Comparison of Water Quality Upstream and Downstream of Coal Refuse in Southwest Virginia's Clinch River Basin

by

Kimberly Joanne Noel

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Approved by:

Carol M. Babyak, Ph.D., Thesis Director

Michael Hambourger, Ph.D., Second Reader

Crystal G. Wilson, M.S., Second Reader

Libby G. Puckett, Ph.D., Honors Committee Chair

Leslie Sargent Jones, Ph.D., Director, The Honors College

Abstract

Water was sampled upstream and downstream of coal refuse areas at Big Stony Creek, Cove Creek, and Shupe Creek in Scott Co., Virginia to determine if coal waste acid mine drainage (AMD) had an impact on water quality before, during, and after a reclamation project removed the refuse material and relocated it to a disposal site. Samples were tested for Cl^- and SO_4^{2-} using ion chromatography (IC), and Al, As, Cd, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, Se, and Zn using inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

In general, Big Stony Creek and Shupe Creek did not have concentrations of AMD related contaminants above acceptance criteria and there was not a significant difference between analyte concentrations upstream and downstream of coal refuse areas. Cove Creek generally did not have analyte concentrations above acceptance criteria, but there was a significant increase in Mg, Na, and SO_4^{2-} at the site downstream of coal refuse relative to the upstream. Overall, AMD was not a water quality problem at these sites, which may be attributable to the age and properties of the coal refuse, presence of acid-neutralizing minerals, and/or established vegetation. Ongoing analysis will provide a water quality record post-reclamation and the effects of coal refuse removal on water quality can be determined.

1. Introduction

1.1 Acid Mine Drainage

1.1.a. The Chemistry of Acid Mine Drainage

Acid mine drainage (AMD) refers to the acidic leachate generated from chemical reactions between sulfide-containing minerals (metal sulfides), oxygen, and water. Oxygen and water can be introduced to metal sulfides via natural geophysical processes, such as faulting or weathering, but human activity, such as mining and construction can also play a role. Acid mine drainage was described as early as 1910 by E.C. Trax, who wrote about the Allegheny, Monongahela, and Youghiogheny rivers in Pennsylvania that were polluted by acidic drainage and waste water from coal mines. [1]

The chemical reactions responsible for AMD have since been well-studied. Iron (II) disulfide (FeS_2), known as pyrite or fool's gold, is the principle mineral responsible for acid mine drainage in coal fields, though pyrrhotite (FeS) and chalcocite (Cu_2S) are other sulfide minerals that may also contribute.[2] The chemical reactions involved in the oxidation of pyrite are as follows.[3]

$$FeS_2(s) + \frac{7}{2}O_2(aq) + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$Fe^{2+} + \frac{1}{4}O_2(aq) + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O \quad (2)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH_3)(s) + 3H^+ \quad (3)$$

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

In the initiation step (reaction 1), S_2^{2-} is oxidized to SO_4^{2-} (sulfate), yielding Fe^{2+} and protons (H^+). The Fe^{2+} ion may also arise from spontaneous dissociation of pyrite, though

FeS_2 is not very soluble, with a pK_{sp} of -15.4.[4] Once Fe^{2+} is generated, it is oxidized to Fe^{3+} (reaction 2), which either reacts with water to form an iron(III) hydroxide ($Fe(OH_3)$) precipitate (reaction 3) or to liberate more Fe^{2+} in solution upon reaction with pyrite (reaction 4). The oxidation of pyrite can become self-propagating as H^+ is generated because the ferric ion is stabilized at low pH.[5]

Philip C. Singer and Werner Stumm found that the rate-determining step for the oxidation of pyrite and release of acid was reaction 2 rather than the initiation step.[3] There are numerous catalysts that can speed up the oxidation of Fe^{2+}, but certain bacteria have been discovered as the most significant. Singer and Stumm found a rate increase on the order of 10^6 when the reaction was performed in the presence of microbes versus sterile conditions.[3] The bacteria thought to be most responsible for pyrite oxidation are *Thiobacillus ferrooxidans.*

1.1.b. Characteristics of AMD

The chemical properties and severity of AMD vary geographically with climate (temperature, oxygen content, water content), mineralogy (type and surface area of metal sulfide, Fe^{3+} activity), presence of bacteria, and the age/exposure of mines or waste piles.[2,3] Once generated, the sulfate-laden acid will eventually be washed out of the rock via water flow and possibly go on to dissolve other chemical species from the surrounding substrate and lead to soil, ground water, and surface water contamination.[3,6] AMD often contains elevated concentrations of aluminum, iron, manganese, and sulfate.[2] Areas heavily impacted by AMD have been known to have effluent sulfate concentrations upwards of 400 mg/L and as high as 18,000 mg/L.[7] Toxic heavy metals may be present in above-average concentrations, but are usually comparatively low.[2, 8]

Environmental contamination due to AMD may be ameliorated naturally when acid-neutralizing carbonate (e.g. $CaCO_3$, $CaMg(CO_3)_2$) and silicate minerals (e.g. $CaAl_2Si_2O_8$) are present.[3, 9] The biological contribution to iron oxidation also may be minimized once the pH drops below the range optimal for bacteria growth.[3] In that case, the presence of AMD can still be determined by measuring the concentration of sulfate anions, which generally remain even in alkaline conditions.[3]

1.1.c. Coal Waste and AMD

Coal mining produces waste known as coal refuse or garbage of bituminous waste (GOB). Generally about 30%, but as much as 60% by mass of the mined material can become refuse.[10] The physical and chemical properties of coal refuse vary depending on its source and how it was processed.[8] Generally, it is made up of coal that does not meet industry criteria as well as rock that was present in or around the coal seam, such as shale, sandstone, and siltstone.[8, 10]

The AMD potential of a coal refuse pile is highly dependent on its oxidizable sulfur content. In addition, the ability of limestone to neutralize acid may mitigate the AMD potential of coal refuse if it is present. The size of the refuse fragments also contribute to the AMD potential, as finer material has a larger surface area that can come in contact with oxygen and water.[8] Older refuse piles tend to have larger fragments and a larger proportion of coal present than newer ones, due to improved separation techniques and ability of modern coal plants to utilize lower-grade coal.[8]

Interested in the feasibility of revegetation, Stewart et al.[10] reported the physical and chemical properties of 27 coal refuse piles from Norton, Wise, and Harlan seams in VA during the 1986-1987 time period. They found that rock fragments were mostly comprised of shale, while sandstone and siltstone were present in lesser amounts. Quartz was the most abundant mineral fragment, while mica and kaolin were present in the clay. Total elemental analysis showed that carbon and silicon were the most abundant elements, SiO_2, Al_2O_3, Fe_2O_3, K_2O, MgO, CaO were present with mean concentrations of 391, 128, 41, 28.9, 3.1, 5.6, and 2.1 g/kg respectively.[10] Copper, zinc, and nickel had mean concentrations of 55.0, 70.3, and 39.2 mg/kg respectively.[10]

1.1.d. Consequences of AMD

AMD can impact surface water and ground water. A visible indication of AMD in surface waters is a yellowish-brown solid settled at the bottom known as "yellowboy."[6] Yellowboy is the iron(III) hydroxide precipitate produced in reaction 3 and can be thick in areas heavily impacted by AMD.

Biotic effects of AMD are of great importance due to the sensitivity of many stream ecosystems and aquatic populations. AMD exerts chemical stresses such as acidity and toxic heavy metals and physical stresses such as metal precipitates that can cover the surfaces of the substrate and bodies of plants and animals.[11] The impact of AMD stress on biological communities can be difficult to measure, and numerous studies attempting to relate AMD stress to benthic biomass, algal metabolism, etc. yield conflicting results due to the complexity of the stream ecosystem and the wide spatial and temporal variation in water chemistry.[11]

Clements et al.[12] performed field and stream microcosm experiments on population and community-level response to metal concentrations in the Arkansas River, CO between 2002 and 2003. They reported that taxa, mayfly, and EPT (*Ephemeroptera, Plecoptera, Trichoptera*) richness were not different between reference sites and metal contaminated sites. These results contrasted with their findings in 2001, which did show significantly lower taxa and EPT richness at a metal contaminated site.[13] Despite the difficulties in quantifying and predicting AMD's impacts on stream ecology, it seems likely that there is some effect on aquatic life that should be considered.

1.1.e. Regulations, Prevention and Treatment of AMD

The Surface Mining Control and Reclamation Act (SMCRA) of 1977 established the Office of Surface Mining Reclamation (OSMRE) to regulate the coal industry throughout the mining process. The EPA first set regulations on mining effluent in 1985 and the Rahall amendment in 1987 specifically incentivized remining and reclamation of abandoned mine lands. EPA regulations sought to reduce acid, iron, manganese, and sulfate, which are the main contaminants discharged from old mines.[14] The maximum one day limits, taken at a single point during the day, for iron and manganese from mining effluent are 7.0 mg/L and 4.0 mg/L respectively. The limit on the average of daily values for 30 consecutive days for iron and manganese are 3.5 mg/L and 2.0 mg/L respectively.

Other mining-related contaminants do not have numeric limitations for mining effluent specified by the EPA, but Table 1 gives the agency's national recommendations for aquatic life in freshwater.[14,15] Limits are reported as criterion continuous concentration (CCC) and criteria maximum concentration (CMC), estimate the highest concentration in surface water that aquatic life can be exposed to indefinitely (CCC) and briefly (CMC), "without resulting in an unacceptable effect."[15]

Table 1. Water quality criteria for freshwater aquatic life recommended by the EPA

Contaminant	CMC (mg/L)	CCC (mg/L)
Al	0.75	0.087
As	0.34	0.15
Cd	0.002	0.00025
Cr (III, VI)	0.57, 0.016	0.074. 0.011
Cu	site specific	site specific
Fe		1
Pb	0.065	0.0025
Ni	0.47	0.052
Se		0.005
Zn	0.12	0.12
Chloride	860	230

The EPA outlines the following Best Management Practices (BMPs) for limiting AMD from pyrite oxidation: (1) preventing pyrite oxidation (2) preventing pyrite exposure to water (3) neutralizing acid with carbonate materials (4) inhibiting bacterial catalysis.[5] Neutralizing acid and maintaining a neutral pH is one of the most effective methods because it inhibits bacterial catalysis and greatly slows the oxidation of pyrite. Sites that have naturally occurring carbonates greater than 3% by volume will produce alkaline rather than acid drainage.[5]

For areas that do not have naturally occurring carbonates, remediation can be achieved by addition of alkaline material at a site with AMD. The type, amount, method and timing of introduction of the material must be carefully chosen.[5] Types of alkaline materials that are used include crushed limestone and limestone products, such as quick lime (CaO) and hydrated lime ($Ca(OH)_2$). Coal ash contains calcium oxide that can be the equivalent of 10-20% $CaCO_3$, by mass. Coal ash can be used as an alkaline material to prevent AMD. However, this material has low solubility and can behave as cement, so care must be taken to spread and mix it properly.[5] Steel slag, phosphate rock, AMD sludge (waste from AMD treatment) and organic wastes, such as whey, lactate, pulped newspaper, sawdust, and mushroom compost, are other potential alkaline materials but are not well tested.[5] Although achieving a neutral or alkaline pH can prevent further AMD, it does not mean that other water quality criteria will be met, such as metals concentrations.[5]

Another AMD control method is induced alkaline drainage, where surface runoff is directed to flow through limestone in a trench or funnel and becomes alkaline. The alkaline water then flows into an effected area, such as a refuse pile or mine overburden. This is a passive method, which requires little maintenance, but it only works after a precipitation event or when there is sufficient surface runoff.[5] Another concern is that the trench can become coated with $Fe(OH)_{3,}$ preventing water contact with the limestone. Many induced alkaline drainage systems are buried to prevent oxidation and the formation of iron hydroxides, these are called anoxic limestone drains (ALDs).

Special handling of acid-producing material is another method for controlling AMD. Techniques include (1) blending naturally occurring carbonate materials with acidic ones, (2) placing acidic materials below the water table, (3) placing them above the water table, (4) redistributing naturally occurring alkaline material from areas of high to low concentration. Method 2 works because it limits dissolved oxygen necessary for pyrite oxidation. Method 3 avoids contact with the water table to AMD transport through groundwater, but does not completely prevent oxidation because of oxygen in bedrock and soil pores below the surface. Burying acidic material above the water table is the most common technique used in the Appalachians, particularly in Pennsylvania.[5] These methods are generally used in combination with each other or with other methods, such as alkaline addition, for best AMD management.[5]

Since bacteria can increase the rate of pyrite oxidation by orders of magnitude, limiting bacterial growth is essential for controlling AMD. Bactericides are used to kill oxidizing bacteria, such as *T. ferrooxidans.* Types of bactericides are surfactants such as sodium lauryl sulfate (SLS), alkyl benzene sulfonate (ABS), and alpha olefin sulfonate (AOS). There have been cases where treatment with bactericides has inhibited AMD production and resulted in increased vegetation in coal refuse piles and surface mines. Bactericides must be continually applied and are not as effective in low oxygen environments.[5]

Revegetation is a required practice for mining permits. Older coal piles, which consist of coarse grain material, tend to have a low water holding capacity and are not readily able to host plant life.[10] Vegetation works to control pyrite oxidation by reducing water infiltration into the soil and exposure to atmospheric oxygen. The roots of well-established vegetation can hold water near the surface and keep it from infiltrating the underlying mine waste or spoil. It also prevents the flow of water into the aquifer below. Revegetation is also an effective means of reducing erosion that can result from mining and waste disposal. Coal refuse piles are prone to erosion and storm runoff if they are exposed.[5]

Coal refuse removal is one of the most effective methods because it eliminates the AMD source.[5] Often, the refuse is sent to a power plant to be burned. It is difficult to remove all of the refuse however, and fine sediment may remain behind. After removal, the site is regraded and revegetated.[5]

1.2. Project Sites and The Clinch River

Based on the standards set forth by The Virginia Coal Surface Mining Control and Reclamation Act of 1979, The Virginia Department of Mines, Minerals, and Energy (DMME), Division of Mined Land Reclamation determined that Big Stony Creek and Cove Creek, located in Scott County, VA were "adversely affected by past coal mining practices."[16] The project goals were to:

a) Remove coal refuse material and place at a disposal site

b) Seal open mine entries

c) Revegetate the land after coal refuse extraction

d) Control erosion and sediment throughout the reclamation[16]

The location of Big Stony Creek, Cove Creek, and Shupe Creek, which were monitored for the research project presented herein, are shown in Figure 1. The Big Stony Creek sites located upstream and downstream of the coal refuse area are labeled BSC 6.55 and BSC 6.35, respectively. The Cove Creek sites upstream and downstream of coal refuse are CC 8.03 and CC 7.75. Shupe Creek, which flows near the disposal site, was monitored when coal waste material began to arrive there; sites labeled SCT 0.94 and SCT 0.56 were upstream and downstream of the disposal area, respectively. The age of the Cove Creek and Big Stony Creek coal refuse piles are not known, but both sites had vegetation that suggested they were at least several decades old, as shown in Figure 2. The coal refuse was extracted with backhoe machinery and transported in dump trucks to the disposal site, where the material was spread out, covered with soil, and seeded with grass (Figures 3 and 4).

These streams are tributaries of the Clinch River, which begins in Virginia and flows southwest to eventually join with the Tennessee River, extending 135 miles.[17] The Clinch

River is ecologically important because of the abundance of rare and endangered aquatic plant and animal species, such as freshwater mussels and fish. The Clinch River Basin is the number-one area for threatened aquatic species in the United States.[18]

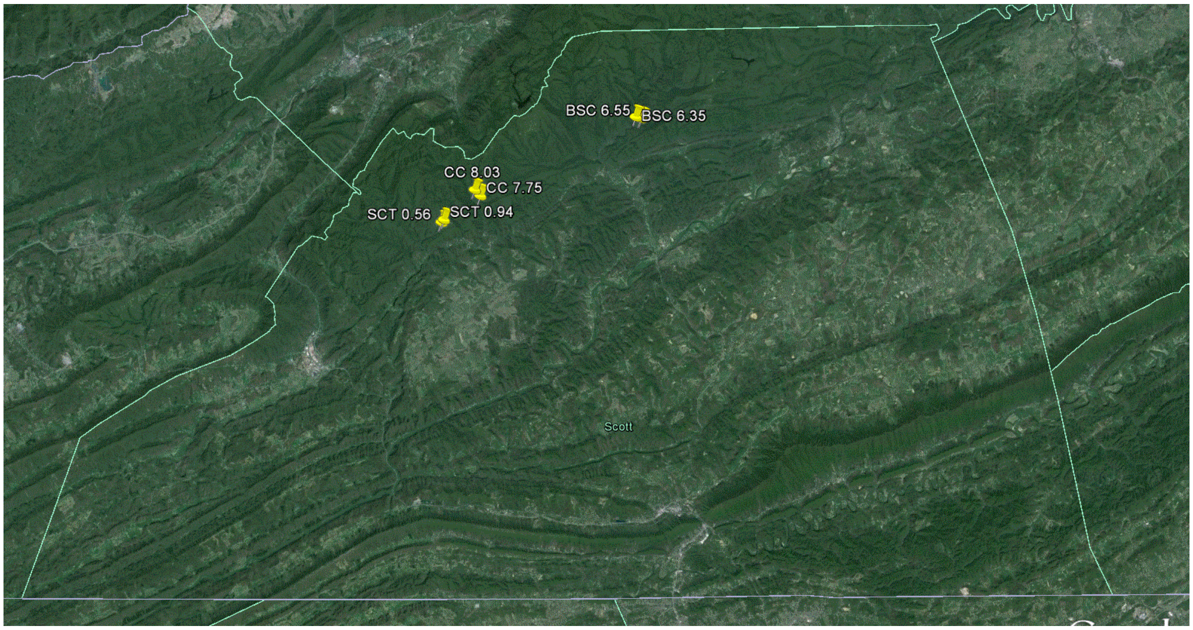

Figure 1. Water quality sampling sites in Scott County, Virginia.

Figure 2. A Big Stony Creek coal refuse pile prior to extraction on 7/25/2013. Note the presence of vegetation and exposed coal refuse.

Figure 3. Coal refuse extraction at the Cove Creek site on 4/21/2014.

Figure 4. Extracted coal refuse being spread out at the disposal site on 4/21/2014.

1.3 Coal History Near Study Sites

Historically, coal mining in Scott County, VA was not as productive as other parts of Southwest VA, due to fewer coal resources (Figure 5) and steep terrain.[19] Railways along Stony Creek and Little Stony Creek were built by Carolina, Clinchfield & Ohio Railroad in 1909 and allowed Virginia Iron, Coal & Coke, and J.S.T Coal Co. to open three coal mines Northeast of the town of Dungannon, VA by 1917. However, the location of the mines did not allow notable coal production until the early 1940s. Production fluctuated after WWII and reached a maximum (123,836 tons) in the mid-1980s, when five coal mines were in operation.[19] There are seven main coal beds in Scott Co., including Burton's Ford, Cove

Creek, Egan, Carter, Tacus, Jawbone and Starns Bed.[20] In the year 2000, 29,985 tons were produced in Scott County.[20] Overall coal production in Virginia has declined steadily since the early 1990s (Figure 6).

Northwest Scott County, where the coal is located, occurs in the Cumberland Plateau Province. This region is characterized flat-lying, alternating sequences of Pennsylvanian dolomite, shale, sandstone, and coal. Oxidizable sulfur content is generally low for coal found in this region.[8] The rest of the county occurs in the Valley and Ridge Province, which consists of folded and faulted sequences of older Paleozoic limestones, shales, and sandstones and lacks coal.[20,21]

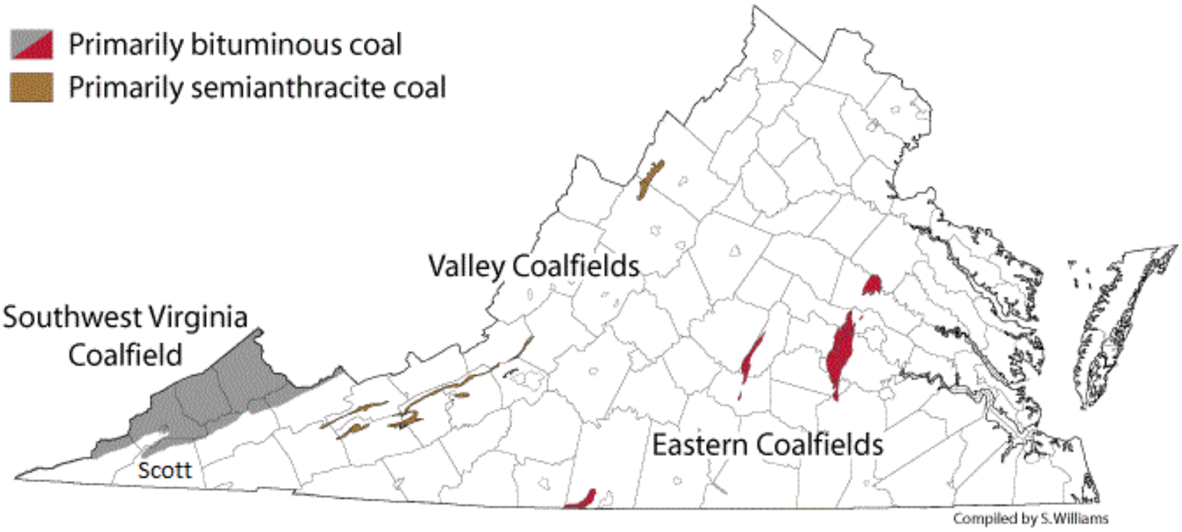

Figure 5. The distribution of bituminous and semianthracite coal beds in Virginia with Scott County labeled.[22]

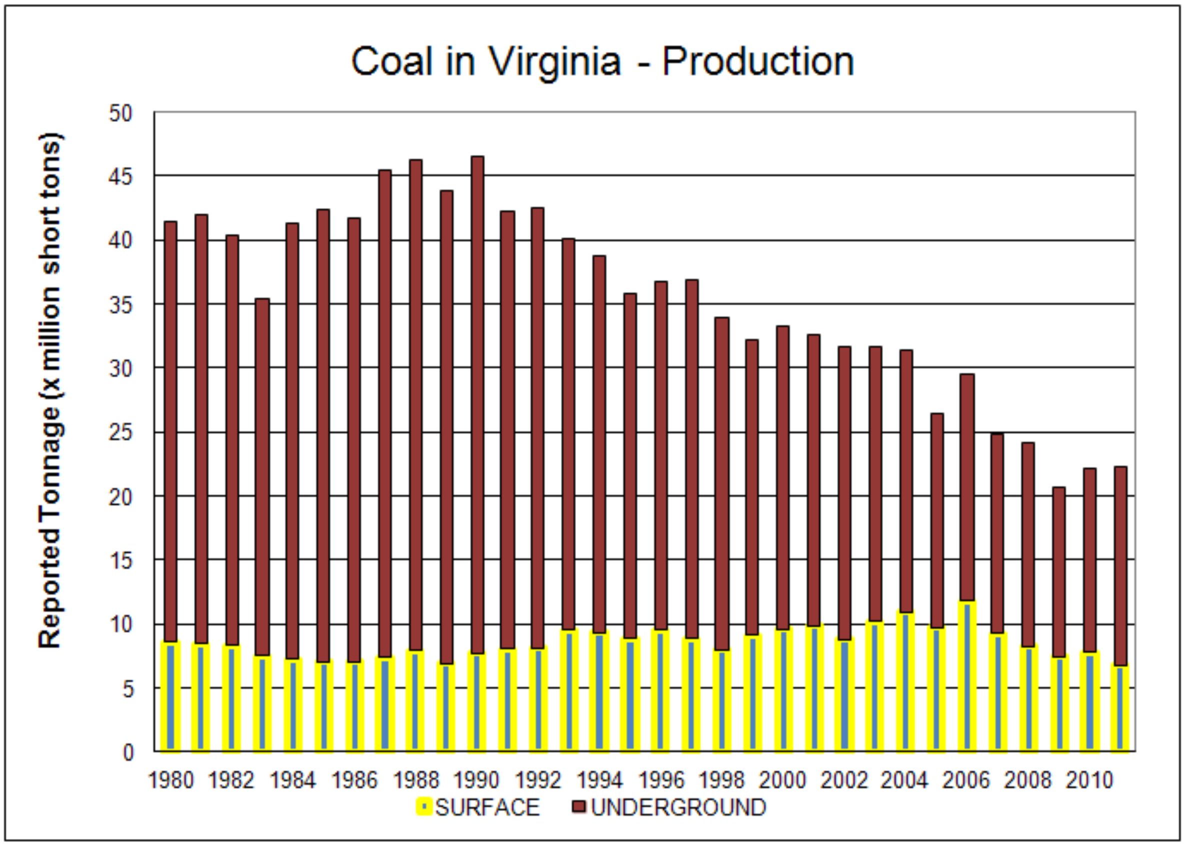

Figure 6. Coal Production in Virginia 1980-2011[23]

1.4.Scope of Work

In collaboration with The Virginia Nature Conservancy, the current research project aimed to monitor water quality before, during, and after coal refuse removal and reclamation activities at Big Stony Creek and Cove Creek. The disposal site, located near Shupe Creek, was also monitored when coal waste material began to arrive there. Water was sampled from each stream at sites upstream and downstream of the coal refuse. Chloride and sulfate were measured by ion chromatography (IC), and aluminum, arsenic, cadmium, chromium, copper, iron, lead, magnesium, manganese, sodium, nickel, selenium, and zinc were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The results are interpreted in the context of understanding the influence of coal refuse on water quality in the Southern Appalachians.

2. Materials and Methods

2.1. Reagents and Chemicals

Stock solutions were obtained from UltraScientific (10,000 mg/L Fe), SCP Science (100 mg/L As, Cd, Cr, Cu, Ni, Pb, Se, Zn, 1000 mg/L Al, 1000 mg/L Mg, 1000 mg/L Mn, and 1000 mg/L Na, 10,000 mg/L Y), Environmental Express (1000 mg/L sulfate), and BDH (1000 mg/L chloride). Concentrated 34-37% hydrochloric acid (HCl) (OmniTrace) and concentrated 67-70% nitric acid (HNO_3) (OmniTrace) were obtained from EMD. Distilled and deionized water was from Thermo-Fisher Nanopure System. High purity grade argon gas for ICP-AES (99.98%) was obtained from Machine and Welding.

2.2. Equipment and Instrumentation

Class A glassware was used throughout each analysis. Micropipettes used were VWR (20-100 μL, 100-1000 μL, 1-5 mL) and Eppendorf (2.0-20 μL). Thermolyne Type 2200 hot plates and SCP Science DigiPREP Jr. Digestion Block, DigiTUBEs, DigiFILTERS, and watchglasses were used for acid digestions. Samples were filtered before ICP-AES using 9 cm quantitative filter paper (VWR) and 25 mm syringe filters with 0.45 μm cellulose acetate membrane (VWR).

A Varian 710-ES Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) equipped with a CETAC ASX-520 AutoSampler, an axial torch (90 degree, 2.4 mm inj), and a Burgener Teflon Mira Mist nebulizer (SCP Science) was used to measure metals concentrations.

A Thermo Scientific (formerly Dionex) Ion Chromatograph, equipped with IonPac AS11-HC Hydroxide-Selective Anion Exchange Analytical Column (4x250 mm), IonPac Guard Column (4x50mm), AERS 500 (4mm) Suppressor (12.1 x 4.5 x 4.0 cm, 112 mA), and Dionex CD25 Conductivity Detector was used to determine chloride and sulfate concentrations. Hydroxide (25.0 mM) was generated by an ECG KOH eluent generator. The flow rate was 1.400 mL/min.

2.3. Sample Collection

Water sampling and quality assurance techniques were followed as directed by the Environmental Protection Agency (EPA).[24-25] For each event, grab samples were collected for anions and metals analysis. Samples for anions analysis were collected in 125-mL plastic bottles and stored in a cooler/refrigerator for up to 28 days. Samples for metals analysis were collected in 250-mL plastic bottles, acidified to a pH ≤2.0 with reagent nitric acid, and stored at room temperature for up to six months. A field reagent blank (FRB) and field duplicate were made for each sampling event.

Samples were collected from CC on 6/5/2013, 6/18/2013, 7/25/2013, 8/30/2013, 11/7/2013, 11/26/2013, 2/5/2014, 3/19/2014, 4/10/2014, 4/17/2014, 4/25/2014, 5/15/2014, 5/30/2014, 6/17/2014, 1/28/2015. Samples were collected from BSC on the same dates excluding 4/10/2014 and 4/17/2014. Remediation of Big Stony Creek began on 4/23/14 and ended on 6/5/14. Cove Creek remediation began on 4/10/14 and ended on 5/20/14. Sample collection from SCT began on 4/10/2014. Storm events occurred on 11/26/13, 2/5/14, 4/25/14, and 5/15/14.

2.4. Chloride and Sulfate Determination

Seven calibration standards were prepared in 25-mL volumetric flasks containing chloride and sulfate with linear ranges of 0.1-100 ppm. A laboratory fortified blank (LFB) containing a known concentration of chloride and sulfate was analyzed to determine if the method produced accurate and precise measurements. A laboratory reagent blank (LRB) containing DI water was analyzed to determine if analytes were introduced via laboratory equipment or reagents. A Field Reagent Blank (FRB) was analyzed to determine if any analytes were introduced via sampling, storage, preservation, and analytical procedure.

The water samples and FRB were filtered using syringeless filters and analyzed with the LFB, and LRB. All measurements were made in triplicate. Microsoft Office Excel was used to create calibration curves ($R^2 > 0.995$) and determine chloride and sulfate concentrations. Method detection limits for chloride and sulfate were 0.015 and 0.01 mg/L respectively.

2.5.Total Metals Determination

2.5.a. Acid Digestion

Acid digestions of water samples for analysis of total metals by ICP-AES followed EPA Method 3005A.[26] All glassware was washed with 50% nitric acid prior to use. Water samples were measured out in 100-mL aliquots and placed in 250-mL glass beakers. A LFB containing each analyte in 1.75% HNO_3 (v/v) was prepared in a 100-mL volumetric flask and then placed in a 250-mL beaker. A LRB digest sample (100-mL of 1.75% HNO_3) was also placed in a 250-mL beaker. Concentrated HNO_3 (2.0 mL) and concentrated HCl (5.0 mL) were added to each beaker via micropipette. The beakers were placed on hot plates, covered with watchglasses, and heated between 90-95°C until reduced to 15-20 mL. After removing beakers from the hot plates and cooling to room temperature, the contents were filtered through 9.0 cm qualitative filter paper into 100-mL volumetric flasks. The digested samples were brought back to 100-mL volumes with DI water and stored in plastic bottles until analysis.

Samples collected after 2/5/2014 were acid digested using a SCP Science DigiPREP Jr. digestion block. Aliquots of each water sample were measured up to the 50-mL mark in class A standard graduated disposable polypropylene DigiTUBEs. LFBs and LRBs were prepared for each digestion and placed into DigiTUBEs. Volumes of 1.0 mL HNO_3 and 0.5 mL HCl were added to each tube before placing them into the DigiPREP Jr. digestion block, set at 96 °C. DigiTUBEs were covered with plastic watchglasses and heated until reduced to a volume of 5.0 mL or less. The digested samples were cooled and filtered into new DigiTUBES using disposable DigiFILTERS, and then diluted to 50.0 mL with deionized and distilled water. Samples were stored in DigiTUBEs until analysis.

2.5.b. ICP-AES

Calibration standards were prepared in 25-mL volumetric flasks containing Al, As, Cd, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, Se, and Zn in 1-2%(v/v) HNO_3. The linear ranges were 0.2-20.0 mg/L for Al, Mg, Mn, Na, Fe, and 0.2-5.0 mg/L for all other metals. Calibration check standards with concentrations within the calibration linear range were made to determine the instrument performance and percent recovery of each analyte. Calibration curves were required to have R^2 values of ≥ 0.995 and a percent error ≤ 50 % per standard.

Yttrium (2.0 ppm) was used as an internal standard and the following were instrument operating conditions: 1100-1200 watts forward power, 15-16 mm viewing height, 15-19 L/min argon coolant flow, 0.6-1 L/min argon aerosol flow, 1-1.8 mL/min sample pumping rate, 10 s measurement time per sample, 220 psi nebulizer pressure. Table 2 gives method detection limits (MDLs).

Table 2. Method Detection Limits for Metals Measured at Given Wavelengths

Analyte (Wavelength Measured, nm)	Method Detection Limit (mg/L)
Al (396.152)	0.02
As(188.980)	0.03
Cd (214.439)	0.0003
Cr (267.716)	0.04
Cu (327.395)	0.09
Fe (238.204)	0.2
Mg (280.270)	0.02
Mn (257.610)	0.01
Na (589.592)	0.05
Ni (231.604)	0.04
Pb (220.353)	0.03
Se (196.026)	0.02
Zn (202.548)	0.01

2.5.c. Statistics

IBM SPSS Statistical Software was used for statistical analysis of the data. Paired sample t-tests were used to determine if there were significant differences between analyte concentrations upstream and downstream of the coal refuse piles at each site. Results were considered significant if $p < 0.05$. SPSS was also used to create boxplots and graphs of the data.

3. Results

3.1. Quality Assurance

A more detailed discussion on quality assurance and Tables A1-A-12 can be found in the Appendix. Briefly, QA parameters (field duplicates, lab duplicates, LRBs, blank digests, LFBs and LFB digests) were generally within acceptance criteria given by the EPA. There were some exceptions, including chloride and sulfate contamination in field blanks and LRBs (Table A1), and Al and Na contamination in field blanks (Table A4). Metals contamination of blank digests were reduced by the use of the DigiPrep acid digestion system (Table A5). Field duplicate relative percent differences (RPDs) (Table A6) were above acceptance criteria for certain metals, particularly Al and Fe. RPDs in lab digest duplicates (Table A7) exceeded acceptance criteria on occasion, but higher field duplicate RPDs indicate that sample collection and storage was a greater source of variability. LFB digest percent recoveries (Table A8) were occasionally outside of acceptance criteria.

3.2. Comparison of Water Quality Above and Below Coal Refuse at BSC, CC, and SCT

3.2.a. Big Stony Creek

Table 3 shows measured chloride concentrations, site averages, and standard deviations. BSC 6.55 (upstream site) had an average chloride concentration of 0.73(±0.26) mg/L, and BSC 6.35 (downstream site) averaged 0.81(±0.32) mg/L. A paired samples t-test showed that the difference was not significant. As seen in Figure 7, BSC 6.55, had a greater range in chloride concentration than BSC 6.35, but an overall similar distribution. The chloride values were far below the EPA recommended CCC and CMC recommended levels.

Table 3. Chloride concentrations at each site with calculated average(±standard deviation)

Chloride Concentrations (mg/L)						
Collection Date	**BSC 6.35**	**BSC 6.55**	**CC 7.75**	**CC 8.03**	**SCT 0.56**	**SCT 0.94**
6/5/2013	0.45	0.51	0.4514	0.473		
6/18/2013	0.360	1.487	0.747	0.766		
7/25/2013	0.734	0.679	0.912	0.821		
8/30/2013	0.990	0.969	0.767	0.728		
11/7/2013	1.21	1.144	0.675	0.73		
11/26/2013	0.826	0.80	0.49	0.54		
2/5/2014	0.626	0.594	0.51	0.499		
3/19/2014	0.636	0.666	0.463	0.483		
4/10/2014			0.458	0.474	0.629	0.600
4/17/2014			0.65	0.68	0.78	0.84
4/25/2014			0.66	0.617	0.732	0.79
5/30/2014	0.98	1.01	0.594	0.596	0.722	0.742
6/17/2014	0.53	0.36	0.284	0.239	0.378	0.327
1/28/2015	0.644	0.651	0.54	0.518	0.588	0.599
Average (±STD)	0.73(±0.26)	0.81(±0.32)	0.59(±0.16)	0.58(±0.15)	0.64(±0.13)	0.65(±0.17)

Sulfate results are given in Table 4. Average sulfate concentrations at BSC 6.35 and BSC 6.55 were 4.5(±0.59) and 4.5(±0.54) mg/L respectively. The sulfate boxplots in Figure 8 show very similar results at BSC 6.35 and BSC 6.55. There was no statistical difference between sulfate concentrations above or below the coal refuse at BSC. Sulfate was low in comparison to concentrations typically found in AMD affected waters.

Table 4. Sulfate concentrations at each site with calculated average(±standard deviation)

Sulfate Concentrations (mg/L)						
Collection Date	**BSC 6.35**	**BSC 6.55**	**CC 7.75**	**CC 8.03**	**SCT 0.56**	**SCT 0.94**
6/5/2013	4.9	5.069	6.06	5.52		
6/18/2013	4.95	4.593	4.50	4.535		
7/25/2013	5.203	5.1	5.95	5.18		
8/30/2013	4.73	4.619	6.234	4.82		
11/7/2013	5.19	4.71	6.1	4.45		
11/26/2013	4.06	4.0	4.9	4.64		
2/5/2014	4.55	4.393	5.39	4.81		
3/19/2014	4.55	4.80	5.10	5.14		
4/10/2014			5.41	5.12	11.2	5.76
4/17/2014			5.77	5.1	7.36	6.94
4/21/2014			5.95	5.02	7.71	6.78
5/30/2014	3.25	3.29	5.04	4.05	6.56	5.67
6/17/2014	4.45	4.77	6.84	4.80	8.99	7.70
1/28/2015	3.96	3.98	5.05	4.58	5.95	5.72
Average (±STD)	4.5(±0.59)	4.5(±0.54)	5.6(±0.64)	4.8(±0.38)	7.96(±1.74)	6.43(±0.765)

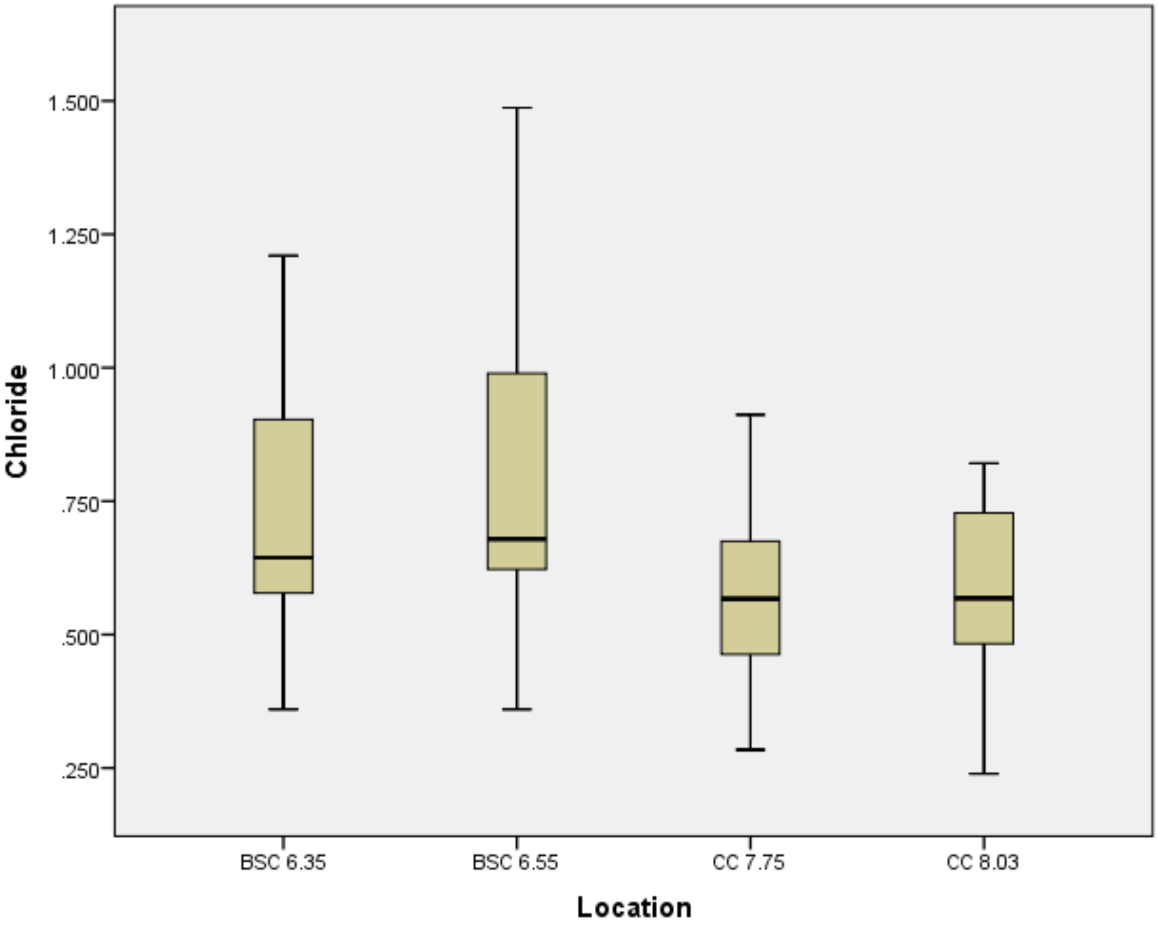

Figure 7. Boxplots showing descriptive statistics for chloride concentrations at BSC and CC.

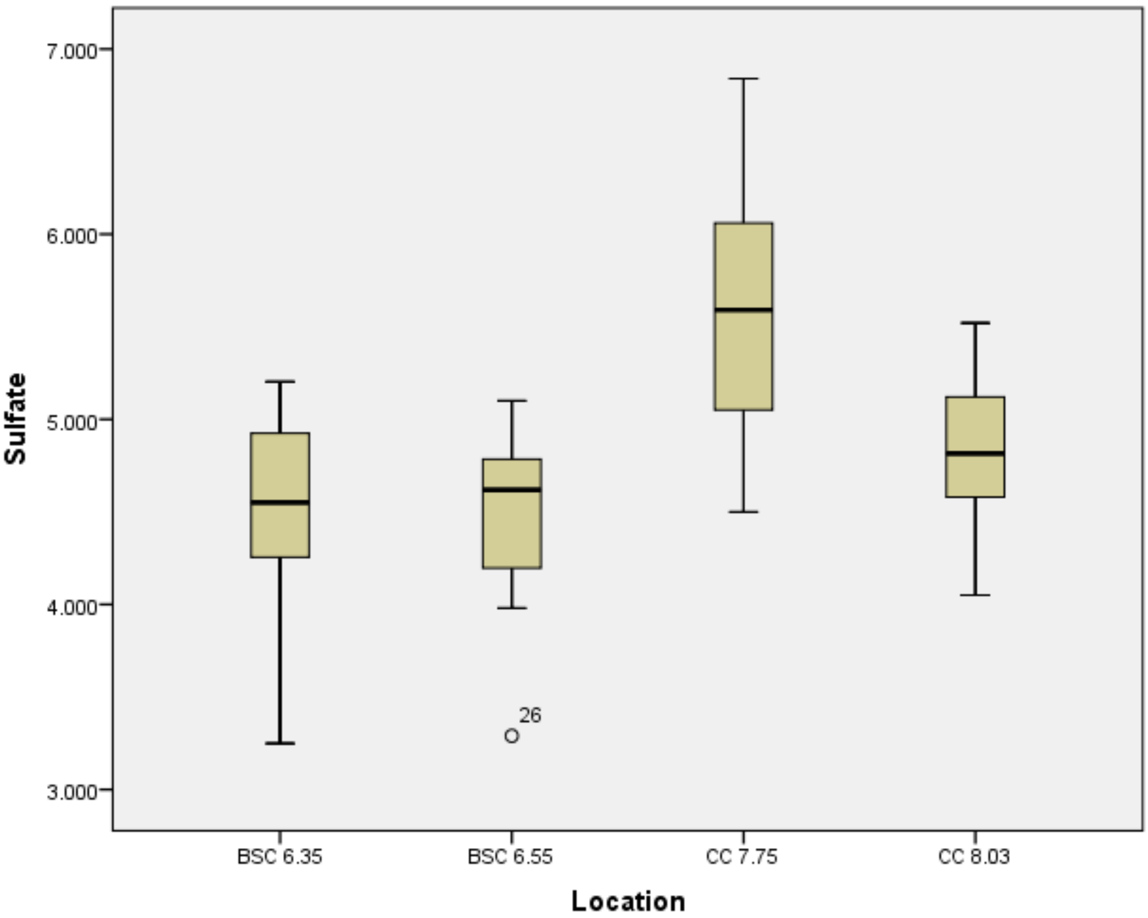

Figure 8. Boxplots showing descriptive statistics for sulfate concentrations at BSC and CC.

All BSC 6.35 and 6.55 metals are is given in ables A9 and A10 respectively. In general, concentrations of As, Cd, Cr, Cu, Ni, Pb, and Se, were near or below the method detection limit (MDL) and therefore will not be discussed. Manganese was detectable 35-65% of the time, and zinc was detectable 20-43% of the time. The other metals, Al, Fe, Mg, and Na, were present in detectable concentrations nearly 100% of the time.

There was a significant difference in iron concentrations between BSC 6.55 and BSC 6.35 (Figure 9): 0.34± 0.35 ppm to 0.27 ± 0.38 ppm, t(11)= -2.471, p=0.031 (Table A11). All other metals showed no significant difference between the upstream and downstream sites. As shown in Figure 9, average iron concentration was higher upstream of the refuse.

A graph of iron concentration vs. collection date (Figure 10) shows that it was generally in steady concentrations with occasional spikes during the periods sampled. The elevated concentrations at both sites on 5/15/14 were likely related to the recent rain event. Iron concentrations were relatively elevated during base flow on 6/18/13; however, they were still below the EPA's mining effluent limits.

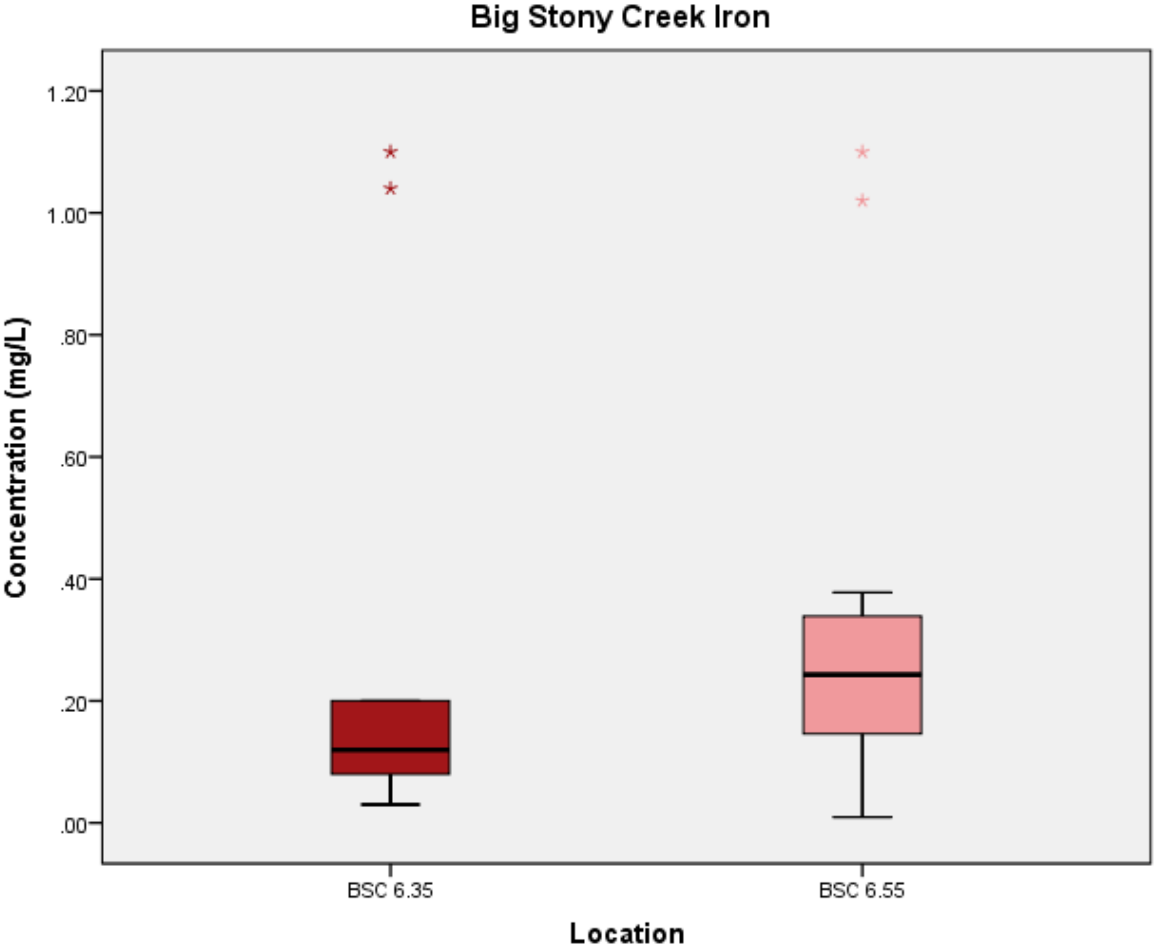

Figure 9. Iron concentrations at BSC 6.35 (downstream) and BSC 6.55 (upstream). Each site had two outliers from 5/15/2014 (storm event) and 6/18/2013. Average concentration was significantly higher upstream of the coal refuse.

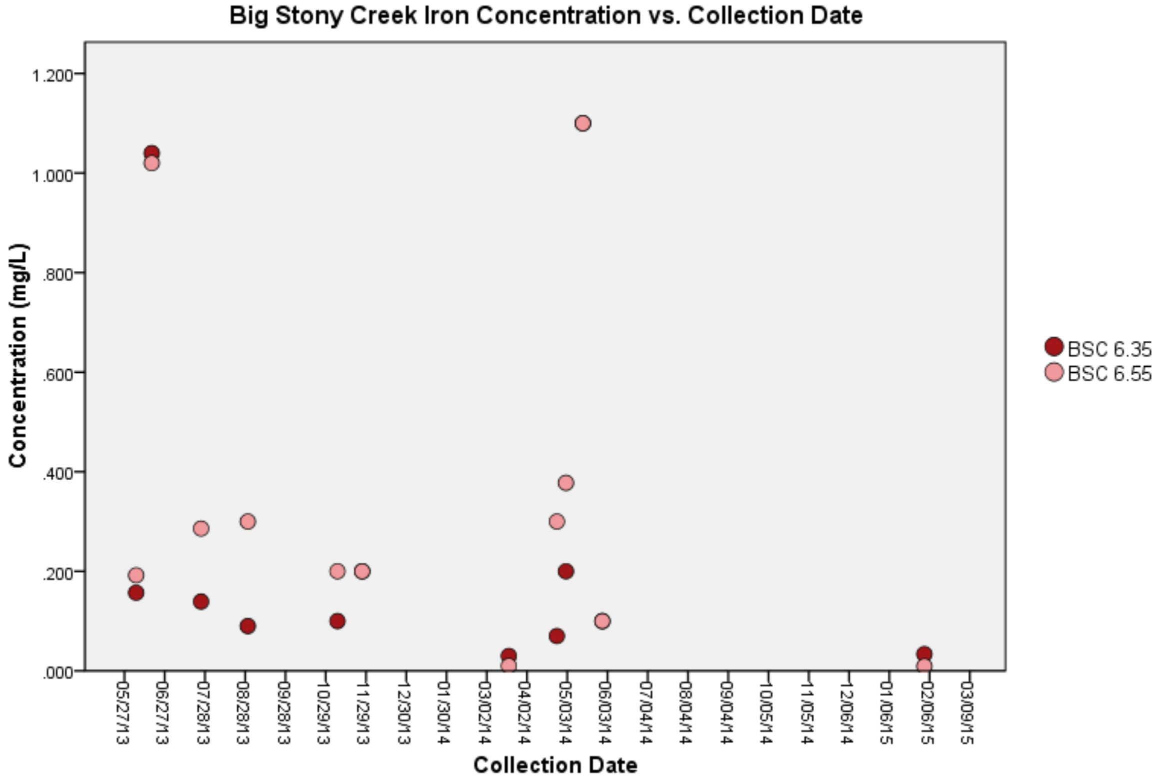

Figure 10. Iron concentration over time at BSC 6.35 and BSC 6.55.

3.2.b. Cove Creek

Average chloride concentrations at CC 7.75 (downstream) and CC 8.03 (upstream) were 0.59(±0.16) and 0.58(±0.15) mg/L, respectively (Table 3). It is evident from Figure 7 that chloride concentrations upstream and downstream sites were similar, and a t-test confirmed that there was not a statistical difference between them. The average sulfate concentrations at CC 7.75 and CC 8.03 were 5.6(±0.64) and 4.8(±0.38) mg/L respectively (Table 4). The sulfate boxplots for Cove Creek (Figure 8) visually represent the difference between the two sites; that difference was found to be significant t(13)=4.605, p<0.000.

Detectable metals from CC 7.75 and CC 8.03 were Al, Fe, Mg, Mn, and Na, shown in Tables A12 and A13. There was a significant difference between CC 8.03 and CC 7.75 concentrations of magnesium (Figure 11): 0.88 ± 0.20 ppm to 1.01 ± 0.26 ppm, $t(12)=4.936$, $p<0.001$ and sodium (Figure 12): 0.533 ± 0.208 ppm to 0.742 ± 0.302 ppm, $t(12)=7.432$, $p<0.000$ (Table A14). In both cases, concentrations downstream exceeded upstream. It is evident from Figure 13, which show plots of concentration vs. collection date, that magnesium and sodium levels were consistently higher downstream of the coal refuse.

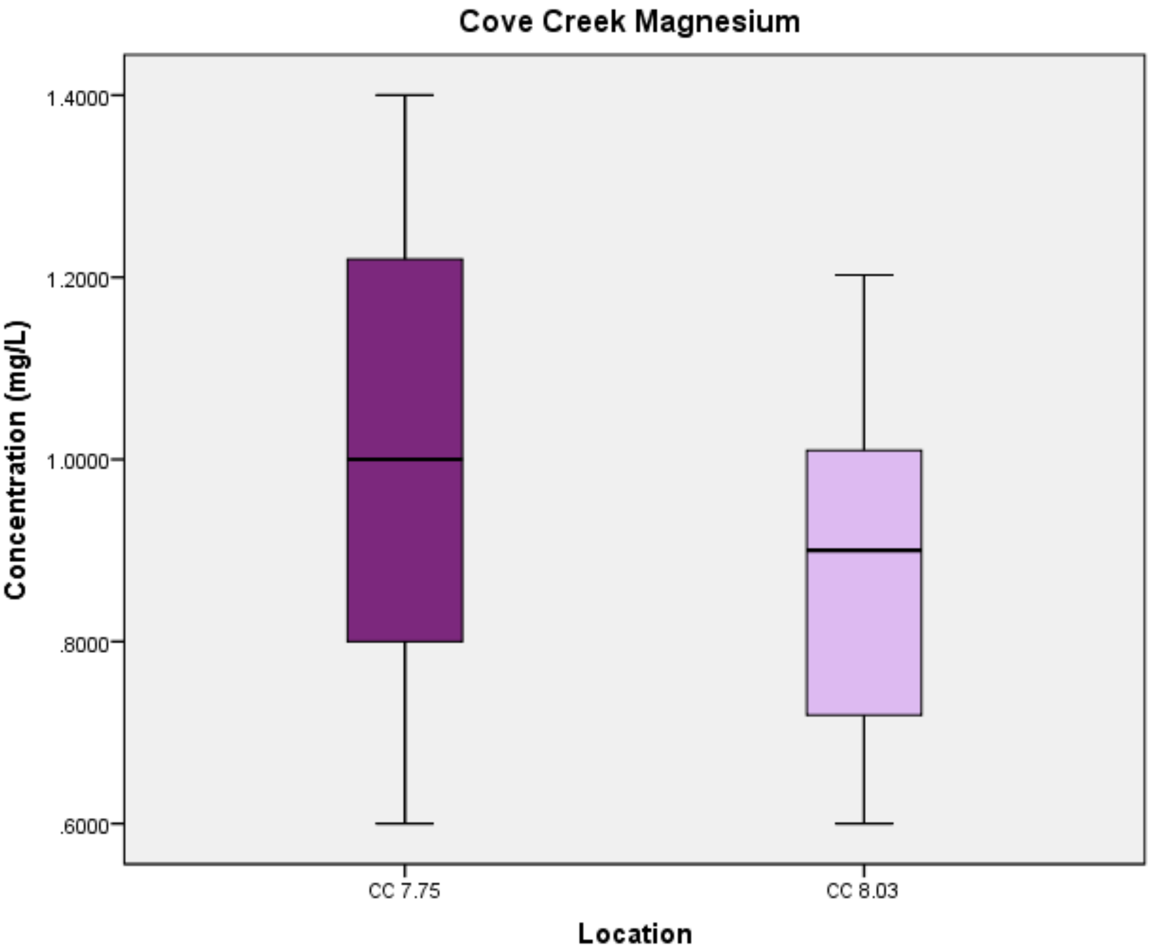

Figure 11. Magnesium concentrations at Cove Creek 7.75 (downstream) and 8.03 (upstream). The average concentration downstream of the coal refuse pile was significantly higher than upstream.

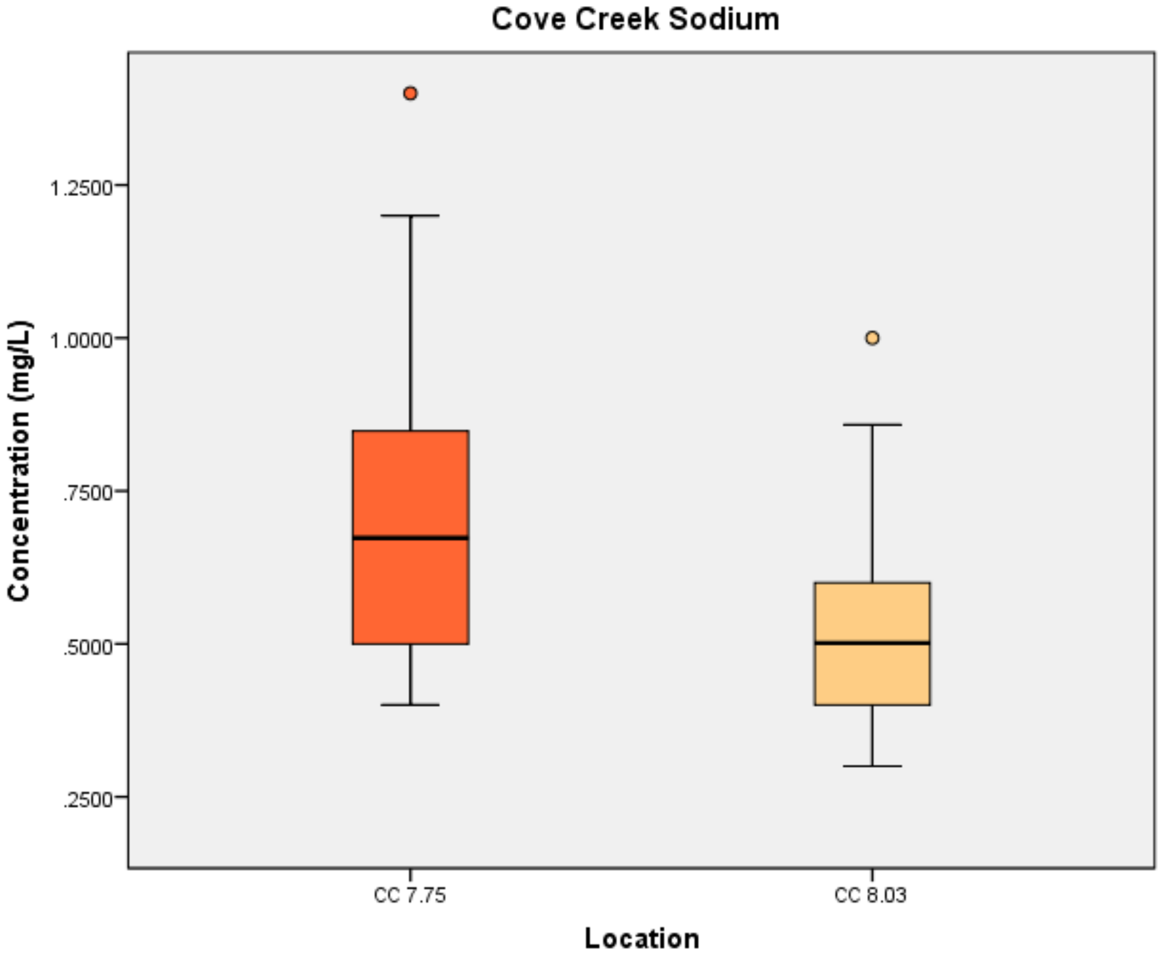

Figure 12. Sodium concentrations at CC 7.75 (downstream) and CC 8.03 (upstream). Outliers were from 8/30/13 for both sites. The average concentration downstream of the coal refuse pile was significantly higher than upstream.

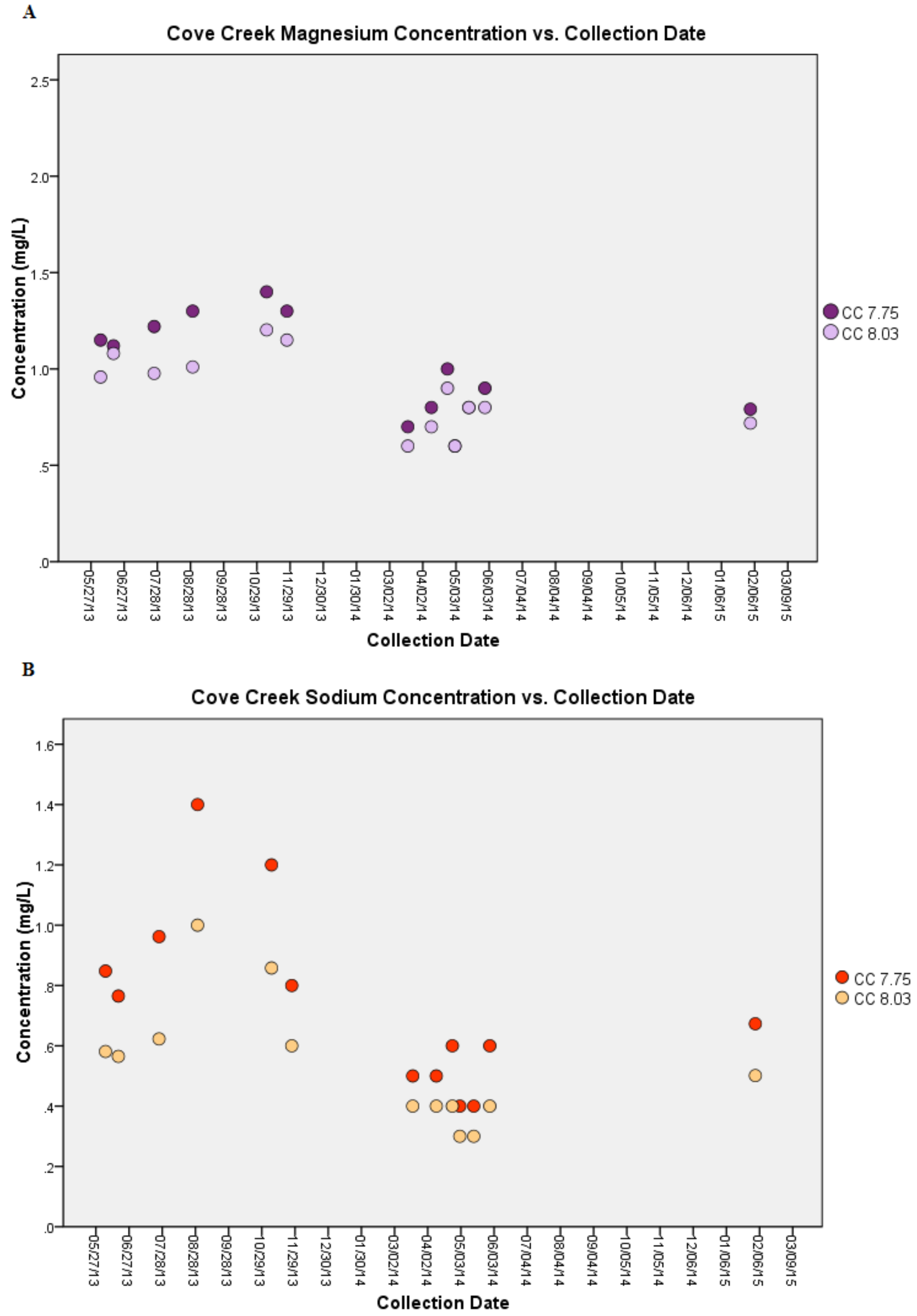

Figure 13 (A) Magnesium and (B) sodium concentrations over time at Cove Creek. Concentrations were higher for at CC 7.75 than CC 8.03 for most sampling events.

Shupe Creek Disposal Site

The disposal sites, SCT 0.56 (downstream) and SCT 0.94 (upstream) had average chloride concentrations of 0.64(±0.13) and 0.65(±0.17) mg/L, and sulfate concentrations of 7.96(±1.74), and 6.43(±0.765) mg/L respectively (Tables 3 and 4). Although the average sulfate concentration at SCT 0.56 was over 1.5 mg/L greater than at SCT 0.94, the difference was not significant, which indicates that the coal refuse material deposited there was not a source of sulfate and chloride.

Metals detected at SCT were Al, Fe, Mg, Mn, and Na (Tables A15 and A16). Magnesium appeared to have higher concentrations below the disposal area, as shown in Figure 14, but the t-test results given in Table A17 show that the difference was not significant.

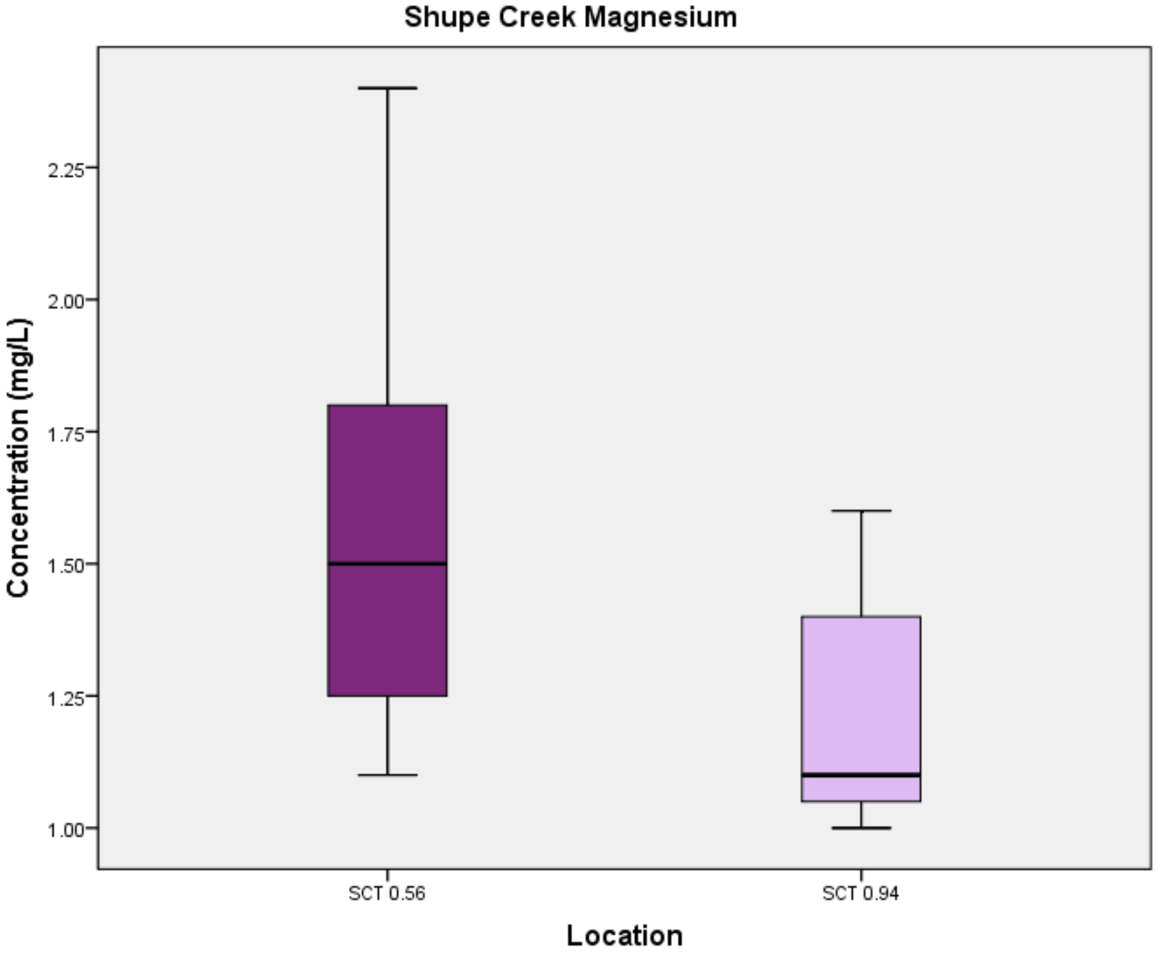

Figure 14 Boxplots of magnesium concentrations at Shupe Creek sites upstream and downstream of the coal refuse disposal area.

4. Discussion

4.1 The Potential Impact of AMD on the Sites

Big Stony Creek results suggest that chloride and sulfate were not leaching at appreciable levels from the coal refuse area. A potential explanation for the higher Fe concentrations above the BSC coal refuse is that weathering and vegetation have reduced the AMD potential of the pile so that it was not leaching metals into the stream. Instead, a natural source close to BSC 6.55 could have been contributing Fe. The results from the disposal site indicated that Shupe Creek was not impacted by AMD resulting from the arrival the coal waste, but future monitoring should be done in case AMD is generated in the future.

Cove Creek may have been impacted by AMD as indicated by elevated concentrations of SO_4^{2-} at the site downstream of the refuse area. Differences in coal refuse chemistry could explain why there were higher concentrations of Na, Mg, and SO_4^{2-} at the downstream CC site and not the downstream BSC site.[10] The sources of Na, Mg, and SO_4^{2-} could be soluble salts not present at BSC.[8] Other potential explanations are that the slope and/or vegetation of coal refuse were different between CC and BSC. Refuse piles with steeper slopes can erode more easily, exposing less-oxidized refuse and generating more AMD than those that lie flat or on more gentle slopes.[8] As discussed previously, vegetation also contributes to weathering and erosion prevention of coal refuse. CC appeared to have more steeply sloping banks than BSC, but differences in vegetation were not apparent.

4.2. Effect of Coal Refuse Removal

The purpose of this project was to monitor not only the effect of coal refuse on downstream sites vs. upstream sites, but to determine the effects of coal refuse removal authorized by Virginia’s DMME. Results so far have established a water quality record prior to refuse extraction, but there is insufficient data (one sample collection) after remediation to make an accurate comparison. Future samples hopefully will allow for a complete water quality analysis post-remediation.

5. Conclusions

Coal refuse piles did not seem to impact water quality in Cove Creek and Big Stony Creek based on analysis of chloride, sulfate, Al, As, Cd, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, Se, and Zn. There was a significantly higher Fe concentration upstream in the BSC GOB, and significantly higher Mg, Na, and SO_4^{2-} concentrations downstream of the CC GOB. Differences in coal refuse chemistry, weathering, slope, or vegetation could explain why the BSC and CC results were different. Although the CC results suggest that there was a source of Mg, Na, and SO_4^{2-} between the upstream and downstream sites, the concentrations were still generally below EPA’s water quality criteria maxima, and AMD did not seem to have a concerning affect on these streams. Any AMD that might have occurred at these sites may have been limited by neutralization due to carbonate material in the surrounding soil, low sulfur content in the coal refuse, weathering, or vegetation of the piles.

6. Future Work

There will be three more sample collections before the conclusion of this research project, which will bring the post-remediation water quality sample size to four. With all of the data, a comparison of water quality before and after remediation should be conducted to determine if reclamation had positive, neutral, or negative effects on these streams.

7. Appendix

7.1. Quality Assurance

7.1.a. Chloride and Sulfate

LRBs and field blanks contained varying concentrations of chloride and sulfate that were generally 0.2-0.4 mg/L and 0.2-0.3 mg/L respectively (Table A1). Chloride LFB percent recoveries ranged from 87.3-103% and sulfate recoveries ranged from 84.3-110% (Table A1). Sulfate recovery was only 70.1% for samples collected 4/17/14 and 4/25/1; however, the overall record for percent recoveries indicates that the method was accurate for detecting both analytes.

Table A1. Quality assurance data for chloride and sulfate LFB recovery, field blank and lab blank concentrations.

	Chloride	Sulfate	Chloride	Sulfate	Chloride	Sulfate
Batch	**LFB Percent Recovery**		**Field Blank Conc. (mg/L)**		**Lab Blank Conc. (mg/L)**	
6/5/13	99.1	98.9	0.028	0.997		
6/18/13	97.1	97.5	0.309	1.002		
7/25/13	97.7	97.1	0.322	1.023		
8/30/13	95.9	95.6	0.50	1.271		
11/7/13	87.3	84.3	0.190	0.89	0.16	0.790
11/26/13	87.3	84.3	0.21	1.1	0.16	0.790
2/5/14	94.8	110	0.220	0.72	0.3	0.86
2/11/14	94.8	110			0.3	0.86
3/19/14	94.8	110	0.226	0.75	0.3	0.86
4/10/14	95.6	110	0.256	0.88	0.27	0.85
4/17/14	97.6	70.3	0.35	0.828	0.4	0.56
4/25/14	97.6	70.3			0.4	0.85
5/30/14	102	97.8	0.218	<DL	0.3	0.03
6/17/14	103	105	<DL	0.59	<DL	<DL
1/28/14	94.9	94.6	0.27	0.23	1.9	0.11

Table A2 gives the chloride and sulfate field duplicate relative percent differences (RPD) for each collection date. Most chloride RPDs were < 20% for samples with concentrations between the minimum reporting level (MRL) and 10xMRL, and < 10% for concentrations above 10xMRL. One exception was the duplicate for BSC 6.35 collected on 6/17/2014 (RPD=40.9%). Sulfate RPDs were < 10% for all concentration ranges with exception of the 4/25/14 CC 7.75 duplicate. Since nearly all of the field duplicate RPDs fell within acceptance criteria given by the EPA, it can be stated that there was precision with sample collection, preservation, storage, and analytical procedures. [25]

Table A2. Chloride and sulfate field duplicate relative percent differences (RPD)

Collection Date	**Chloride RPD**	**Sulfate RPD**
6/5/2013	0.1	2.4
6/18/2013	0.8	0.7
7/25/2013	3.9	6.9
8/30/2013	5.9	6.2
11/7/2013	13.8	2.8
11/26/2013	8.3	1.3
2/5/2014	0.2	2.9
2/11/2014		
3/19/2014	11.4	9.7
4/10/2014	8.4	1.2
4/17/2014	2.5	0.3
4/25/2014	7.6	22.9
5/30/2014	3.4	2.0
6/17/2014	40.9	4.2
1/28/2014	7.5	3.7

7.1.b. Metals

Table A3 shows the concentrations of each metal in the LRBs, which consisted of dilute HNO_3 (1-2%) in DI water. All metals were generally present in concentrations less than the MDL. Al, Cd, and Mn were detected above their MDLs on only one analysis batch and Se was detected at or above the MDL on three batches. While Al, Cd, Mn, and Se occasionally had concentrations above their respective MDLs, they were very near the detection limit and do not suggest a contamination problem with the reagents used.

Table A3. LRB concentrations per batch

Batch	**Al**	**As**	**Cd**	**Cr**	**Cu**	**Fe**	**Mg**	**Mn**	**Na**	**Ni**	**Pb**	**Se**	**Zn**
6/5/2013	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.02	<MDL
6/17/2013		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.02	<MDL
7/25/2013													
8/30/2013	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/7/2013	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
11/26/2013	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
2/5/14, 6/17/14	<MDL	<MDL	0.0008	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
3/19/14, 4/10/14	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
4/25/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	
5/2/14, 5/15/14	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
5/30/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
5/30/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
1/28/2014	0.05	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.02	<MDL	<MDL	<MDL	0.03	<MDL

As shown in Table A4, field blank concentrations per collection day were less than the MDL for As, Cr, Cu, Fe, Ni, and Pb. Other metal concentrations were also less than the MDL, with the exception of Al and Na, which ranged 0.02-0.1 mg/L and 0.05-0.3 mg/L on a number of collection dates. Cd, Mg, Mn, Se, and Zn were occasionally detected above the MDL. The repeated presence of aluminum and sodium in fairly high concentrations indicates that there was contamination introduced in sample collection, storage, or laboratory analysis.

Table A4. Field blank concentrations per sample collection date

Batch	Al	As	Cd	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Se	Zn
6/5/2013	0.1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.2	<MDL	<MDL	<MDL	
6/17/2013	0.1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.1	<MDL	<MDL	<MDL	
7/25/2013	0.1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.1063	
8/30/2013	0.05	<MDL	<MDL	<MDL	<MDL	<MDL	0.0268	<MDL	0.2	<MDL	<MDL	<MDL	0.02
11/7/2013	0.04	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.01	0.3	<MDL	<MDL	<MDL	<MDL
11/26/2013	0.04	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.3	<MDL	<MDL	<MDL	<MDL
2/5/2014	<MDL	<MDL	0.0007	<MDL	<MDL	<MDL	0.03	<MDL	0.3	<MDL	<MDL	<MDL	0.02
3/19/2014	0.02	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.08	<MDL	<MDL	<MDL	<MDL
4/10/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.08	<MDL	<MDL	<MDL	<MDL
4/25/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.08	<MDL	<MDL	<MDL	
5/2/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.05	<MDL	<MDL	<MDL	<MDL
5/15/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
5/30/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
6/17/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
1/28/2014	0.05	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.01	<MDL	<MDL	<MDL	0.02	0.03

Metals concentrations in the blank digest samples were generally ess than the MDL. As seen in Table A5, Al, As, Fe, Na, and Zn exceeded their MDLs frequently in the blank digests, while Cr, Mg, Mn, and Se only exceeded the MDL once. The blank digests contained the same reagents as the lab blanks discussed earlier (1-2% HNO_3), except having gone through acid digestion and storage; therefore, greater concentrations of metals in the blank digest means they were introduced during those stages. Detectable Al, As, Fe, Na, and Zn were more common in the blank digests analyzed 6/5/13-11/26/13 than in 2/5/14-1/28/15, which was when the acid digestion method changed to the DigiPrep technique. Prior to switching to the DigiPrep acid digestion, the samples came in contact with more equipment, graduated cylinder, glass beakers, filter paper, and volumetric flasks before being stored in plastic bottles. The DigiPrep digestion materials, were certified to be ultra low in leachable metals, which likely reduced the amount of contamination introduced during acid digestion and storage. Blank digests prepared with the DigiPrep still had occasional concentrations of Al, Cr, Fe, Mn, and Zn, but the technique clearly allowed for a cleaner acid digestion.

Table A5. Blank digest concentrations per sample collection date

Batch	Al	As	Cd	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Se	Zn
6/5/2013	0.5	0.03	<MDL	<MDL	<MDL	0.2	0.02	<MDL	0.2	<MDL	<MDL	<MDL	<MDL
6/17/2013	0.03	0.03	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.05	<MDL	<MDL	<MDL	0.02
7/25/2013	<MDL	0.02	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.04	0.7
8/30/2013	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.2	<MDL	<MDL	<MDL	0.06
11/7/2013	<MDL	<MDL	<MDL	<MDL	<MDL	0.2	<MDL	<MDL	0.2	<MDL	<MDL	<MDL	0.01
11/26/2013	0.04	<MDL	<MDL	<MDL	<MDL	0.04	<MDL	<MDL	0.3	<MDL	<MDL	<MDL	0.02
2/5/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
3/19/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
4/10/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
4/25/2014	<MDL	<MDL	<MDL	0.05	<MDL	0.2	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	
5/2/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
5/15/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
5/30/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.01
6/17/2014	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
1/28/2014	0.05	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.01	<MDL	<MDL	<MDL	<MDL	0.02

The relative percent differences for the field duplicates taken on each collection day are given in Table A6. The cells labeled "n.a" did not contain analytes in detectable concentrations or concentrations greater than the MDL, and therefore a RPD calculation was not performed. For metals that were present above their reporting levels RPDs were < 10% for Mg, and < 20% For Na and Se, with only one sample > 10% for each. Field duplicate Al RPDs were an average of 20%, ranging 2.2-59%. Arsenic had one instance of a measurable RPD (79%), Fe RPDs averaged 25% and ranged from 4.3-117%, Mn RPDs ranged 0.5-54% with a 14% average, and Zn had RPDs of 53 and 95%. Any RPDs above 10% for concentrations 10x-MRL to the highest calibration standard are considered unacceptable, which was the case for many field duplicates.

Table A6. Field duplicate RPDs per sample collection date

Batch	Al	As	Cd	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Se	Zn
6/5/2013	**41**	n.a	n.a.	n.a	n.a	4.3	2.9	n.a	9.2	n.a	n.a	n.a	n.a
6/17/2013	**37**	n.a	n.a	n.a	n.a	8.4	n.a	4.6	1.3	n.a	n.a	1.3	n.a
7/25/2013	**21**	**79**	n.a	n.a	n.a	n.a	2.2	n.a	0.07	n.a	n.a	n.a	n.a
8/30/2013	19	n.a	n.a	n.a	n.a	17	0.48	28	3.8	n.a	n.a	n.a	**53**
11/7/2013	3.4	n.a	n.a	n.a	n.a	**117**	n.a	0.5	14	n.a	n.a	3.7	n.a
11/26/2013	4.7	n.a	n.a	n.a	n.a	7.1	0.69	12	1.7	n.a	n.a	n.a	n.a
2/5/2014	7.9	n.a	n.a	n.a	n.a	n.a	2.0	n.a	0.96	n.a	n.a	n.a	n.a
3/19/2014	**22**	n.a	n.a	n.a	n.a	n.a	0.1	n.a	0.1	n.a	n.a	n.a	n.a
4/10/2014	4.5	n.a	n.a	n.a	n.a	7.8	0.6	7.9	3.4	n.a	n.a	n.a	n.a
4/25/2014	16	n.a	n.a	n.a	n.a	**33**	1.7	5.3	1.7	n.a	n.a	n.a	n.a
5/2/2014	**59**	n.a	n.a	n.a	n.a	n.a	1.3	n.a	0.15	n.a	n.a	n.a	n.a
5/15/2014	2.2	n.a	n.a	n.a	n.a	24	6.1	12	0.4	n.a	n.a	n.a	n.a
5/30/2014	**24**	n.a	n.a	n.a	n.a	6.7	0.1	54	2.7	n.a	n.a	n.a	n.a
6/17/2014	**30**	n.a	n.a	n.a	n.a	n.a	0.21	n.a	2.4	n.a	n.a	n.a	n.a
1/28/2014	11	n.a	n.a	n.a	n.a	n.a	1.3	3.4	0.76	n.a	n.a	19	**95**

According to EPA Method 300.0, the analysis must be redone when RPDs do not meet acceptance criteria.[25] Since reanalysis was not performed, the conclusion drawn from these data is that there was much variation in Al and Fe between samples and their field duplicates, and some, but not a concerning or consistent level of variation in As, Mn, Na, and Se.

The laboratory digest duplicate RPDs are given in Table A7. Only Al, Fe, Mg, Na, and Zn had measurable RPDs. The digest duplicate results were similar to those of the field duplicate, with Al RPDs ranging 0.4-26% with 11% average, Fe ranging 0.5-11% with 6% average, Mn ranging 0.7-12% with 4% average, and Zn with two RPDs of 14 and 2.7%. Magnesium RPDs were < 10%, falling within the EPA's acceptance criteria. These RPDs are lower than those of the field duplicate, indicating that there was a greater loss of precision in sample collection and storage than in laboratory analysis.

Table A7. Digest duplicate relative percent recoveries per sample collection date

Batch	**Al**	**As**	**Cd**	**Cr**	**Cu**	**Fe**	**Mg**	**Mn**	**Na**	**Ni**	**Pb**	**Se**	**Zn**
6/5/2013													
6/17/2013													
7/25/2013													
8/30/2013													
11/7/2013													
11/26/2013													
2/5/2014	5.5	n.a	n.a	n.a	n.a	4.7	1.6	n.a	1.2	n.a	n.a	n.a	**14**
3/19/2014	**26**	n.a	n.a	n.a	n.a	**11**	2.8	n.a	3.0	n.a	n.a	n.a	n.a
4/10/2014	3.9	n.a	n.a	n.a	n.a	n.a	1.1	n.a	1.0	n.a	n.a	n.a	n.a
4/25/2014													
5/2/2014	**11**	n.a	n.a	n.a	n.a	n.a	1.6	n.a	2.6	n.a	n.a	n.a	n.a
5/15/2014	**12**	n.a	n.a	n.a	n.a	6.0	5.8	**12**	**17**	n.a	n.a	n.a	n.a
5/30/2014	**24**	n.a	n.a	n.a	n.a	n.a	3.2	n.a	0.56	n.a	n.a	n.a	n.a
6/17/2014	0.4	n.a	n.a	n.a	n.a	0.5	2.0	0.7	0.9	n.a	n.a	n.a	2.7
1/28/2014	0.88	n.a	n.a	n.a	n.a	n.a	0.46	0.17	3.4	n.a	n.a	n.a	n.a

Control limits for LFB percent recoveries given in EPA Method 300.0 are 75-125% for concentrations in between the MRL and 10xMRL and 85-115% for concentrations between 10xMRL and the highest calibration level.[25] Most LFB digests were 10xMRL-highest calibration level. Percent recoveries that did not fall within acceptance criteria are bolded in Table A8, where it can be seen that percent recoveries were generally 85-115% for each metal, indicating good accuracy in the method. Percent recoveries were outside of the control limits once for Al, As, Fe, and Mn, twice for Mg, and four times for Na.

Table A8. LFB digest percent recoveries for each batch

Batch	Al	As	Cd	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Se	Zn
6/5/13	110	**84.1**	86.4	88.2	92.1	91.2	94.6	92.6	87.7	91.3	91.6	85.8	**84.2**
6/17/13	**137**	94.5	96.1	97.9	98.1	99.8	107	98.9	101	97.7	97.8	89.6	109
7/25/13	94.1					92.3	97.9	99.4	103				
8/30/13	107	102	100	106	105	111	106	103	114	101	101	101	100
11/7/13	100.9	99.9	99.3	105.0	102.9	**115.5**	100.8	100.2	108.4	100.6	101.3	98.8	98.0
11/26/13	103	98	99	101	102	103	101	101	118	100	99.6	96	99
2/4/14, 6/17/14	93.5	106.8	109.4	97.4	108.6	99.0	84.6	95.6	**67.6**	102.8	107.0	105.9	109.5
3/19/14, 4/10/14	102					96		95					
4/25/14	109.7	98.0	99.7	101.9	104.4	101.5	115.3	104.2	92.6	102.2	102.7	98.8	
5/2/14, 5/15/14	**80.4**	108.3	105.0	97.6	107.0	99.2	**78.4**	83.9	**63.7**	100.8	101.4	108.6	105.8
5/30/14	100.9	93.7	88.1	86.8	90.0	92.5	89.7	97.6	**78.3**	87.5	88.3	91.8	89.5
1/28/15	**120.8**	102.8	105.9	106.3	108.7	100.9	102.1	105.8	108.2	104.3	104.8	101.7	104.9

7.2. Metals Results and Statistical Analysis

Table A9. BSC 6.35 metals concentrations per collection date

Coll. Date	Al	As	Cd	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Se	Zn
6/5/2013	0.511	<MDL	<MDL	<MDL	<MDL	0.157	0.765	<MDL	0.593	<MDL	<MDL	<MDL	<MDL
6/17/2013	4.75	<MDL	<MDL	<MDL	<MDL	1.04	0.809	0.048	0.539	<MDL	<MDL	<MDL	<MDL
7/25/2013	<MDL	0.05	<MDL	0.1	<MDL	0.1	0.7	<MDL	0.6	0.06	<MDL	<MDL	0.03
8/30/2013	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.8	<MDL	1.1	<MDL	<MDL	<MDL	0.02
11/7/2013	0.09	<MDL	<MDL	<MDL	<MDL	<MDL	0.8	0.02	1.7	<MDL	<MDL	<MDL	0.01
11/26/2013	0.1	<MDL	<MDL	<MDL	<MDL	0.2	0.6	0.01	0.97	<MDL	<MDL	<MDL	<MDL
2/5/2014	0.2	<MDL	<MDL	<MDL	<MDL	<MDL	0.5	<MDL	0.4	<MDL	<MDL	<MDL	0.02
3/19/2014	0.05	<MDL	<MDL	<MDL	<MDL	<MDL	0.6	<MDL	0.4	<MDL	<MDL	<MDL	<MDL
4/25/2014	0.05	<MDL	<MDL	<MDL	<MDL	<MDL	0.8	<MDL	0.5	<MDL	<MDL	<MDL	
5/2/2014	0.07	<MDL	<MDL	<MDL	<MDL	0.2	0.5	<MDL	0.4	<MDL	<MDL	<MDL	<MDL
5/15/2014	1.0	<MDL	<MDL	<MDL	<MDL	1.1	0.5	0.03	0.3	<MDL	<MDL	<MDL	<MDL
5/30/2014	0.10	<MDL	<MDL	<MDL	<MDL	0.1	0.5	<MDL	0.4	<MDL	<MDL	<MDL	<MDL
6/17/2014	0.05	<DL	<MDL	<MDL	<MDL	<MDL	0.5	<MDL	0.4	<MDL	<MDL	<MDL	<MDL
1/28/2015	0.07	<MDL	<MDL	<MDL	<MDL	<MDL	0.6	0.01	0.6	<MDL	<MDL	0.03	0.03

Table A10. BSC 6.55 metals concentrations per collection date

Coll. Date	Al	As	Cd	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Se	Zn
6/5/2013	0.415	<MDL	<MDL	<MDL	<MDL	0.192	0.723	<MDL	0.826	<MDL	<MDL	<MDL	<MDL
6/17/2013	4.58	<MDL	<MDL	<MDL	<MDL	1.02	0.801	0.051	0.568	<MDL	<MDL	<MDL	<MDL
7/25/2013	<MDL	<MDL	<MDL	0.498	<MDL	0.286	0.740	0.013	0.592	0.343	<MDL	0.062	0.045
8/30/2013	0.2	<MDL	<MDL	<MDL	<MDL	0.3	0.80	0.02	1.0	<MDL	<MDL	<MDL	0.02
11/7/2013	0.03	<MDL	<MDL	0.04	<MDL	0.2	0.8	0.01	1.4		<MDL	<MDL	<MDL
11/26/2013	0.1	<MDL	<MDL	<MDL	<MDL	0.2	0.7	0.02	1.0	<MDL	<MDL	<MDL	<MDL
2/5/2014	0.2	<MDL	<MDL	<MDL	<MDL	0.2	0.5	<MDL	0.4	<MDL	<MDL	<MDL	<MDL
3/19/2014	0.03	<MDL	<MDL	<MDL	<MDL	<MDL	0.5	<MDL	0.4	<MDL	<MDL	<MDL	<MDL
4/25/2014	0.06	<MDL	<MDL	0.05	<MDL	0.3	0.7	0.01	0.5	<MDL	<MDL	<MDL	
5/2/2014	0.2	0.03	<MDL	<MDL	<MDL	0.4	2.0	0.01	1.4	<MDL	<MDL	<MDL	0.02
5/15/2014	0.8	<MDL	<MDL	<MDL	<MDL	1.1	0.6	0.03	0.3	<MDL	<MDL	<MDL	<MDL
5/30/2014	0.08	<MDL	<MDL	<MDL	<MDL	0.1	0.5	<MDL	0.4	<MDL	<MDL	<MDL	<MDL
6/17/2014	0.05	<MDL	<MDL	<MDL	<MDL	0.15	0.6	<MDL	0.4	<MDL	<MDL	<MDL	0.01
1/28/2015	0.08	0.02	0.0003	<MDL	<MDL	<MDL	0.6	0.01	0.5	<MDL	<MDL	0.03	0.01

Table A11 Paired samples T-tests for metals upstream and downstream of Big Stony Creek refuse.

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Al6.35 - Al6.55	0.036	0.0953	0.030	-0.031	0.1049	1.217	9	0.254
Pair 2	As6.35 - As6.55	-0.00803	0.0130	0.0075	-0.0404	0.02435	-1.068	2	0.397
Pair 4	Cr6.35 - Cr6.55	-0.04525	0.1196	0.0366	-0.1256	0.03510	-1.255	10	0.238
Pair 5	Cu6.35 - Cu6.55	-0.0013	0.00115	0.00066	-0.0042	0.0015	-2.000	2	0184
Pair 6	Fe6.35 - Fe6.55	-0.0695	0.0975	0.0281	-0.1315	-0.0076	-2.471	11	0.031
Pair 7	Mg6.35 - Mg6.55	-0.1250	0.4493	0.129	-0.4105	0.1604	-0.964	11	0.356
Pair 8	Mn6.35 - Mn6.55	-0.0008	0.0053	0.0017	-0.0049	0.0032	-0.470	8	0.651
Pair 9	Na6.35 - Na6.55	-0.0702	0.3050	0.0880	-0.2641	0.1235	-0.798	11	0.442
Pair 10	Ni6.35 - Ni6.55	-0.0415	0.1050	0.0397	-0.1388	0.0557	-1.045	6	0.336
Pair 11	Pb6.35 - Pb6.55	-0.0027	0.0040	0.0020	-0.0090	0.0036	-1.361	3	0.267
Pair 13	Zn6.35 - Zn6.55	-0.0026	0.0130	0.0053	-0.0163	0.0110	-0.505	5	0.635

Table A12. CC 7.75 metals concentrations per collection date

Coll. Date	Al	As	Cd	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Se	Zn
6/5/2013	0.9	<MDL	<MDL	<MDL	<MDL	0.2	1.1	<MDL	0.8	<MDL	<MDL	<MDL	<MDL
6/17/2013	5.1	<MDL	<MDL	<MDL	<MDL	1.2	1.1	0.05	0.8	<MDL	<MDL	<MDL	<MDL
7/25/2013	<MDL	<MDL	<MDL	0.1	<MDL	<MDL	1.2	<MDL	0.96	0.08	<MDL	<MDL	0.02
8/30/2013	0.3	<MDL	<MDL	<MDL	<MDL	0.3	1.3	0.015	1.4	<MDL	<MDL	<MDL	0.02
11/7/2013	0.03	<MDL	<MDL	<MDL	<MDL	<MDL	1.4	0.01	1.2	<MDL	<MDL	<MDL	0.01
11/26/2013	2.3	<MDL	<MDL	<MDL	<MDL	2.6	1.3	0.17	0.8	<MDL	<MDL	<MDL	<MDL
2/5/2014	0.2	<MDL	<MDL	<MDL	<MDL	0.2	0.7	<MDL	0.4	<MDL	<MDL	<MDL	0.03
3/19/2014	0.05	<MDL	<MDL	<MDL	<MDL	<MDL	0.7	<MDL	0.5	<MDL	<MDL	<MDL	<MDL
4/10/2014	0.05	<MDL	<MDL	<MDL	<MDL	<MDL	0.8	<MDL	0.5	<MDL	<MDL	<MDL	<MDL
4/25/2014	0.06	<MDL	<MDL	<MDL	<MDL	<MDL	1.0	<MDL	0.6	<MDL	<MDL	<MDL	
5/2/2014	0.08	<MDL	<MDL	<MDL	<MDL	<MDL	0.6	<MDL	0.4	<MDL	<MDL	<MDL	<MDL
5/15/2014	0.3	<MDL	<MDL	<MDL	<DL	0.4	0.8	0.02	0.4	<MDL	<MDL	<MDL	0.03
5/30/2014	0.04	<MDL	<MDL	<MDL	<MDL	<MDL	0.9	<MDL	0.6	<MDL	<MDL	<MDL	<MDL
6/17/2014	0.08	<MDL	<MDL	<MDL	<MDL	<MDL	1.2	<MDL	0.9	<MDL	<MDL	<MDL	0.01
1/28/2015	0.08	0.02	0.0003	0.02	<MDL	<MDL	0.8	0.01	0.7	<MDL	<MDL	0.03	0.03

Table A13. CC 8.03 metals concentrations per collection date

Coll. Date	Al	As	Cd	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Se	Zn
6/5/2013	0.9	<MDL	<MDL	<MDL	<MDL	0.3	1.0	0.01	0.6	<MDL	<MDL	<MDL	<MDL
6/17/2013	5.3	<MDL	<MDL	<MDL	<DL	1.2	1.1	0.05	0.6	<MDL	<MDL	<MDL	<MDL
7/25/2013	0.06	0.06	<MDL	<MDL	<MDL	<MDL	1.0	<MDL	0.6	<MDL	<MDL	<MDL	
8/30/2013	0.2	<MDL	<MDL	0.06	<MDL	0.4	1.01	0.02	1.0	<MDL	<MDL	<MDL	0.06
11/7/2013	0.02	<MDL	<MDL	<MDL	<MDL	<MDL	1.2	0.01	0.9	<MDL	<MDL	<MDL	<MDL
11/26/2013	2.1	<MDL	<MDL	<MDL	<MDL	2.3	1.15	0.15	0.6	<MDL	<MDL	<MDL	<MDL
2/5/2014	0.3	<MDL	<MDL	<MDL	<MDL	0.3	0.6	<MDL	0.3	<MDL	<MDL	<MDL	<MDL
3/19/2014	0.05	<MDL	<MDL	<MDL	<MDL	<MDL	0.6	<MDL	0.4	<MDL	<MDL	<MDL	<MDL
4/10/2014	0.1	<MDL	<MDL	<MDL	<MDL	<MDL	0.7	<MDL	0.4	<MDL	<MDL	<MDL	<MDL
4/25/2014	0.05	<MDL	<MDL	<MDL	<MDL	<MDL	0.9	<MDL	0.4	<MDL	<MDL	<MDL	
5/2/2014	0.1	<MDL	<MDL	<MDL	<MDL	<MDL	0.6	<MDL	0.3	<MDL	<MDL	<MDL	<MDL
5/15/2014	0.5	<MDL	<MDL	<MDL	<MDL	0.7	0.8	0.03	0.3	<MDL	<MDL	<MDL	<MDL
5/30/2014	0.2	<MDL	<MDL	<MDL	<MDL	0.3	0.8	0.02	0.4	<MDL	<MDL	<MDL	<MDL
6/17/2014	0.07	<MDL	<MDL	<MDL	<DL	<MDL	1.0	<MDL	0.6	<MDL	<MDL	<MDL	<MDL
1/28/2015	0.09	<MDL	<MDL	<MDL	<MDL	<MDL	0.7	0.01	0.5	<MDL	<MDL	<MDL	0.01

Table A14. Paired Samples T-Test for metals upstream and downstream of Cove Creek refuse

Paired Samples Test

		Paired Differences							
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference		t	df	Sig. (2-tailed)
					Lower	Upper			
Pair 1	Al7.75 - Al8.03	-0.0146	0.1112	0.0321	-0.0853	0.0560	-0.456	11	0.657
Pair 2	As7.75 - As8.03	0.00103	0.00171	0.00098	-0.00321	0.00529	1.048	2	0.405
Pair 3	Cd7.75 - Cd8.03	0.00011	0.00006	0.00004	-0.00041	0.00063	2.702	1	0.226
Pair 4	Cr7.75 - Cr8.03	0.00094	0.02765	0.00767	-0.01576	0.01766	0.124	12	0.904
Pair 5	Cu7.75 - Cu8.03	0.00055	0.0017	0.0008	-0.00218	0.00328	.641	3	0.567
Pair 6	Fe7.75 - Fe8.03	-0.0384	0.1502	0.0433	-0.13387	0.0570	-0.886	11	0.394
Pair 7	Mg7.75 - Mg8.03	0.1218	0.0890	0.0246	0.06809	0.1757	4.936	12	0.000
Pair 8	Mn7.75 - Mn8.03	-0.0017	0.0089	0.0026	-0.00776	0.0042	-0.662	10	0.523
Pair 9	Na7.75 - Na8.03	0.2092	0.1015	0.0281	0.14787	0.2705	7.432	12	0.000
Pair 10	Ni7.75 - Ni8.03	0.0036	0.0191	0.0060	-0.01007	0.0173	0.603	9	0.562
Pair 11	Pb7.75 - Pb8.03	-0.0030	0.0014	0.0010	-0.01570	0.0097	-3.000	1	0.205
Pair 13	Zn7.75 - Zn8.03	-0.0427	0.1062	0.0433	-0.15426	0.0687	-0.986	5	0.369

Table A15. SCT 0.56 metals concentrations per collection date

Coll. Date	Al	As	Cd	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Se	Zn
4/10/2014	0.4	<MDL	<MDL	<MDL	<MDL	0.9	2.4	0.2	0.7	<MDL	<MDL	<MDL	<MDL
4/25/2014	0.3	<MDL	<MDL	<MDL	<MDL	0.4	1.7	0.02	0.6	<MDL	<MDL	<MDL	
5/2/2014	0.4	<MDL	<MDL	<MDL	<MDL	0.6	1.1	0.02	0.4	<MDL	<MDL	<MDL	<MDL
5/15/2014	0.9	<MDL	<MDL	<MDL	<MDL	1.2	1.3	0.04	0.4	<MDL	<MDL	<MDL	<MDL
5/30/2014	0.3	<MDL	<MDL	<MDL	<MDL	0.4	1.5	0.02	0.6	<MDL	<MDL	<MDL	<MDL
6/17/2014	1.3	<MDL	<MDL	<MDL	<MDL	1.4	1.9	0.05	0.8	<MDL	<MDL	<MDL	<MDL
1/28/2015	0.2	<MDL	<MDL	<MDL	<MDL	0.2	1.2	0.02	0.7	<MDL	<MDL	0.02	0.02

Table A16. SCT 0.94 metals concentrations per collection date

Coll. Date	Al	As	Cd	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Se	Zn
4/10/2014	0.4	<MDL	<MDL	<MDL	<MDL	0.5	1.1	0.03	0.6	<MDL	<MDL	<MDL	<MDL
4/25/2014	0.2	<MDL	<MDL	<MDL	<MDL	0.3	1.5	0.03	0.6	<MDL	<MDL	<MDL	
5/2/2014	0.3	<MDL	<MDL	0.02	<MDL	0.5	1.0	0.02	0.5	<MDL	<MDL	<MDL	<MDL
5/15/2014	0.9	<MDL	<MDL	<MDL	<MDL	1.2	1.0	0.05	0.4	<MDL	<MDL	<MDL	<MDL
5/30/2014	0.2	<MDL	<MDL	<MDL	<MDL	0.3	1.3	0.02	0.5	<MDL	<MDL	<MDL	<MDL
6/17/2014	0.3	<MDL	<MDL	<MDL	<MDL	0.4	1.6	0.02	0.6	<MDL	<MDL	<MDL	<MDL
1/28/2015	0.2	0.02	<MDL	<MDL	<MDL	0.2	1.1	0.03	0.7	<MDL	<MDL	<MDL	0.01

Table A17. Paired Samples T-test for metals upstream and downstream of SCT disposal area

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Al_SCT_0.94 - Al_SCT_0.56	-0.2166	0.3868	0.15793	-0.6226	0.1893	-1.372	5	0.228
Pair 2	Fe_SCT_0.94 - Fe_SCT_0.56	-0.2833	0.3763	0.15365	-0.6783	0.1116	-1.844	5	0.125
Pair 3	Mg_SCT_0.94 - Mg_SCT_0.56	-0.400	0.44721	0.18257	-0.8693	0.06932	-2.191	5	0.080
Pair 4	Mn_SCT_0.94 - Mn_SCT_0.56	-0.030	0.07014	0.02863	-0.1036	0.04361	-1.048	5	0.343
Pair 5	Na_SCT_0.94 - Na_SCT_0.56	-0.050	0.10488	0.04281	-0.1600	0.0600	-1.168	5	0.296

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