from element concentration downstream (µg/mL) / element concentration at point of effluents discharge (µg/mL).

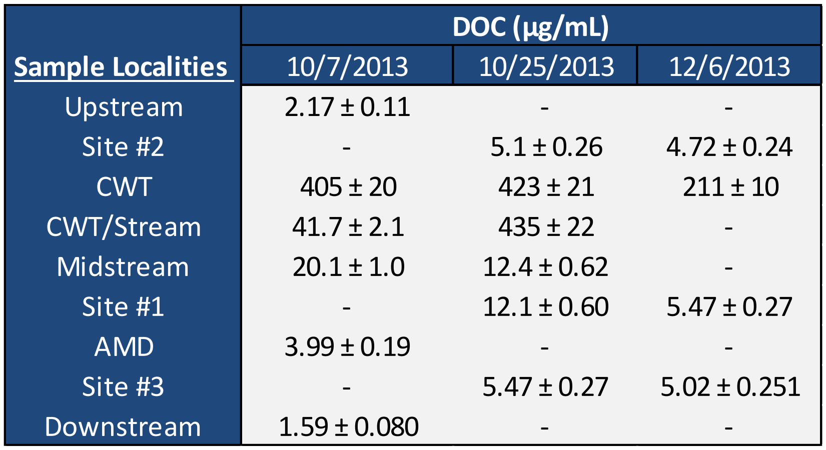
	Cl			SO_4			Br		
Locations	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Upstream	-	-	-	-	-	-	-	-	-
Site #2	-	-	-	-	-	-	-	-	-
CWT	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
CWT/Stream	0.48	0.84	-	0.38	1.22	-	0.18	0.78	-
Midstream	0.06	0.03	-	0.37	0.21	-	0.05	0.02	-
Site #1	-	0.01	0.01	-	0.16	0.12	-	0.01	0.01
AMD	-	-	-	-	-	-	-	-	-
Site #3	-	0.00	0.00	-	0.16	0.16	-	0.00	0.00
Downstream	0.00	-	-	0.23	-	-	0.00	-	-

A “-“ in the chart indicates there was no sample taken from location on that sampling date or it was located upstream from discharge point.

Table 7: Dilution ratios downstream from point of effluents discharge. Dilution ratio was generated from element concentration downstream (µg/mL) / element concentration at point of effluents discharge (µg/mL).

	Na			**DOC**		
Samples	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Upstream	-	-	-	-	-	-
Site #2	-	-	-	-	-	-
CWT	1.00	1.00	1.00	1.00	1.00	1.00
CWT/Stream	0.206	0.921	-	0.103	1.03	-
Midstream	0.065	0.031	-	0.050	0.029	-
Site #1	-	0.013	0.006	-	0.029	0.026
AMD	-	-	-	-	-	-
Site #3	-	0.006	0.005	-	0.013	0.024
Downstream	0.00	-	-	0.004	-	-

A “-“ in the chart indicates there was no sample taken from location on that sampling date or it was located upstream from discharge point.



Sample Localities	DOC (µg/mL)		
	10/7/2013	10/25/2013	12/6/2013
Upstream	2.17 ± 0.11	-	-
Site #2	-	5.1 ± 0.26	4.72 ± 0.24
CWT	405 ± 20	423 ± 21	211 ± 10
CWT/Stream	41.7 ± 2.1	435 ± 22	-
Midstream	20.1 ± 1.0	12.4 ± 0.62	-
Site #1	-	12.1 ± 0.60	5.47 ± 0.27
AMD	3.99 ± 0.19	-	-
Site #3	-	5.47 ± 0.27	5.02 ± 0.251
Downstream	1.59 ± 0.080	-	-

Table 8: Concentration of DOC (µg DOC/mL) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

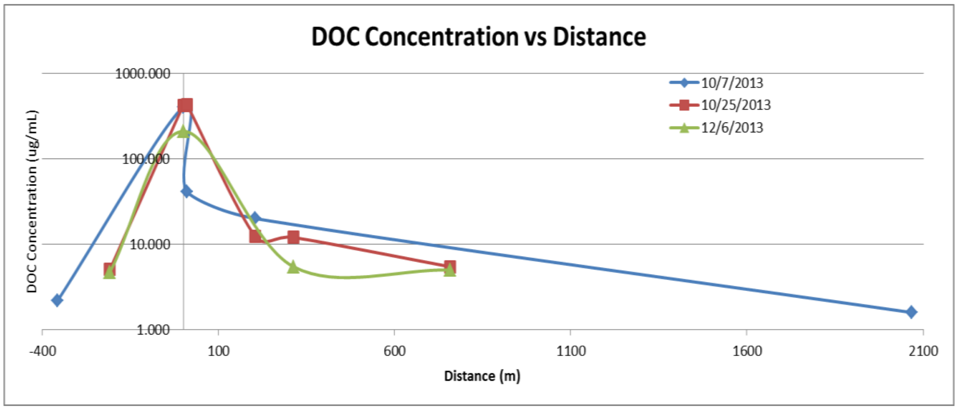


Figure 14: Concentration of DOC (µg/mL) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

The values for exchangeable ions, amorphous oxide, and organic bound Fe in the sediment are given in Table 9. The concentrations were calculated from data collected on the ICP-AES. The results were given in ppm (µg/mL). The results were then converted into mol/L by each element's molecular weight. After this value was calculated, the results were converted into numbers of moles found in the sample by the total solution volume in liters. The solution volumes for each fraction were as follows: Exchangeable fraction was 10mL, Amorphous fraction was 10 mL, and Organic-bound fraction was 35 mL. The results were then divided by the total weight of each sample that was run. All other data in regards to different phases from the sediment grab samples can be seen in Appendix A. The different phases of Fe in the sediment did not exhibit any significantly higher values or anomalies.

Table 9: Exchangeable fraction, amorphous oxide and organic bound results for Fe from sequential extraction on soil grab samples of Blacklick Cree. Each fraction was measure in mol/g of sample (smp)

	Fe (mol/g smp)		
	10/7/2013	10/25/2013	12/6/2013
Exchangeable Ions	35.8E-12 ± 1.8E-12	-	-
	-	1.7E-9 ± 85.9E-12	-
	-	-	-
	-	BD	-
	BD	4.7E-9 ± 236.4E-12	-
	-	BD	-
	-	-	-
	-	15.7E-9 ± 784.3E-12	-
	BD	-	-
	Fe (mol/g smp)		
	10/7/2013	10/25/2013	12/6/2013
Amorphous Oxide	1.3E-3 ± 67.1E-6	-	-
	-	799.5E-6 ± 40.0E-6	-
	-	-	-
	-	711.5E-6 ± 35.6E-6	-
	236.2E-6 ± 11.8E-6	240.3E-6 ± 12.0E-6	-
	-	193.1E-6 ± 9.7E-6	-
	-	-	-
	-	479.4E-6 ± 24.0E-6	-
	711.5E-6 ± 35.6E-6	-	-
	Fe (mol/g smp)		
	10/7/2013	10/25/2013	12/6/2013
Organic Bound	1.1E-3 ± 55.6E-6	-	-
	-	221.6E-6 ± 11.1E-6	-
	-	-	-
	-	9.0E-6 ± 452.0E-9	-
	26.5E-6 ± 1.3E-6	22.8E-6 ± 1.1E-6	-
	-	21.0E-6 ± 1.1E-6	-
	-	-	-
	-	24.1E-6 ± 1.2E-6	-
	100.6E-6 ± 5.0E-6	-	-

A "-" in the chart indicates there was no sample taken from location on that sampling date or it was located upstream from discharge point.

The XRD analysis on the 10/25 CWT white precipitate sample gave a peak that was easily identified as Halite. There is a small amount of quartz that is also identified within the chart too. The data collected from the analysis can be seen in Figure 15.

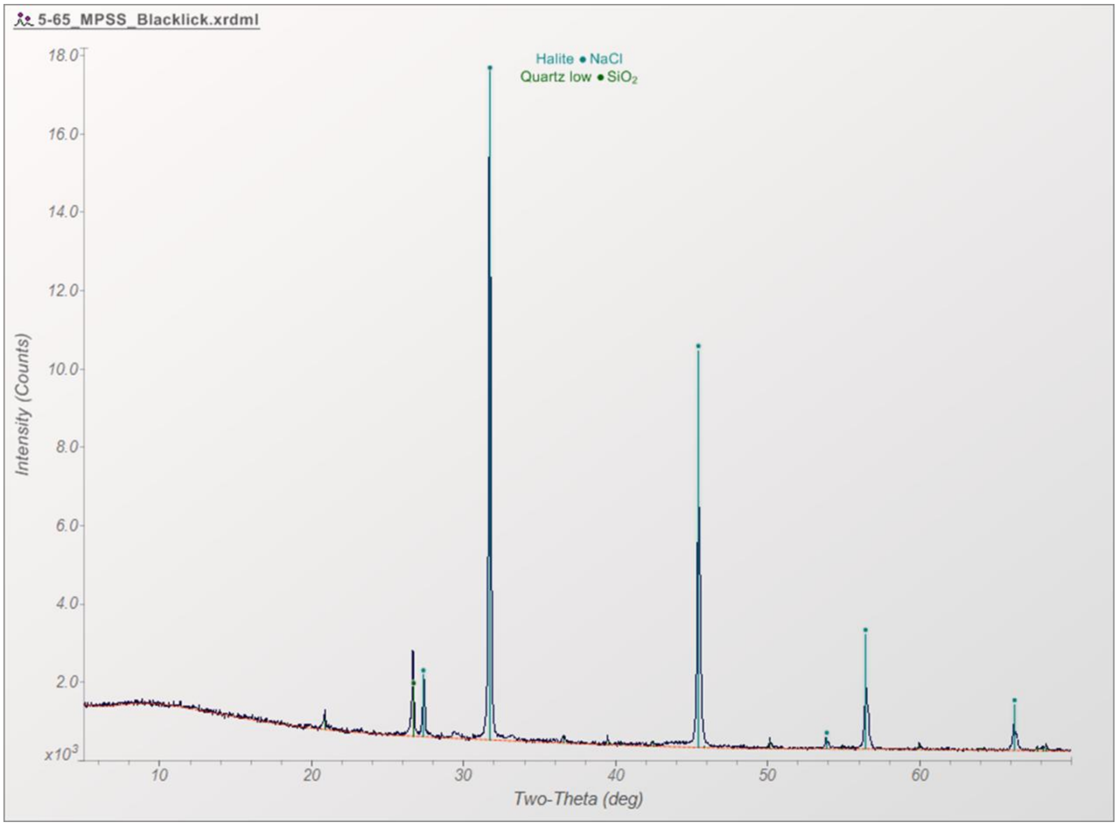


Figure 15: XRD chart run on CWT white precipitate collected on 10/25.

Discussion

The concentrations of major cations(Ca^{2+}, Na^{+}, Sr^{2+}) and anions (Cl^{-}, $Br^{=}$, SO_4^{2-}) in the treated effluent wastewaters varied throughout the three sampling events. The three sampling dates allowed for a more diverse stream flow vs. concentration profile to be generated. These concentrations were seen several thousand times larger than what was seen in upstream sample locations. For example, chloride concentrations upstream were low (19.9 - 26.9 µg/mL) throughout the three sampling dates on Blacklick Creek. The chloride concentration from the effluent discharge increased tremendously (15,960 - 91,130 µg/mL) (Table 1). The dilution ratios of Cl decreased much slower downstream than with the other elements in Tables 6 and 7. The ratios for Cl show the normal dilution ratios that are seen along the stream since it should not be reacting with anything. However, the other elements seen diluting faster could be an example of other elements being removed by other processes. Some of these processes could be the precipitation of barite downstream.

Bromide concentration upstream was low enough not to be detected by the IC - which has a detection limit of 0.1 ppm. The concentration at the effluent discharge ranged between 57 - 441 Br µg/L (Table 1). Br has generated major concern because of its ability to generate carcinogenic brominated disinfectant byproducts. Even with a concentration of 0.1 mg/L , chlorination of water can result in the production of these byproducts (Bonacquisti 2006). Although, the relative concentration is much lower, there is still an effect that can be seen further downstream in the Pittsburgh municipal waste treatment facilities (Cyprych et al 2013).

Water samples collected downstream from the effluents discharge showed a significant dilution effect. The variability of streamflow in Blacklick Creek plays a crucial role in potentially remediating the effluents effectively. The downstream concentrations during a high stream flow date are going to be much lower at a shorter distance than during a low stream flow date. The stream does an effective job at remediating the concentrations of some anions and cations back to background levels. However, several anions and cations do not return to background levels within the sampling area (~2067m). The wastewater effluents has a discernible impact on the enrichment of certain ions downstream. Cl, DOC, Na, and Br play a crucial role in reducing the quality of downstream surface water. The Josephine Brine Treatment plant has received citations in the past for the concentration levels of their effluent discharge.

The DOC found in the samples downstream exhibited the same dilution compared to the salts from the effluents. This result can be seen in Figures 1 - 6 and 14. The decrease of Cl from the discharge to Midstream (205m) downstream showed a factor of 0.03; in contrast, DOC decreased over that same distance by 0.029. The DOC concentrations followed the same linear dilution effect that is seen with a majority of the anions and cations.

The conservative nature of chloride and bromide allow for unique mixing trends to be generated when Cl/Br ratios are plotted against Cl concentrations . Ionic concentrations of Cl and Br have been accepted as an effective geochemical tool in correctly identifying groundwater salinization sources (Llewellyn 2014). On Figure 13, the lower mixing curve area is allotted for Appalachian Brines. The samples from the CWT for the three different sampling dates, plotted within the lower mixing curve. Marcellus Shale wastewater correspond close to Appalachian Brines. Gas wells from the Marcellus Shale have exhibited flow-back chemistry very similar to the Appalachian Brines (Llewellyn 2014). The major anions and cations concentrations from the point of effluent discharge resemble concentrations similar to wastewater prior to May 2011 that the treatment plant was receiving (Warner et al 2013). Although, they were accepting both unconventional and conventional wastewater at that time, the concentrations prior to 2011 are comparable with today.

Interaction between the effluents and the stream bed were not observed. The hypothesis that there was an interaction between the Fe rich stream bed and the effluents is incorrect. The downstream sediment exhibited lower or was consistent with concentrations of the different phases of Fe with upstream samples.

Conclusions

In summary, the effluents discharge from the Josephine Brine Treatment plant into Blacklick Creek has an impact on the water quality. The treatment process overall reduces a majority of the major anions and cations concentration, but does not dilute every major anion and cation to background levels. This generates a contamination issue that could potentially cause problems further downstream. The downstream concentration from the point of discharge is heavily reliant on the variability of the stream flow seen in Blacklick Creek.

Future studies should explore the DOC and salt content further in Blacklick Creek. There is some type of process that is occurring which is allowing certain salts to dilute rapidly downstream. Since there is a rapid decrease, there could be some process occurring (reaction, volatilization, or consumption) that is removing the salts rapidly from the system. There could be more of an interaction with the sediments found in the middle of the stream rather than the sediments found closer to the embankment.

Water management for conventional and unconventional gas extraction are still key issues that dominate environmental debates. CWTs and different types of remediation are being used to try to combat the concern of vast salt quantities related to the wastewater. As time goes on, oil and gas exploration is becoming more popular and necessary. The need to find the most successful remediation technique for this wastewater will likely intensify. It is important to maintain pristine streams and creeks to their natural conditions and to avoid the adverse environmental effects associated with oil and gas wastewater remediation.

References Cited

Agency USEP. 2012. Key documents about mid-atlantic oil and gas extraction.

Bonacquisti TP. 2006. A drinking water utility's perspective on bromide, bromate, and ozonation. *Toxicology* 221: 145-48

Cyprych G, Stoner M, Wydra F, Kuchta J, Monnell J, Casson L. 2013. Marcellus Shale drilling and brominated THMs in Pittsburgh, Pa., drinking water (PDF). *Journal-American Water Works Association* 105: E432-E48

Ellsworth WL. 2013. Injection-Induced Earthquakes. *Science* 341

Ferrar KJ, Michanowicz DR, Christen CL, Mulcahy N, Malone SL, Sharma RK. 2013. Assessment of Effluent Contaminants from Three Facilities Discharging Marcellus Shale Wastewater to Surface Waters in Pennsylvania. *Environmental Science & Technology* 47: 3472-81

Folger P, Humphries M, Copeland C, Tiemann M, Meltz R, Brougher C. 2009. Unconventional Gas Shales: Development, Technology, and Policy Issues.

Haluszczak LO, Rose AW, Kump LR. 2013. Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Applied Geochemistry* 28: 55-61

Hladik ML, Focazio MJ, Engle M. 2014. Discharges of produced waters from oil and gas extraction via wastewater treatment plants are sources of disinfection by-products to receiving streams. *Science of The Total Environment* 466–467: 1085-93

Kargbo DM, Wilhelm RG, Campbell DJ. 2010. Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities. *Environmental Science & Technology* 44: 5679-84

Llewellyn G. 2014. Evidence and mechanisms for Appalachian Basin brine migration into shallow aquifers in NE Pennsylvania, USA. *Hydrogeology Journal*: 1-12

Lutz BD, Lewis AN, Doyle MW. 2013. Generation, transport, and disposal of wastewater associated with Marcellus Shale gas development. *Water Resources Research* 49: 647-56

Robart J. 2012. *Water Management Economics in the Development and Production of Shale Resources*. Presented at IAEE Energy Forum, First Quarter

Soeder DJ, Kappel WM. 2009. *Water resources and natural gas production from the Marcellus Shale*: US Department of the Interior, US Geological Survey Reston, Virginia

USEPA. 2011. USEPA settlement Josephine Brine Remediation.

Vidic RD, Brantley SL, Vandenbossche JM, Yoxtheimer D, Abad JD. 2013. Impact of Shale Gas Development on Regional Water Quality. *Science* 340

Warner NR, Christie CA, Jackson RB, Vengosh A. 2013. Impacts of Shale Gas Wastewater Disposal on Water Quality in Western Pennsylvania. *Environmental Science & Technology*

Appendix A: All Relevant Tables and Graphs

Table 10: Concentrations of major anions Cl and SO_4 (mol/L) from water samples collected at Blacklick Creek.

Sample Localities	Cl (mol/L)			SO_4 (mol/L)		
	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Upstream	760.5E-6 ± 38.0E-6	-	-	2.2E-3 ± 111.6E-6	-	-
Site #2	-	562.1E-6 ± 28.1E-6	507.0E-6 ± 25.3E-6	-	1.6E-3 ± 81.2E-6	352.7E-6 ± 17.6E-6
CWT	2.4E+0 ± 117.6E-3	2.6E+0 ± 128.5E-3	450.1E-3 ± 22.5E-3	9.6E-3 ± 477.7E-6	10.2E-3 ± 507.8E-6	2.8E-3 ± 139.8E-6
CWT/Stream	1.1E+0 ± 56.6E-3	2.1E+0 ± 107.4E-3	-	3.6E-3 ± 181.4E-6	12.4E-3 ± 619.9E-6	-
Midstream	134.7E-3 ± 6.7E-3	69.0E-3 ± 3.4E-3	-	3.5E-3 ± 176.6E-6	2.1E-3 ± 105.9E-6	-
Site #1	-	31.0E-3 ± 1.6E-3	2.4E-3 ± 118.6E-6	-	1.6E-3 ± 82.4E-6	333.5E-6 ± 16.7E-6
AMD	603.7E-6 ± 30.2E-6	-	-	3.8E-3 ± 188.9E-6	-	-
Site #3	-	12.7E-3 ± 634.6E-6	2.0E-3 ± 98.8E-6	-	1.6E-3 ± 81.2E-6	442.9E-6 ± 22.1E-6
Downstream	841.3E-6 ± 42.1E-6	-	-	2.2E-3 ± 108.8E-6	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 11: Concentrations of major anions Br and NO_3 (mol/L) from water samples collected at Blacklick Creek.

Sample Localities	**Br (mol/L)**			**NO_3 (mol/L)**		
	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Upstream	2.4E-6 ± 122.1E-9	-	-	23.4E-6 ± 1.2E-6	-	-
Site #2	-	BD	BD	-	44.8E-6 ± 2.2E-6	82.4E-6 ± 4.1E-6
CWT	5.5E-3 ± 276.0E-6	6.2E-3 ± 310.8E-6	715.9E-6 ± 35.8E-6	BD	BD	57.5E-6 ± 2.9E-6
CWT/Stream	997.9E-6 ± 49.9E-6	4.8E-3 ± 241.2E-6	-	BD	BD	-
Midstream	264.6E-6 ± 13.2E-6	145.5E-6 ± 7.3E-6	-	BD	BD	-
Site #1	-	59.5E-6 ± 3.0E-6	8.1E-6 ± 406.9E-9	-	44.2E-6 ± 2.2E-6	75.5E-6 ± 3.8E-6
AMD	2.8E-6 ± 137.8E-9	-	-	BD	-	-
Site #3	-	27.5E-6 ± 1.4E-6	3.1E-6 ± 156.9E-9	-	46.0E-6 ± 2.3E-6	115.7E-6 ± 5.8E-6
Downstream	1.3E-6 ± 67.0E-9	-	-	25.0E-6 ± 1.3E-6	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

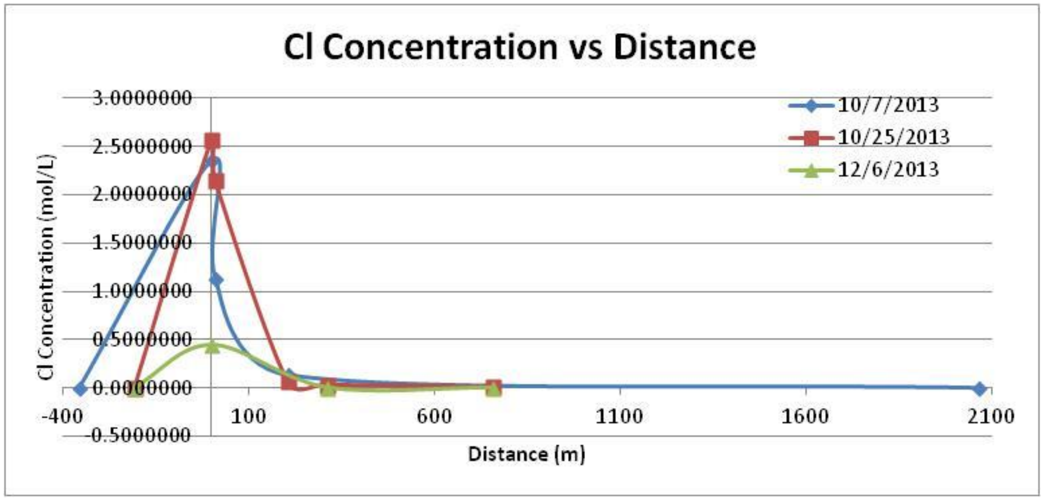


Figure 16: Concentrations of Cl (mol/L) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

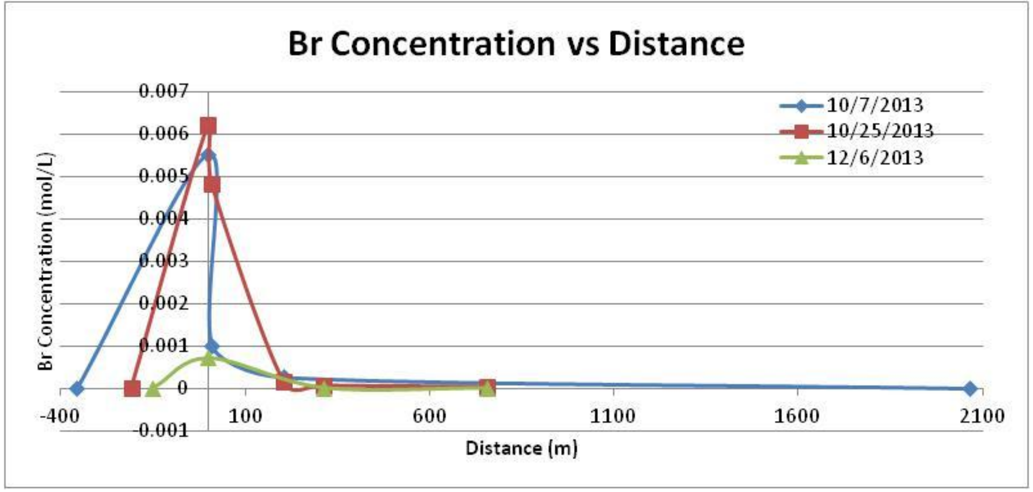


Figure 17: Concentrations of Br (mol/L) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

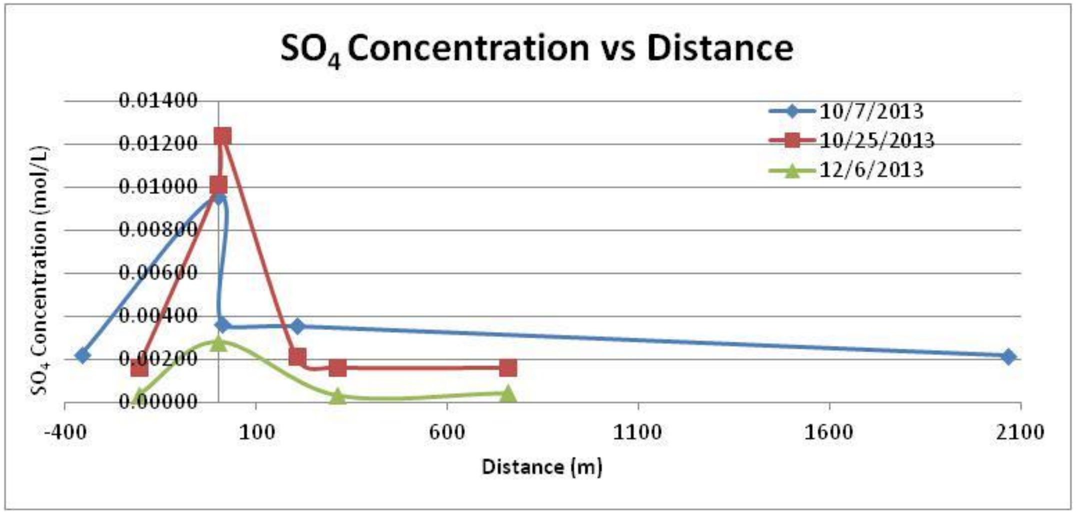


Figure 18: Concentrations of SO_4 (mol/L) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

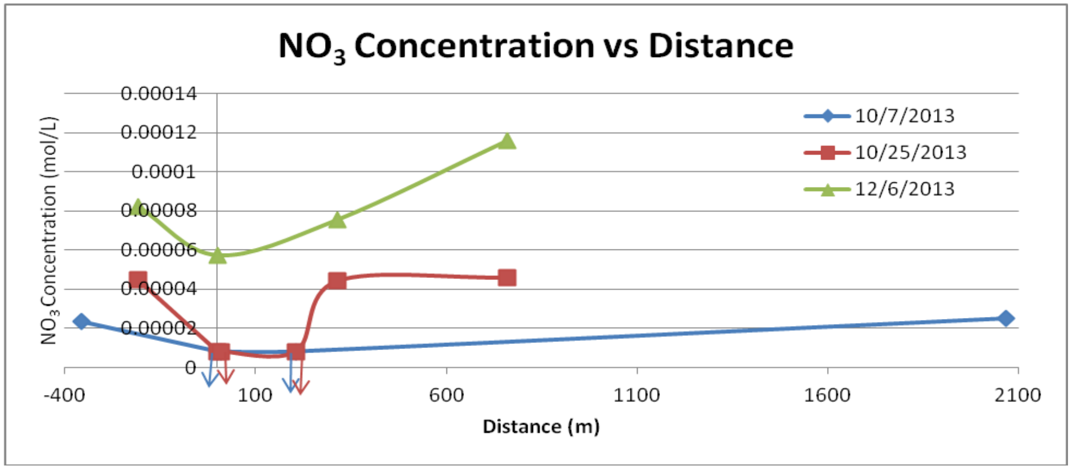


Figure 19: Concentrations of NO_3 (mol/L) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

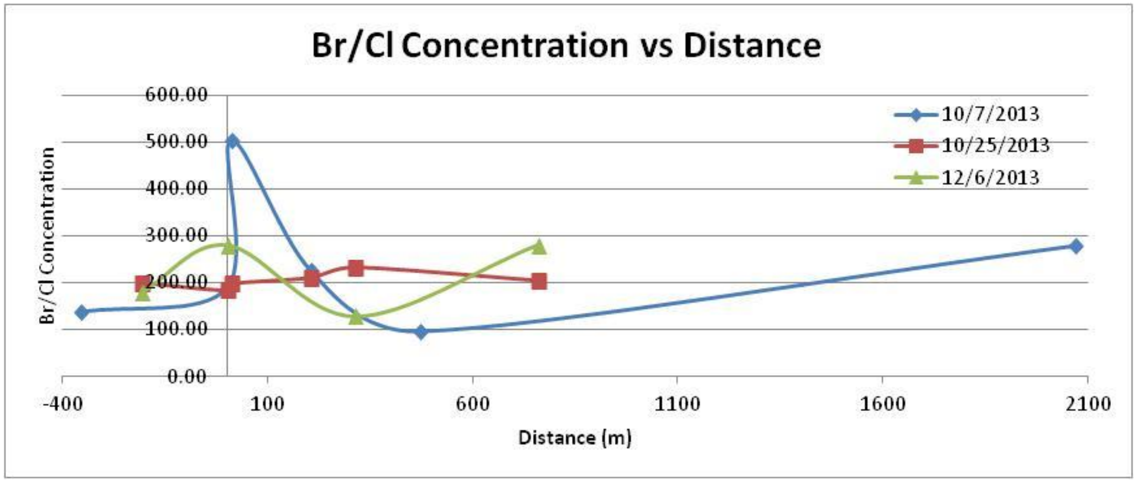


Figure 17: Concentrations of Br/Cl vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

Table 12: Concentrations of major cations Al, Fe and K (µg/mL) from water samples collected at Blacklick Creek.

Sample Localities	Al (µg/mL)			Fe (µg/mL)			K (µg/mL)		
	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Upstream	1.15 ± 0.034	-	-	0.0837 ± 0.0025	-	-	4.94 ± 0.15	-	-
Site #2	-	BD	0.0432 ± 0.0013	-	0.680 ± 0.020	0.0650 ± 0.0033	-	3.16 ± 0.095	2.39 ± 0.072
CWT	0.767 ± 0.023	3.11 ± 0.093	0.163 ± 0.0049	0.196 ± 0.0059	0.251 ± 0.0075	0.00860 ± 0.00043	403 ± 12.1	378 ± 11	42.1 ± 1.3
CWT/Stream	0.209 ± 0.0063	0.403 ± 0.012	-	0.211 ± 0.00634	0.246 ± 0.0074	-	57.5 ± 1.7	239 ± 7.2	-
Midstream	BD	0.0494 ± .0015	-	0.0457 ± 0.0014	0.349 ± 0.010	-	6.87 ± 0.21	11.3 ± 0.34	-
Site #1	-	BD	0.031 ± 0.000930	-	0.225 ± 0.0068	0.0392 ± 0.0020	-	7.30 ± 0.22	2.36 ± 0.071
AMD	10.5 ± 0.32	-	-	0.119 ± 0.0036	-	-	3.93 ± 0.12	-	-
Site #3	-	BD	0.0315 ± 0.000945	-	1.06 ± 0.032	0.0276 ± 0.0014	-	5.17 ± 0.26	2.36 ± 0.071
Downstream	0.892 ± 0.027	-	-	0.0245 ± 0.00074	-	-	4.58 ± 0.14	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 13: Concentrations of major cations Mg, Mn and P (µg/mL) from water samples collected at Blacklick Creek.

	Mg (µg/mL)			Mn (µg/mL)			P (µg/mL)		
Sample Localities	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Upstream	16.4 ± 0.49	-	-	0.687 ± 0.0343	-	-	0.167 ± 0.00836	-	-
Site #2	-	12.5 ± 0.38	4.27 ± 0.13	-	0.364 ± 0.0182	BD	-	0.198 ± 0.00992	0.0746 ± 0.0037
CWT	1,059 ± 31.8	1,100 ± 33	247 ± 7.4	BD	BD	BD	14.0 ± 0.701	16.5 ± 0.825	35.2 ± 1.76
CWT/Stream	206 ± 6.2	913 ± 27	-	BD	BD	-	0.134 ± 0.00671	12.6 ± 0.630	-
Midstream	67.5 ± 2.0	43.3 ± 1.3	-	BD	0.352 ± 0.0176	-	3.70 ± 0.185	0.649 ± 0.0324	-
Site #1	-	25.5 ± 0.77	5.32 ± 0.16	-	0.343 ± 0.0172	BD	-	0.143 ± 0.00715	0.0424 ± 0.00212
AMD	30.3 ± 0.91	-	-	1.68 ± 0.0838	-	-	0.0285 ± 0.00143	-	-
Site #3	-	18.5 ± 0.55	5.18 ± 0.16	-	0.358 ± 0.0179	BD	-	BD	0.0508 ± 0.00254
Downstream	16.0 ± 0.48	-	-	0.689 ± 0.0345	-	-	0.192 ± 0.00962	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 14: Concentrations of major cations Si (µg/mL) from water samples collected at Blacklick Creek.

	Si (µg/mL)		
Sample Localities	10/7/2013	10/25/2013	12/6/2013
Upstream	6.94 ± 0.347	-	-
Site #2	-	3.44 ± 0.172	2.55 ± 0.127
CWT	5.87 ± 0.293	28.2 ± 1.41	1.89 ± 0.0944
CWT/Stream	10.0 ± 0.501	4.29 ± 0.214	-
Midstream	8.90 ± 0.445	3.16 ± 0.158	-
Site #1	-	3.35 ± 0.168	2.44 ± 0.122
AMD	13.9 ± 0.695	-	-
Site #3	-	3.64 ± 0.182	2.56 ± 0.128
Downstream	5.56 ± 0.278	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A "-" in the chart indicates no sample was taken from the location on that sampling date.

Table 15: Concentrations of major cations Al, Fe and K (mol/L) from water samples collected at Blacklick Creek.

Sample Localities	Al (mol/L)			Fe (mol/L)			K (mol/L)		
	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Upstream	42.4E-6 ± 1.3E-6	-	-	1.5E-6 ± 44.8E-6	-	-	126.6E-6 ± 3.8E-6	-	-
Site #2	-	BD	1.6E-6 ± 48.0E-6	-	12.1E-6 ± 364.3E-6	1.2E-6 ± 34.8E-6	-	81.1E-6 ± 2.4E-6	61.2E-6 ± 1.8E-6
CWT	28.4E-6 ± 852.4E-6	115.1E-6 ± 3.5E-6	6.0E-6 ± 180.6E-6	3.5E-6 ± 104.8E-6	4.5E-6 ± 134.3E-6	153.6E-6 ± 4.6E-6	10.3E-6 ± 309.7E-6	9.7E-6 ± 290.5E-6	1.1E-6 ± 32.4E-6
CWT/Stream	7.8E-6 ± 232.7E-6	14.9E-6 ± 447.3E-6	-	3.8E-6 ± 113.1E-6	4.4E-6 ± 131.6E-6	-	1.5E-6 ± 44.2E-6	6.1E-6 ± 184.0E-6	-
Midstream	BD	1.8E-6 ± 54.9E-6	-	816.1E-6 ± 24.5E-6	6.2E-6 ± 186.7E-6	-	176.2E-6 ± 5.3E-6	290.6E-6 ± 8.7E-6	-
Site #1	-	BD	1.1E-6 ± 34.4E-6	-	4.0E-6 ± 120.6E-6	700.0E-6 ± 21.0E-6	-	187.1E-6 ± 5.6E-6	60.6E-6 ± 1.8E-6
AMD	388.6E-6 ± 11.7E-6	-	-	2.1E-6 ± 64.0E-6	-	-	100.8E-6 ± 3.0E-6	-	-
Site #3	-	BD	1.2E-6 ± 35.0E-6	-	18.9E-6 ± 565.7E-6	492.9E-6 ± 14.8E-6	-	132.5E-6 ± 4.0E-6	60.4E-6 ± 1.8E-6
Downstream	33.0E-6 ± 990.8E-6	-	-	437.5E-6 ± 13.1E-6	-	-	117.5E-6 ± 3.5E-6	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 16: Concentrations of major cations Mg, Mn and P (mol/L) from water samples collected at Blacklick Creek.

Sample Localities	Mg (mol/L)			Mn (mol/L)			P (mol/L)		
	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Upstream	684.2E-6 ± 20.5E-6	-	-	12.5E-6 ± 374.7E-6	-	-	5.4E-6 ± 161.7E-6	-	-
Site #2	-	521.2E-6 ± 15.6E-6	177.9E-6 ± 5.3E-6	-	6.6E-6 ± 198.3E-6	BD	-	6.4E-6 ± 192.0E-6	2.4E-6 ± 72.2E-6
CWT	44.1E-6 ± 1.3E-6	46.0E-6 ± 1.4E-6	10.3E-6 ± 308.2E-6	BD	BD	BD	452.3E-6 ± 13.6E-6	532.4E-6 ± 16.0E-6	1.1E-6 ± 34.0E-6
CWT/Stream	8.6E-6 ± 257.9E-6	38.0E-6 ± 1.1E-6	-	BD	BD	-	4.3E-6 ± 129.9E-6	405.8E-6 ± 12.2E-6	-
Midstream	2.8E-6 ± 84.4E-6	1.8E-6 ± 54.1E-6	-	BD	6.4E-6 ± 192.1E-6	-	119.3E-6 ± 3.6E-6	20.9E-6 ± 627.9E-6	-
Site #1	-	1.1E-6 ± 31.9E-6	221.8E-6 ± 6.7E-6	-	6.2E-6 ± 187.1E-6	BD	-	4.6E-6 ± 138.4E-6	1.4E-6 ± 41.0E-6
AMD	1.3E-6 ± 37.8E-6	-	-	30.5E-6 ± 914.6E-6	-	-	919.4E-6 ± 27.6E-6	-	-
Site #3	-	769.6E-6 ± 23.1E-6	215.7E-6 ± 6.5E-6	-	6.5E-6 ± 195.4E-6	BD	-	BD	1.6E-6 ± 49.2E-6
Downstream	668.0E-6 ± 20.0E-6	-	-	12.5E-6 ± 375.9E-6	-	-	6.2E-6 ± 186.1E-6	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A "-" in the chart indicates no sample was taken from the location on that sampling date.

Table 17: Concentrations of major cations Si (mol/L) from water samples collected at Blacklick Creek.

	Si (mol/L)		
Sample Localities	10/7/2013	10/25/2013	12/6/2013
Upstream	247.9E-6 ± 7.4E-6	-	-
Site #2	-	122.8E-6 ± 3.7E-6	91.0E-6 ± 2.7E-6
CWT	209.5E-6 ± 6.3E-6	1.0E-6 ± 30.2E-6	67.4E-6 ± 2.0E-6
CWT/Stream	358.2E-6 ± 10.7E-6	153.1E-6 ± 4.6E-6	-
Midstream	317.7E-6 ± 9.5E-6	112.7E-6 ± 3.4E-6	-
Site #1	-	119.8E-6 ± 3.6E-6	87.0E-6 ± 2.6E-6
AMD	496.3E-6 ± 14.9E-6	-	-
Site #3	-	130.1E-6 ± 3.9E-6	91.4E-6 ± 2.7E-6
Downstream	198.7E-6 ± 6.0E-6	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

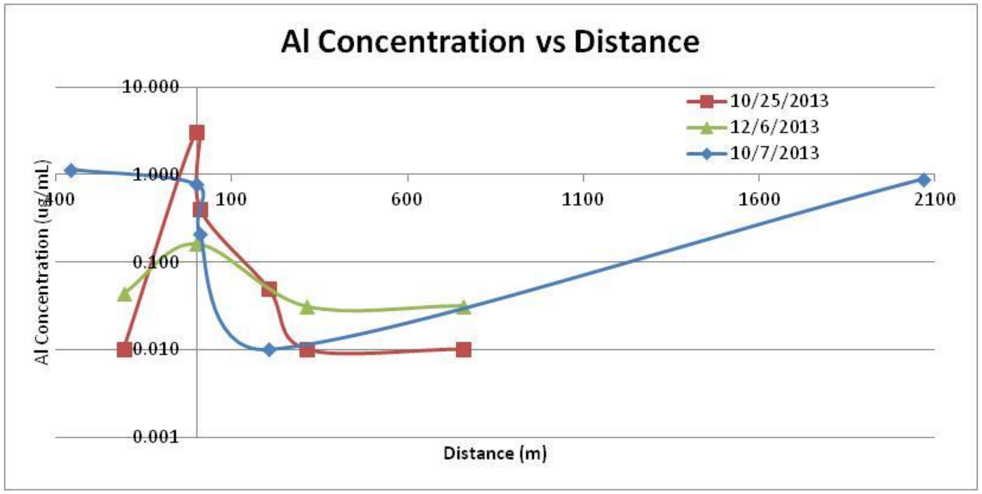


Figure 17: Concentrations of Al (μg/mL) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

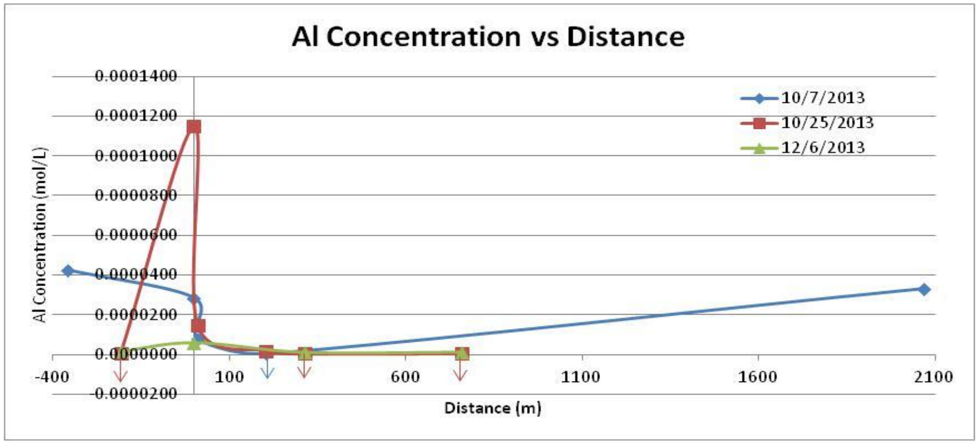


Figure 18: Concentrations of Al (mol/L) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

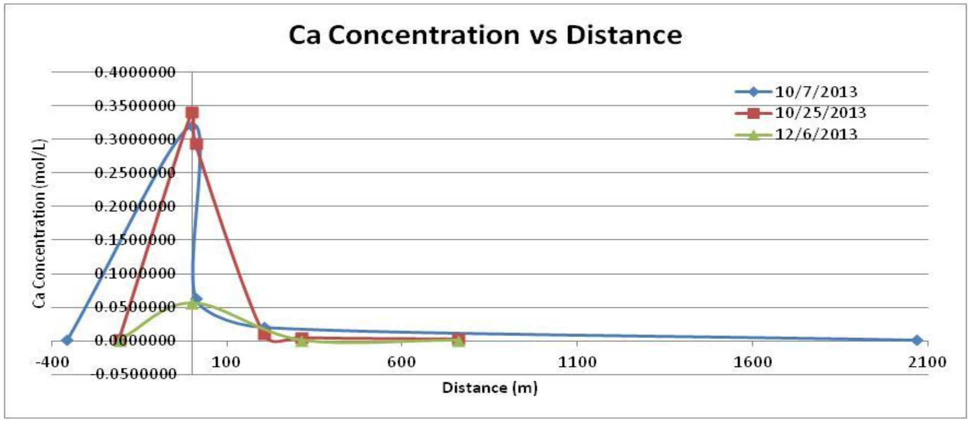


Figure 19: Concentrations of Al (mol/L) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

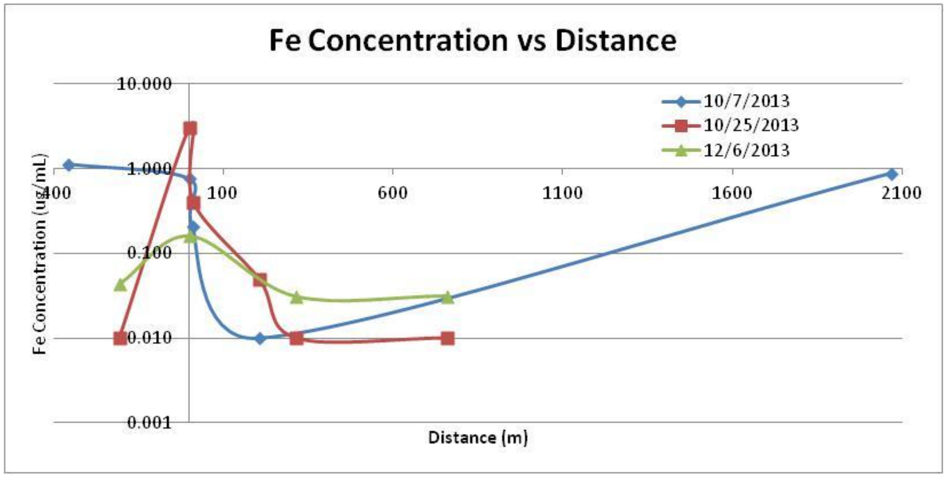


Figure 20: Concentrations of Fe (µg/mL) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

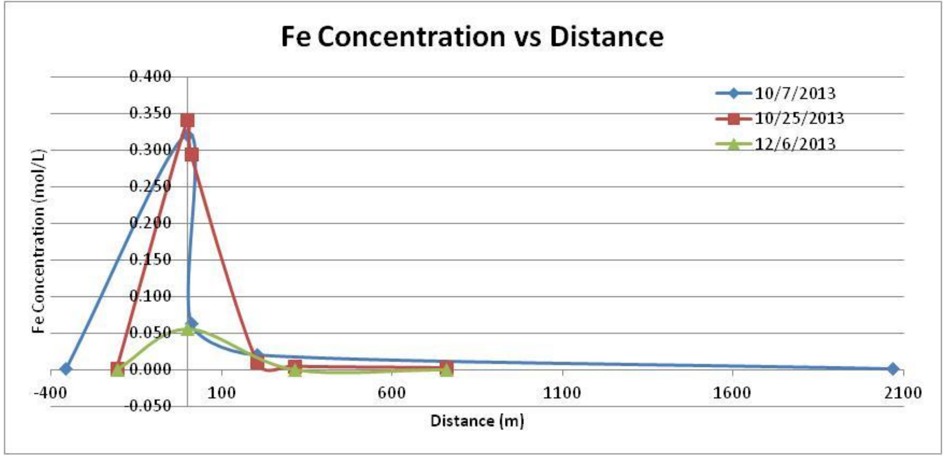


Figure 21: Concentrations of Fe (mol/L) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

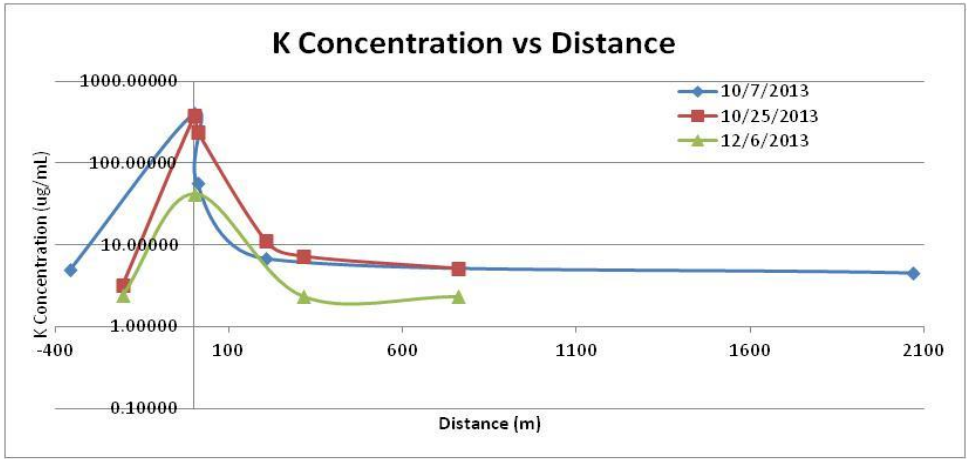


Figure 22: Concentrations of K (µg/mL) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

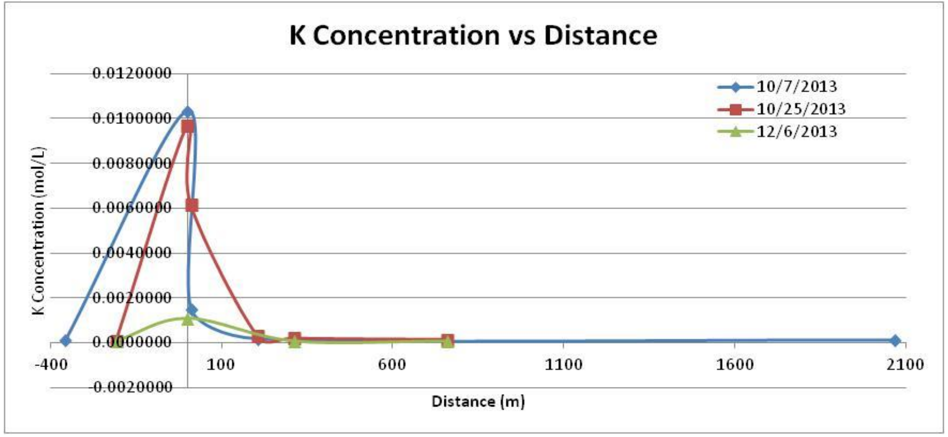


Figure 23: Concentrations of K (mol/L) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

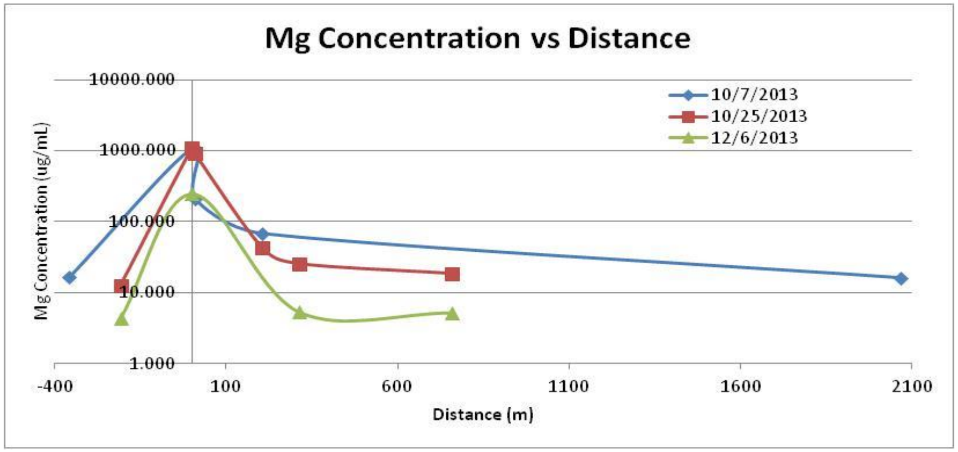


Figure 24: Concentrations of Mg (µg/mL) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

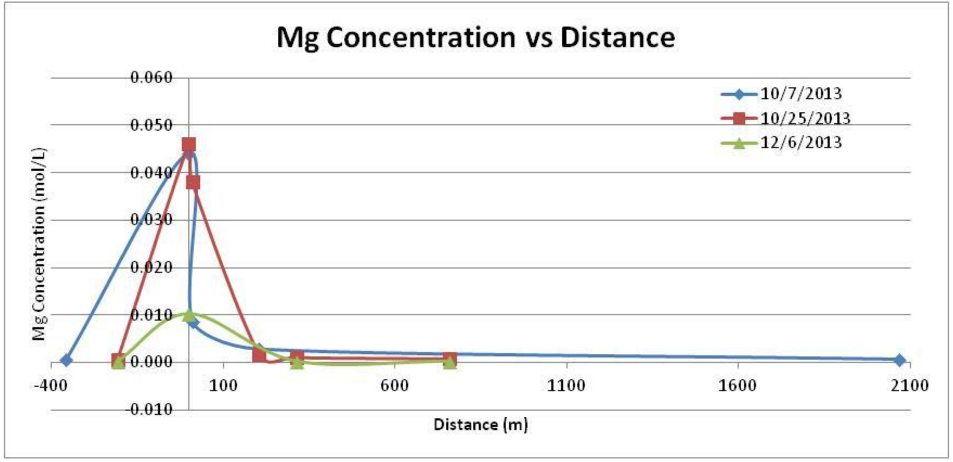


Figure 25: Concentrations of Mg (mol/L) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

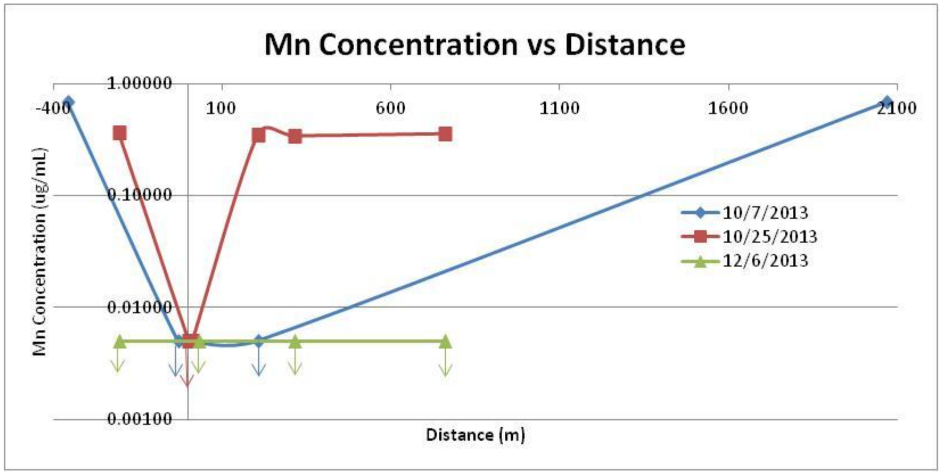


Figure 26: Concentrations of Mn (µg/mL) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

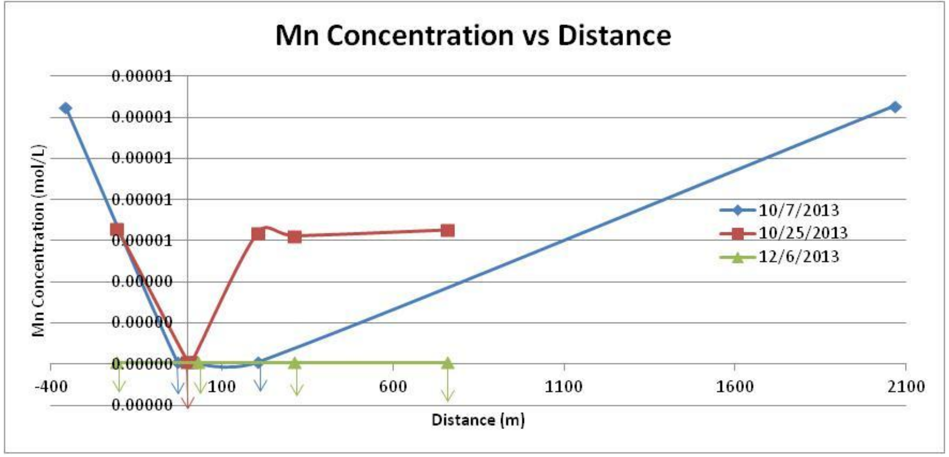


Figure 27: Concentrations of Mn (mol/L) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

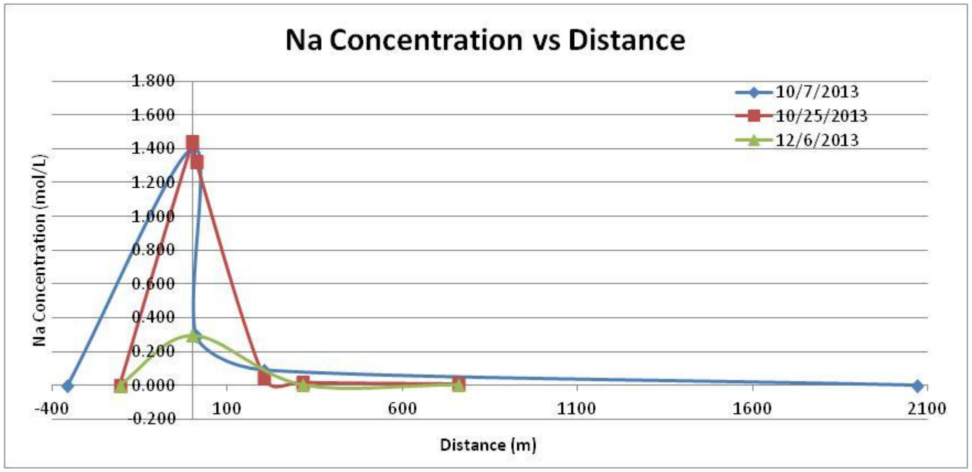


Figure 28: Concentrations of Na (mol/L) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

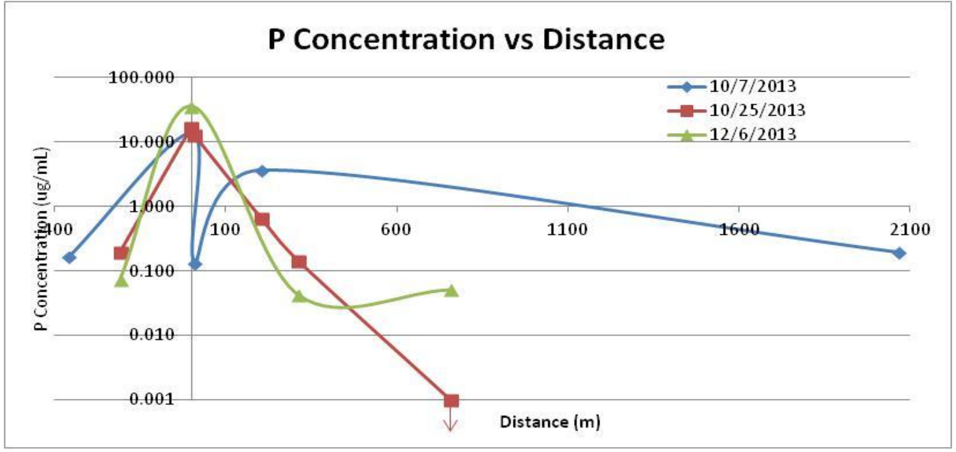


Figure 29: Concentrations of P (µg/mL) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

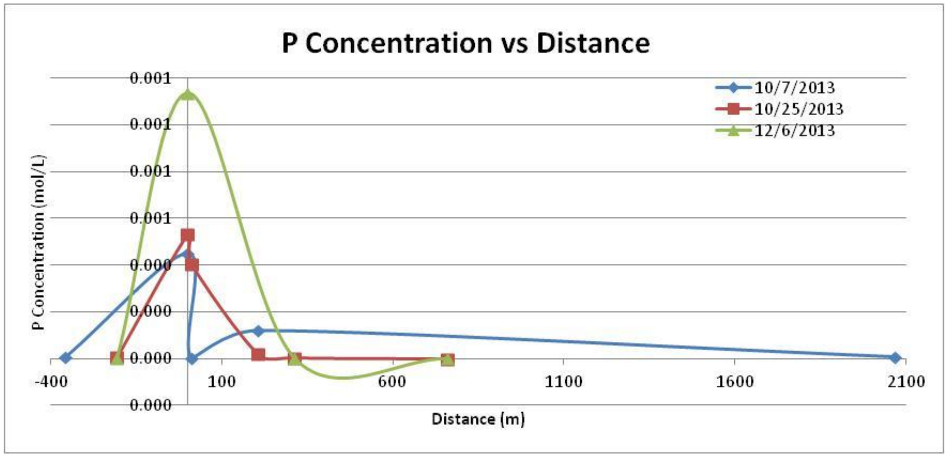


Figure 30: Concentrations of P (mol/L) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

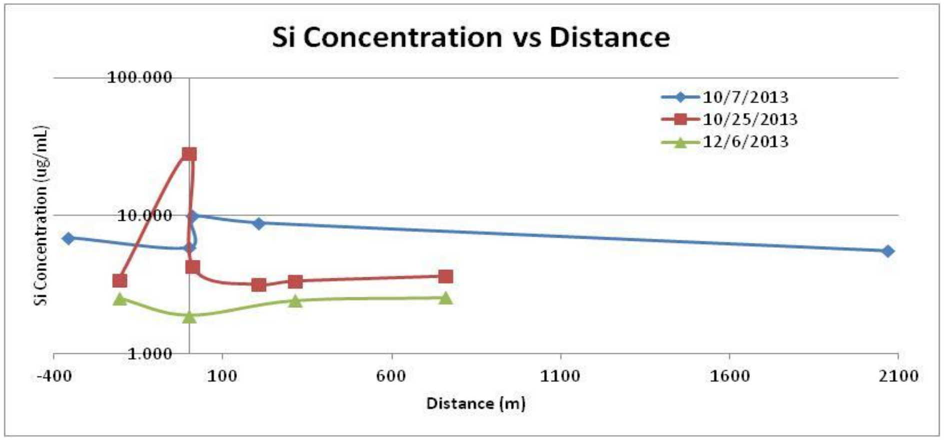


Figure 31: Concentrations of Si (μg/mL) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

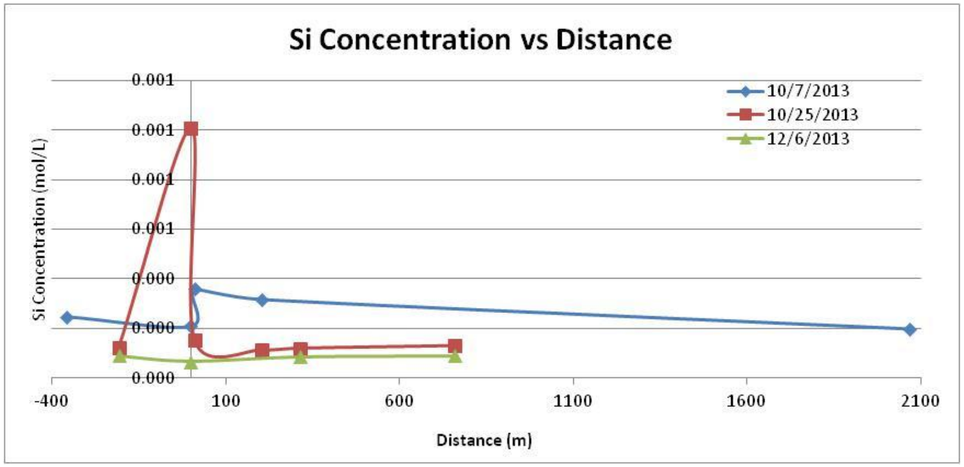


Figure 32: Concentrations of Si (mol/L) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

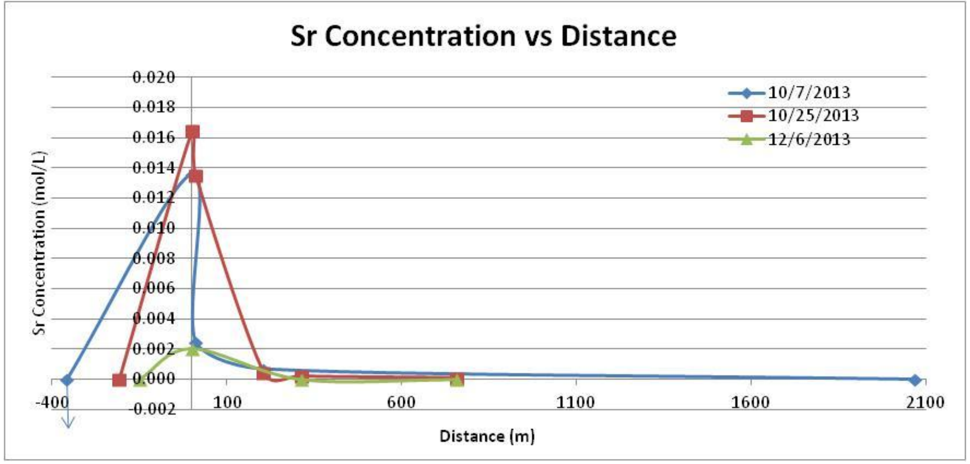


Figure 33: Concentrations of Sr (mol/L) vs. distance in Blacklick Creek from data collected 10/7, 10/25, 12/6

Table 18: Organic bound results for Al, Ba and Ca from sequential extraction on soil grab samples of Blacklick Creek. Each fraction was measure in mol/g of sample (smp)

		Al (mol/g smp)			Ba (mol/g smp)			Ca (mol/g smp)		
	Sample Localities	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Organic Bound	Upstream	197.4E-6 ± 5.9E-6	-	-	3.7E-6 ± 110.8E-9	-	-	17.7E-9 ± 530.7E-12	-	-
	Site #2	-	71.3E-6 ± 2.1E-6	-	-	103.2E-9 ± 3.1E-9	-	-	25.8E-9 ± 773.7E-12	-
	CWT	-	-	-	-	-	-	-	-	-
	CWT/Stream	-	5.6E-6 ± 169.2E-9	-	-	227.5E-9 ± 6.8E-9	-	-	56.9E-9 ± 1.7E-9	-
	Midstream	12.0E-6 ± 359.5E-9	10.2E-6 ± 306.5E-9	-	237.1E-9 ± 7.1E-9	81.2E-9 ± 2.4E-9	-	59.3E-9 ± 1.8E-9	20.3E-9 ± 608.9E-12	-
	Site #1	-	11.8E-6 ± 355.1E-9	-	-	37.3E-9 ± 1.1E-9	-	-	9.3E-9 ± 279.7E-12	-
	AMD	-	-	-	-	-	-	-	-	-
	Site #3	-	12.6E-6 ± 378.5E-9	-	-	151.6E-9 ± 4.5E-9	-	-	37.9E-9 ± 1.1E-9	-
	Downstream	32.8E-6 ± 984.8E-9	-	-	49.6E-9 ± 1.5E-9	-	-	12.4E-9 ± 372.1E-12	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 19: Organic bound results for Fe, K and Mg from sequential extraction on soil grab samples of Blacklick Creek. Each fraction was measure in mol/g of sample (smp)

		Fe (mol/g smp)			K (mol/g smp)			Mg (mol/g smp)		
	Sample Localities	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Organic Bound	Upstream	1.1E-3 ± 33.4E-6	-	-	534.4E-9 ± 16.0E-9	-	-	BD	-	-
	Site #2	-	221.6E-6 ± 6.6E-6	-	-	1.5E-6 ± 45.6E-9	-	-	2.1E-6 ± 63.6E-9	-
	CWT	-	-	-	-	-	-	-	-	-
	CWT/Stream	-	9.0E-6 ± 271.2E-9	-	-	1.3E-6 ± 39.5E-9	-	-	2.9E-6 ± 87.1E-9	-
	Midstream	26.5E-6 ± 793.8E-9	22.8E-6 ± 684.1E-9	-	473.2E-9 ± 14.2E-9	388.5E-9 ± 11.7E-9	-	836.5E-9 ± 25.1E-9	487.1E-9 ± 14.6E-9	-
	Site #1	-	21.0E-6 ± 631.1E-9	-	-	1.1E-6 ± 32.6E-9	-	-	553.7E-9 ± 16.6E-9	-
	AMD	-	-	-	-	-	-	-	-	-
	Site #3	-	24.1E-6 ± 722.5E-9	-	-	1.2E-6 ± 35.1E-9	-	-	785.6E-9 ± 23.6E-9	-
	Downstream	100.6E-6 ± 3.0E-6	-	-	1.7E-6 ± 49.8E-9	-	-	1.2E-6 ± 35.7E-9	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 20: Organic bound results for Mn, Na and P from sequential extraction on soil grab samples of Blacklick Creek. Each fraction was measure in mol/g of sample (smp)

	Sample Localities	**Mn (mol/g smp)**			**Na (mol/g smp)**			**P (mol/g smp)**		
		10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Organic Bound	Upstream	4.3E-6 ± 129.9E-9	-	-	3.8E-6 ± 115.1E-9	-	-	10.1E-6 ± 304.0E-9	-	-
	Site #2	-	1.7E-6 ± 52.0E-9	-	-	3.1E-6 ± 93.7E-9	-	-	10.0E-6 ± 299.8E-9	-
	CWT	-	-	-	-	-	-	-	-	-
	CWT/Stream	-	237.5E-9 ± 7.1E-9	-	-	4.9E-6 ± 147.1E-9	-	-	3.7E-6 ± 111.0E-9	-
	Midstream	380.7E-9 ± 11.4E-9	339.7E-9 ± 10.2E-9	-	2.8E-6 ± 84.1E-9	2.6E-6 ± 77.2E-9	-	5.3E-6 ± 158.8E-9	3.8E-6 ± 115.3E-9	-
	Site #1	-	1.2E-6 ± 35.5E-9	-	-	2.4E-6 ± 71.8E-9	-	-	3.2E-6 ± 97.4E-9	-
	AMD	-	-	-	-	-	-	-	-	-
	Site #3	-	213.8E-9 ± 6.4E-9	-	-	3.0E-6 ± 90.8E-9	-	-	4.1E-6 ± 121.7E-9	-
	Downstream	661.3E-9 ± 19.8E-9	-	-	3.6E-6 ± 106.8E-9	-	-	6.8E-6 ± 205.3E-9	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 21: Organic bound results for Si, Sr and Ti from sequential extraction on soil grab samples of Blacklick Creek. Each fraction was measure in mol/g of sample (smp)

		Si (mol/g smp)			Sr (mol/g smp)			Ti (mol/g smp)		
	Sample Localities	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Organic Bound	Upstream	83.1E-6 ± 2.5E-6	-	-	11.0E-9 ± 329.3E-12	-	-	88.7E-9 ± 2.7E-9	-	-
	Site #2	-	29.5E-6 ± 884.2E-9	-	-	19.7E-9 ± 591.8E-12	-	-	34.8E-9 ± 1.0E-9	-
	CWT	-	-	-	-	-	-	-	-	-
	CWT/Stream	-	7.0E-6 ± 209.6E-9	-	-	19.4E-6 ± 581.1E-9	-	-	36.1E-9 ± 1.1E-9	-
	Midstream	8.4E-6 ± 251.4E-9	6.9E-6 ± 206.9E-9	-	204.3E-9 ± 6.1E-9	30.9E-9 ± 928.3E-12	-	57.1E-9 ± 1.7E-9	47.7E-9 ± 1.4E-9	-
	Site #1	-	6.6E-6 ± 199.4E-9	-	-	22.2E-9 ± 665.8E-12	-	-	53.2E-9 ± 1.6E-9	-
	AMD	-	-	-	-	-	-	-	-	-
	Site #3	-	7.5E-6 ± 223.8E-9	-	-	41.8E-9 ± 1.3E-9	-	-	55.0E-9 ± 1.6E-9	-
	Downstream	18.1E-6 ± 542.6E-9	-	-	16.0E-9 ± 479.7E-12	-	-	100.0E-9 ± 3.0E-9	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 22: Organic bound results for Zn and Zr from sequential extraction on soil grab samples of Blacklick Creek. Each fraction was measure in mol/g of sample (smp)

Organic Bound

	Zn (mol/g smp)			Zr (mol/g smp)		
Sample Localities	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Upstream	963.2E-9 ± 28.9E-9	-	-	20.5E-9 ± 616.2E-12	-	-
Site #2	-	523.0E-9 ± 15.7E-9	-	-	21.4E-9 ± 641.5E-12	-
CWT	-	-	-	-	-	-
CWT/Stream	-	109.4E-9 ± 3.3E-9	-	-	6.8E-9 ± 205.4E-12	-
Midstream	179.5E-9 ± 5.4E-9	117.8E-9 ± 3.5E-9	-	4.3E-9 ± 129.2E-12	BD	-
Site #1	-	170.4E-9 ± 5.1E-9	-	-	3.6E-9 ± 108.5E-12	-
AMD	-	-	-	-	-	-
Site #3	-	128.5E-9 ± 3.9E-9	-	-	3.7E-9 ± 110.8E-12	-
Downstream	292.2E-9 ± 8.8E-9	-	-	2.9E-9 ± 87.7E-12	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 23: Exchangeable fraction results for Al, Ba and Ca from sequential extraction on soil grab samples of Blacklick Creek. Each fraction was measure in mol/g of sample (smp)

		Al (mol/g smp)			Ba (mol/g smp)			Ca (mol/g smp)		
	Sample Localities	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Exchangable Ions	Upstream	14.8E-9 ± 740.7E-12	-	-	11.1E-9 ± 553.3E-12	-	-	2.8E-9 ± 138.3E-12	-	-
	Site #2	-	14.8E-9 ± 740.7E-12	-	-	50.7E-9 ± 2.5E-9	-	-	12.7E-9 ± 634.1E-12	-
	CWT	-	-	-	-	-	-	-	-	-
	CWT/Stream	-	14.8E-9 ± 740.7E-12	-	-	428.9E-9 ± 21.4E-9	-	-	107.2E-9 ± 5.4E-9	-
	Midstream	14.8E-9 ± 740.7E-12	14.8E-9 ± 740.7E-12	-	100.2E-9 ± 5.0E-9	75.2E-9 ± 3.8E-9	-	25.0E-9 ± 1.3E-9	18.8E-9 ± 939.8E-12	-
	Site #1	-	14.8E-9 ± 740.7E-12	-	-	44.4E-9 ± 2.2E-9	-	-	11.1E-9 ± 554.4E-12	-
	AMD	-	-	-	-	-	-	-	-	-
	Site #3	-	14.8E-9 ± 740.7E-12	-	-	8.1E-9 ± 403.6E-12	-	-	2.0E-9 ± 100.9E-12	-
	Downstream	14.8E-9 ± 740.7E-12	-	-	34.9E-9 ± 1.7E-9	-	-	8.7E-9 ± 436.1E-12	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 24: Exchangeable fraction results for Fe, K and Mg from sequential extraction on soil grab samples of Blacklick Creek. Each fraction was measure in mol/g of sample (smp)

		Fe (mol/g smp)			K (mol/g smp)			Mg (mol/g smp)		
	Sample Localities	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Exchangable Ions	Upstream	35.8E-12 ± 1.8E-12	-	-	4.3E-6 ± 214.9E-9	-	-	7.4E-6 ± 371.9E-9	-	-
	Site #2	-	1.7E-9 ± 85.9E-12	-	-	3.6E-6 ± 179.7E-9	-	-	8.4E-6 ± 418.7E-9	-
	CWT	-	-	-	-	-	-	-	-	-
	CWT/Stream	-	BD	-	-	12.9E-6 ± 647.4E-9	-	-	100.5E-6 ± 5.0E-6	-
	Midstream	BD	4.7E-9 ± 236.4E-12	-	1.9E-6 ± 95.6E-9	2.9E-6 ± 146.3E-9	-	9.4E-6 ± 472.4E-9	11.9E-6 ± 594.7E-9	-
	Site #1	-	BD	-	-	1.1E-6 ± 56.3E-9	-	-	1.3E-6 ± 66.1E-9	-
	AMD	-	-	-	-	-	-	-	-	-
	Site #3	-	15.7E-9 ± 784.3E-12	-	-	4.0E-6 ± 198.1E-9	-	-	18.7E-6 ± 933.8E-9	-
	Downstream	BD	-	-	2.8E-6 ± 141.9E-9	-	-	8.4E-6 ± 420.3E-9	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 25: Exchangeable fraction results for Mn, Na and P from sequential extraction on soil grab samples of Blacklick Creek. Each fraction was measure in mol/g of sample (smp)

		Mn (mol/g smp)			Na (mol/g smp)			P (mol/g smp)		
	Sample Localities	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Exchangable Ions	Upstream	3.3E-6 ± 164.6E-9	-	-	11.5E-6 ± 574.7E-9	-	-	169.5E-9 ± 8.5E-9	-	-
	Site #2	-	3.3E-6 ± 164.4E-9	-	-	3.6E-6 ± 180.9E-9	-	-	96.9E-9 ± 4.8E-9	-
	CWT	-	-	-	-	-	-	-	-	-
	CWT/Stream	-	192.0E-9 ± 9.6E-9	-	-	1.6E-3 ± 80.8E-6	-	-	653.5E-9 ± 32.7E-9	-
	Midstream	164.9E-9 ± 8.2E-9	243.1E-9 ± 12.2E-9	-	128.0E-6 ± 6.4E-6	290.8E-6 ± 14.5E-6	-	348.7E-9 ± 17.4E-9	366.8E-9 ± 18.3E-9	-
	Site #1	-	66.9E-9 ± 3.3E-9	-	-	7.8E-6 ± 391.9E-9	-	-	44.1E-9 ± 2.2E-9	-
	AMD	-	-	-	-	-	-	-	-	-
	Site #3	-	1.0E-6 ± 52.3E-9	-	-	234.8E-6 ± 11.7E-6	-	-	508.1E-9 ± 25.4E-9	-
	Downstream	518.2E-9 ± 25.9E-9	-	-	4.8E-6 ± 238.5E-9	-	-	152.9E-9 ± 7.6E-9	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 26: Exchangeable fraction results for Si, Sr and Ti from sequential extraction on soil grab samples of Blacklick Creek. Each fraction was measure in mol/g of sample (smp)

	Sample Localities	**Si (mol/g smp)**			**Sr (mol/g smp)**			**Ti (mol/g smp)**		
		10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Exchangable Ions	Upstream	2.2E-6 ± 110.3E-9	-	-	64.1E-9 ± 3.2E-9	-	-	6.6E-9 ± 332.4E-12	-	-
	Site #2	-	3.2E-6 ± 159.8E-9	-	-	79.2E-9 ± 4.0E-9	-	-	10.2E-9 ± 510.3E-12	-
	CWT	-	-	-	-	-	-	-	-	-
	CWT/Stream	-	1.2E-6 ± 62.2E-9	-	-	32.1E-6 ± 1.6E-6	-	-	9.5E-9 ± 474.5E-12	-
	Midstream	3.0E-6 ± 148.4E-9	2.2E-6 ± 107.8E-9	-	1.7E-6 ± 83.2E-9	2.6E-6 ± 130.8E-9	-	7.3E-9 ± 364.7E-12	4.8E-9 ± 239.7E-12	-
	Site #1	-	1.1E-6 ± 53.0E-9	-	-	344.0E-9 ± 17.2E-9	-	-	5.9E-9 ± 296.1E-12	-
	AMD	-	-	-	-	-	-	-	-	-
	Site #3	-	2.6E-6 ± 131.3E-9	-	-	1.4E-6 ± 70.7E-9	-	-	3.7E-9 ± 185.3E-12	-
	Downstream	2.6E-6 ± 131.5E-9	-	-	185.8E-9 ± 9.3E-9	-	-	7.8E-9 ± 391.7E-12	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 27: Exchangeable fraction results for Zn and Zr from sequential extraction on soil grab samples of Blacklick Creek. Each fraction was measure in mol/g of sample (smp)

		Zn (mol/g smp)			Zr (mol/g smp)		
	Sample Localities	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Exchangable Ions	Upstream	8.2E-9 ± 409.2E-12	-	-	BD	-	-
	Site #2	-	BD	-	-	BD	-
	CWT	-	-	-	-	-	-
	CWT/Stream	-	4.5E-9 ± 223.1E-12	-	-	BD	-
	Midstream	4.1E-9 ± 206.2E-12	8.7E-9 ± 435.4E-12	-	BD	BD	-
	Site #1	-	3.2E-9 ± 160.0E-12	-	-	BD	-
	AMD	-	-	-	-	-	-
	Site #3	-	35.6E-9 ± 1.8E-9	-	-	BD	-
	Downstream	BD	-	-	BD	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 28: Amorphous fraction results for Al, Ba and Ca from sequential extraction on soil grab samples of Blacklick Creek. Each fraction was measure in mol/g of sample (smp)

	Sample Localities	Al (mol/g smp)			Ba (mol/g smp)			Ca (mol/g smp)		
		10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Amorphous Oxide	Upstream	1.0E-3 ± 30.6E-6	-	-	366.2E-9 ± 11.0E-9	-	-	91.6E-9 ± 2.7E-9	-	-
	Site #2	-	640.8E-6 ± 19.2E-6	-	-	743.7E-9 ± 22.3E-9	-	-	185.9E-9 ± 5.6E-9	-
	CWT	-	-	-	-	-	-	-	-	-
	CWT/Stream	-	52.0E-6 ± 1.6E-6	-	-	300.3E-9 ± 9.0E-9	-	-	75.1E-9 ± 2.3E-9	-
	Midstream	128.4E-6 ± 3.9E-6	93.3E-6 ± 2.8E-6	-	4.1E-6 ± 122.2E-9	1.8E-6 ± 54.6E-9	-	1.0E-6 ± 30.5E-9	454.7E-9 ± 13.6E-9	-
	Site #1	-	74.4E-6 ± 2.2E-6	-	-	584.8E-9 ± 17.5E-9	-	-	146.2E-9 ± 4.4E-9	-
	AMD	-	-	-	-	-	-	-	-	-
	Site #3	-	191.8E-6 ± 5.8E-6	-	-	906.7E-9 ± 27.2E-9	-	-	226.7E-9 ± 6.8E-9	-
	Downstream	635.3E-6 ± 19.1E-6	-	-	729.4E-9 ± 21.9E-9	-	-	182.4E-9 ± 5.5E-9	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 29: Amorphous fraction results for Fe, K and Mg from sequential extraction on soil grab samples of Blacklick Creek. Each fraction was measure in mol/g of sample (smp)

		Fe (mol/g smp)			K (mol/g smp)			Mg (mol/g smp)		
	Sample Localities	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Amorphous Oxide	Upstream	1.3E-3 ± 40.2E-6	-	-	1.2E-6 ± 37.3E-9	-	-	-	-	-
	Site #2	-	799.5E-6 ± 24.0E-6	-	-	2.0E-6 ± 61.2E-9	-	-	19.6E-6 ± 588.3E-9	-
	CWT	-	-	-	-	-	-	-	-	-
	CWT/Stream	-	711.5E-6 ± 21.3E-6	-	-	3.5E-6 ± 105.3E-9	-	-	245.5E-6 ± 7.4E-6	-
	Midstream	236.2E-6 ± 7.1E-6	240.3E-6 ± 7.2E-6	-	1.3E-6 ± 38.6E-9	1.7E-6 ± 52.3E-9	-	4.6E-6 ± 138.4E-9	1.8E-6 ± 53.1E-9	-
	Site #1	-	193.1E-6 ± 5.8E-6	-	-	1.6E-6 ± 48.7E-9	-	-	3.2E-6 ± 96.7E-9	-
	AMD	-	-	-	-	-	-	-	-	-
	Site #3	-	479.4E-6 ± 14.4E-6	-	-	1.1E-6 ± 33.7E-9	-	-	2.7E-6 ± 80.8E-9	-
	Downstream	711.5E-6 ± 21.3E-6	-	-	1.3E-6 ± 39.2E-9	-	-	50.0E-6 ± 1.5E-6	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 30: Amorphous fraction results for Mn, Na and P from sequential extraction on soil grab samples of Blacklick Creek. Each fraction was measure in mol/g of sample (smp)

		Mn (mol/g smp)			Na (mol/g smp)			P (mol/g smp)		
	Sample Localities	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Amorphous Oxide	Upstream	24.0E-6 ± 719.7E-9	-	-	679.9E-9 ± 20.4E-9	-	-	2.1E-6 ± 62.4E-9	-	-
	Site #2	-	14.3E-6 ± 429.2E-9	-	-	1.0E-6 ± 30.2E-9	-	-	4.4E-6 ± 131.6E-9	-
	CWT	-	-	-	-	-	-	-	-	-
	CWT/Stream	-	7.9E-6 ± 236.7E-9	-	-	11.7E-6 ± 351.4E-9	-	-	875.0E-9 ± 26.2E-9	-
	Midstream	5.6E-6 ± 168.6E-9	1.6E-6 ± 48.4E-9	-	1.8E-6 ± 54.5E-9	2.9E-6 ± 87.9E-9	-	858.0E-9 ± 25.7E-9	503.1E-9 ± 15.1E-9	-
	Site #1	-	10.6E-6 ± 317.6E-9	-	-	767.7E-9 ± 23.0E-9	-	-	484.0E-9 ± 14.5E-9	-
	AMD	-	-	-	-	-	-	-	-	-
	Site #3	-	1.2E-6 ± 36.7E-9	-	-	2.0E-6 ± 59.5E-9	-	-	1.7E-6 ± 50.1E-9	-
	Downstream	5.9E-6 ± 176.6E-9	-	-	971.5E-9 ± 29.1E-9	-	-	3.1E-6 ± 92.3E-9	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 31: Amorphous fraction results for Si, Sr and Ti from sequential extraction on soil grab samples of Blacklick Creek. Each fraction was measure in mol/g of sample (smp)

		Si (mol/g smp)			Sr (mol/g smp)			Ti (mol/g smp)		
	Sample Localities	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Amorphous Oxide	Upstream	286.4E-6 ± 8.6E-6	-	-	71.9E-9 ± 2.2E-9	-	-	12.6E-9 ± 377.4E-12	-	-
	Site #2	-	183.4E-6 ± 5.5E-6	-	-	156.1E-9 ± 4.7E-9	-	-	35.7E-9 ± 1.1E-9	-
	CWT	-	-	-	-	-	-	-	-	-
	CWT/Stream	-	45.3E-6 ± 1.4E-6	-	-	86.2E-6 ± 2.6E-6	-	-	15.0E-9 ± 450.6E-12	-
	Midstream	61.3E-6 ± 1.8E-6	40.0E-6 ± 1.2E-6	-	2.4E-6 ± 72.0E-9	810.6E-9 ± 24.3E-9	-	20.3E-9 ± 609.4E-12	19.4E-9 ± 582.1E-12	-
	Site #1	-	30.5E-6 ± 915.2E-9	-	-	213.3E-9 ± 6.4E-9	-	-	18.6E-9 ± 556.8E-12	-
	AMD	-	-	-	-	-	-	-	-	-
	Site #3	-	51.0E-6 ± 1.5E-6	-	-	340.2E-9 ± 10.2E-9	-	-	34.1E-9 ± 1.0E-9	-
	Downstream	220.2E-6 ± 6.6E-6	-	-	369.7E-9 ± 11.1E-9	-	-	39.0E-9 ± 1.2E-9	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.

Table 32: Amorphous fraction results for Zn and Zr from sequential extraction on soil grab samples of Blacklick Creek. Each fraction was measure in mol/g of sample (smp)

		Zn (mol/g smp)			Zr (mol/g smp)		
	Sample Localities	10/7/2013	10/25/2013	12/6/2013	10/7/2013	10/25/2013	12/6/2013
Amorphous Oxide	Upstream	3.2E-6 ± 95.2E-9	-	-	7.9E-9 ± 238.0E-12	-	-
	Site #2	-	3.4E-6 ± 101.6E-9	-	-	14.3E-9 ± 429.9E-12	-
	CWT	-	-	-	-	-	-
	CWT/Stream	-	407.4E-9 ± 12.2E-9	-	-	2.4E-9 ± 71.2E-12	-
	Midstream	1.1E-6 ± 33.6E-9	344.0E-9 ± 10.3E-9	-	549.5E-12 ± 16.5E-12	2.4E-9 ± 71.2E-12	-
	Site #1	-	494.7E-9 ± 14.8E-9	-	-	1.8E-9 ± 54.1E-12	-
	AMD	-	-	-	-	-	-
	Site #3	-	343.1E-9 ± 10.3E-9	-	-	5.4E-9 ± 162.9E-12	-
	Downstream	2.3E-6 ± 68.6E-9	-	-	8.9E-9 ± 268.4E-12	-	-

BD in the chart indicates that particular element showed up below the detection limit for the machine. A “-“ in the chart indicates no sample was taken from the location on that sampling date.