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Determining a Total Dissolved Solids Release Index from Overburden in Appalachian Coal Fields

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Determining a Total Dissolved Solids Release Index from Overburden in Appalachian Coal Fields

Jessica L. Odenheimer

**Thesis submitted
to the Davis College of Agriculture, Natural Resources, and Design
At West Virginia University**

in partial fulfillment of the requirements for the degree of

**Master of Science in
Plant and Soil Science**

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2013

Keywords: Total Dissolved Solids, Electrical Conductivity, Weathering, Overburden, Acid-Base Account

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ABSTRACT

Determining an Index for Total Dissolved Solids Weathered from Overburden in Appalachian Coal Fields

Jessica L. Odenheimer

The Appalachian coal industry has been very successful in developing technologies to identify, handle, treat and isolate potentially acid-forming overburden materials at coal mines in the region. However, the techniques to predict acid mine drainage potential may not adequately predict the release of total dissolved solids (TDS). High concentrations of TDS have been linked to a decrease in survival of aquatic macroinvertebrates. Our objective was to determine the effect of different solutions on overburden dissolution, and to develop a TDS release index. Forty-one overburden samples were collected from surface mines in West Virginia, Virginia, and Kentucky. Samples were grinded to a > 2mm particle size and combined with dilute HNO₃, EDTA, and digested in the microwave to obtain the most efficient laboratory experiment to determine an index for TDS released. Supernatants were analyzed for pH, Electrical Conductivity (EC), and other selected ions from the three solutions. Results were compared to Acid-Base Accounting parameters; i.e. maximum potential acidity and neutralization potential, as well as leaching column data from Virginia Tech to determine which parameter(s) were correlated to TDS release. EC was converted to TDS, and results showed that Maximum Potential Acidity (MPA) and TDS had the strongest relationship to TDS release. We determined a low, moderate, and high TDS release index using MPA ranging from 0.0-1.0, 1.0 – 3.0, and 3.0 +, respectively.

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1. Introduction and Literature Review

1.1. Coal and Surface Mining Regulation

Coal is the most abundant fossil fuel produced in the United States and contributes to 42% of the 4 trillion kilowatt-hours of electricity generated nationwide (U.S. Energy Information Administration, 2013). On a world scale, China produces the most coal at 3,471 million tons, the United States is second with 1,004 million tons, and India comes in third with 585 million tons (World Coal Association, 2012). China is responsible for 47% of global coal consumption, which is almost as much as the entire rest of the world combined (World Coal Association, 2012). In the United States, Wyoming, West Virginia, and Kentucky are the three major coal-producing states (U.S. Energy Information Administration, 2012). Wyoming is part of the western coal region which has subbituminous and bituminous coal seams up to 31 meters thick under gently rolling plains and steep mountains. Large area mines and some contour mines dominate the western coal region. Kentucky and West Virginia are part of the Appalachian coal region, which is underlain by relatively thin bands of bituminous coal ranging on average from 0.3 to 1.5 meters thick. Due to the very steep and narrow valleys of the Appalachian coal mining region, local mining industries tend to extract coal via underground, mountaintop, and surface contour mining operations.

West Virginia is the largest coal-producing state in the Appalachian coal region (U.S. Energy Information Administration, 2012). West Virginia produced 139,424,080 short tons of coal, and employed 20,334 people in 2011 (West Virginia Coal Association, 2012). The coal industry is the backbone of West Virginia's industrial economy, and has played a major leadership role in the state's political and social history (McGehee, 2010). The coal industry has also been at the forefront of controversy concerning human and environmental health and safety.

Deforestation, leveling mountains, acid mine drainage, erosion, subsidence, acid rain, air pollution, and the burying of streams are just a few of the environmental impacts caused by the extraction and burning of coal. West Virginia was the first state in the nation to pass laws regulating surface mining in 1939. Surrounding states followed this example, and laws and regulations evolved throughout the nation. Almost forty years later, a federal surface mining law was passed in 1977 called the Surface Mining Control and Reclamation Act (SMCRA). SMCRA enacted mandatory performance standards for all coal mining operations in the nation. These standards include permitting requirements and resource inventories on geology, soils, vegetation, and water resources before mining, as well as operation and mining plans during mining to minimize disturbances, and a reclamation plan to develop a suitable post-mining land use (OSM, 2012). Operation and performance standards (including air, land, soil, and water quality) must be met during the mining and reclamation phases in order to achieve successful closure of the site.

1.1.2. Mining Procedures and Overburden Material

Proper planning prior to coal mining can help alleviate or minimize many environmental impacts. Proper planning includes the identification and consideration of resources such as stream locations, water quality, water wells, homes and structures, geologic and soil conditions, and ecosystem components such as rare and endangered species.

During surface mining activities, the rock units which cover the coal seam, otherwise known as overburden material, are blasted apart and moved in order to expose the coal. All of the blasted overburden cannot be put back into the same place because of the increase in volume (Merricks et al., 2007). This excess material is commonly placed in valley fills or other constructed fills (Robins, 1979; White and Barata, 1995; Peng, 2000; Messinger and Paybins, 2003; Pond et al., 2008). Once the overburden material has been blasted, it is then subject to

accelerated weathering processes due to the smaller particle size, larger surface area, and greater exposure to the sun, the atmosphere, and precipitation. The physical and chemical weathering of the overburden material promotes the release of soluble constituents into the environment. Depending on the chemical composition of the rock, weathering of these broken rocks can promote acid mine drainage, alkaline mine drainage (Berhhardst et al., 2012) as well as the release of heavy metals, and total dissolved solids (TDS).

1.2. Overburden Analysis and Acid-Base Accounting

The application of innovative procedures has helped alleviate negative impacts of coal mining activities. Researchers from West Virginia University formulated the Acid-Base Account (ABA) to better understand the chemical production potential of overburden material and to determine potential topsoil substitutes (Smith et al., 1974). Overburden cores in areas which are to be mined are extracted and used to gather information about rock layers before they are disturbed. The geologic layers of each core are identified by rock color, hardness, fizz, and pH, and samples from these layers are then analyzed for total sulfur or maximum potential acidity (MPA) and neutralization potential (NP).

The ABA procedure is a method used to determine the total amount of acidity and alkalinity that may be produced from overburden material upon weathering (Skousen et al., 1997). The acidity or MPA (metric ton (mt) per 1000 mt of material) comes from total sulfur analysis, and the alkalinity or NP (mt per 1000 mt of material) is a measure of alkaline carbonates, exchangeable bases, and weatherable silicates present in the overburden material. The ABA accurately quantifies potential acidity when all of the sulfur in the rock is present as pyritic minerals (sulfides). However, the ABA overestimates MPA when the overburden is also comprised of organic sulfur, and/or sulfates. To calculate NP, a sample is treated with a known

amount of standardized hydrochloric acid and hydrogen peroxide to rid the sample of organic matter and oxides. Once these samples are treated with acids they are then neutralized with sodium hydroxide. The amount of acid consumed is used to calculate NP.

Toxic and alkaline materials are defined using MPA and NP parameters. Subtracting the MPA from the NP yields a net neutralizing potential (NNP). A positive NNP indicates potentially acid-neutralizing rock units, and a negative NNP indicates a potential acid-producing rock unit.

The ABA functions under certain assumptions: 1) If the overburden sample consumes acid in the laboratory, it will generate alkalinity in the field. 2) All of the sulfur in the overburden sample will react to form acid. 3) The rate of pyrite oxidation is less than or equal to the rate of carbonate mineral dissolution (Perry, 1985).

Many studies have been conducted to test whether MPA, NP, or a combination or ratio of parameters can best predict post-mining water quality. Skousen et al. (2002) found in a study of 56 surface coal mining sites that MPA was poorly correlated to post-mining water quality, NP was moderately correlated, and the NP to MPA ratio and NNP were equally good in predicting water quality from overburden. They found that in general, an NP to MPA ratio of < 1 will primarily generate acidic drainage. NP to MPA ratio of 1-2 will primarily generate alkaline drainage, and ratios > 2 will generally produce alkaline drainage (Skousen et al., 2002). The application of ABA has been successful in helping operators minimize acid mine drainage and alkaline mine drainage from surface mines (Skousen et al., 1987).

1.3. Total Dissolved Solids

ABA is the most common method for predicting post-mining water quality (Perry, 1985) and as mentioned has been very successful in its implementation to minimize water quality

impacts from mining. In recent years, however, researchers have determined that TDS are responsible for polluting waterways and harming aquatic insects. Therefore, the United States Environmental Protection Agency (USEPA) has attempted to regulate the release of TDS from surface mines by setting effluent standards through their interpretation and implementation of the Clean Water Act. In order to regulate TDS discharge standards, the USEPA, researchers and operators need a better understanding of how TDS constituents are released from mined and reclaimed overburden materials and how these constituents enter streams. Unfortunately, no such method currently exists for the prediction of TDS release from overburden material.

TDS are defined as the total sum of cations and anions in solution, but more specifically as any inorganic and/or organic constituent in water that can pass through a 2.0 micron filter (APHA, 1992). Common ions are SO_4^{2-} , HCO_3^- , Cl^- , Ca^{2+} , K^+ , Na^+ , and Mg^{2+} , but any element that is present in solution will contribute to TDS. Depending on the properties of rock, physical and chemical weathering can produce high concentrations of TDS in streams. Physical weathering is the physical breakdown of rock into smaller particle sizes via climate, flora, and fauna. Chemical weathering may promote TDS release via proton-promoted dissolution, ligand-promoted dissolution, hydroxide-promoted dissolution, and/or redox-promoted dissolution.

The approximate concentration of TDS found in most of the world's rivers is 120 mg L^{-1} (Wetzel, 1983). When TDS exceeds $1,000 \text{ mg L}^{-1}$, the water body is termed brackish. In North America, the major ion found in natural waters is bicarbonate (HCO_3^-) at an average of 68 mg L^{-1} . Sulfate is the second most common ion found in natural waters with an average concentration of 20 mg L^{-1} . Calcium is the most common cation found in fresh water with an average concentration of 21 mg L^{-1} (Wetzel, 1983).

The gravimetric procedure for measuring TDS involves filtering out the total suspended solids from solution and collecting the filtrate. The filtrate is then transferred to a pre-weighed beaker and evaporated in an oven at 180°C, until a constant weight is maintained. Once the beaker has cooled, the beaker is reweighed. TDS is calculated in mg L⁻¹ (APHA, 2002). Since ion concentrations control electrical conductivity (EC) in water, EC can be used to estimate TDS with a conversion factor of 640. The number 640 in the equation comes from the number 64, which represents the average equivalent weight of salts commonly found in natural waters and is multiplied by the constant 10. Equation (1) is used when EC is less than 1 dS m⁻¹, and equation (2) is used when EC is greater than 1 dS m⁻¹. However, this conversion factor generally underestimates TDS in chloride-rich solutions, and overestimates TDS in sulfate-rich solutions.

$$\text{TDS} = 640 * \text{EC (dS m}^{-1}\text{)} \quad (1)$$

$$\text{TDS} = 640 * [\text{EC (dS m}^{-1}\text{)}]^{1.087} \quad (2)$$

TDS is only one of many water quality parameters that can create stress in aquatic ecosystems and it is not independent of other stressors in Central Appalachian streams. TDS is a difficult parameter to monitor because there may be one dominate ion in solution, or a couple of ions that are controlling the TDS of a stream. It is likely that a certain ion concentration or an ionic ratio may be more critical to understanding aquatic health effects than a total TDS value. In some cases, a single constituent such as SO₄²⁻ can be the dominate stressor in polluted streams, contributing up to 50% (w/v) of the TDS (Timpano et al., 2010). Therefore, a laboratory or field technique for estimating TDS release potentials from coal overburden material would be helpful

for mine planning, the placement of high-producing TDS rocks, and abatement procedures for coal operators.

1.3.1. TDS Effects on Human Health

Congress passed the Safe Drinking Water Act in 1974, which requires the USEPA to determine safe levels of chemicals in drinking water. TDS is considered a secondary pollutant with a maximum criteria limit of 500 mg L^{-1} . TDS is not expected to harm human health at this level, but may be toxic to aquatic life and can damage water treatment equipment (USEPA, 2012). Appalachian streams not influenced by coal mining commonly have TDS concentrations less than 75 mg L^{-1} and are primarily comprised of HCO_3^- , SO_4^{2-} , Ca^{2+} , and Cl^- . TDS levels in streams that are impacted by coal mining can range from $400 - 2,000 \text{ mg L}^{-1}$ and TDS of mining-impacted streams are primarily made up of SO_4^{2-} , HCO_3^- , and Ca^{2+} (Timpano et al., 2010; Pond et al., 2008).

Current West Virginia water quality standards can be found in the Requirements Governing Water Quality Standards Rule – Title 47CRS2. These rules establish requirements concerning the release of sewage, industrial wastes, and other wastes into the waters of West Virginia. Table 1.1 displays a summary of aquatic and human health criteria for metals effective June 27, 2011. All of these parameters (in addition to other constituents not included in this table) account for the TDS in waters of West Virginia.

Table 1.1: Summary of Aquatic Life and Human Health Criteria for Metals[†]

Parameter	Use Designation					
	Aquatic Life				Human Health	
	B1, B4		B2		C ³	A ⁴
	Acute	Chronic	Acute	Chronic		
Dissolved Aluminum (µg/l)	750	750	750	87		
Antimony (µg/L)					4300	14
Arsenic (µg/L)					10	10
Barium (mg/L)						1.0
Beryllium (mg/L)	130		130			0.0077
Chloride (mg/L)	860	230	860	230	250	250
Copper (µg/L)						1000
Cyanide	22	5.0	22	5.0	5.0	5.0
Fluoride (mg/L)						1.4
Iron (mg/L)		1.5		1.0		1.5
Lead (µg/L)						50
Manganese (mg/L)						1.0
Nickel (µg/L)					4600	510
Nitrate (mg/L)						10
Nitrite (mg/L)	1.0	1.0	0.060	0.060		
Selenium (µg/L)	20	5	20	5		50

[†] Title 47 Legislative Rule DEP Water Resources 47CSR2 Appendix E, Table 1

All metals must be converted to a dissolved concentration by multiplying each numerical value by the appropriate conversion factor

A: Water supply for human consumption

B1: Warm water fishery streams

B2: Trout waters

B4: Wetlands

C: Water contact recreation

1.3.2 TDS Effects on Aquatic Health

Aquatic organisms are affected by TDS on a cellular level. Aquatic organisms must perform osmotic regulation to maintain homeostasis. High concentrations of TDS in the water will promote the diffusion of water out of the organism's cells and into the surrounding water, causing the cells of an aquatic organism to shrink. However, low concentrations of TDS are also problematic, where water can move into the cell, causing cellular swelling. TDS becomes toxic because of the increase in salinity (Potts, 1954).

Indicator species are commonly used in lab toxicity tests to determine levels that are toxic to these organisms over a range of TDS concentrations. Common indicator species are benthic macroinvertebrates. Pond et al. (2008) found that mining activity impacted benthic macroinvertebrate communities with a strong correlation to ionic strength. Background EC in the Appalachian region are generally less than 0.075 dS m^{-1} , compared to up to 30 times over background levels downstream of mountain top mining sites (Pond et al., 2008). Aquatic insects make up a large portion of benthic macroinvertebrates. Ephemeroptera (mayflies), Plecoptera (stoneflies), and Trichoptera (caddisflies) are orders of aquatic insects that are collectively termed EPT. These aquatic insects are often indicators of the highest quality streams in the Appalachian region (Pond, 2010). These organisms are the foundation for many food chains, and are critical for the processing and cycling of nutrients (WVDEP, 2012). These three orders in particular are commonly analyzed because of their sensitivity to pollution. Using Pearson Product-Moment correlations for biological metrics and water quality parameters, Timpano et al. (2010) found that the number of EPT taxa had a strong negative correlation to TDS (-0.76) as well as to individual ions Ca^{2+} (-0.81), SO_4^{2-} (-0.81), and Mg^{2+} (-0.79).

Other common macroinvertebrates used for TDS toxicity tests include *Ceriodaphnia dubia* (water flea), *Chironomids* (midge), and *Corbicula* (freshwater clam). Kennedy et al. (2002) found that the mean survival of *Ceriodaphnia* is inversely related to TDS. Research suggests that EC levels that exceed about 3.7 dS m^{-1} will impair sensitive invertebrates (Kennedy et al., 2002). Fish have also been tested for TDS toxicity. For fathead minnow (*Pimephales promelas*), researchers saw a significant decrease in percent survival at about 6.18 dS m^{-1} , and a significant decrease in mean reproduction growth at about 4.84 dS m^{-1} (Kennedy et al., 2002). However, rainbow trout were not significantly impaired at a maximum TDS concentration of

2,000 mg L⁻¹ (Chapman et al., 1999). Mount et al. (2009) found that in general, relative ion toxicity was found to be in the order of $K^+ > HCO_3^- = Mg^{2+} > Cl^- > SO_4^{2-}$, and cations Ca^{2+} and Na^+ produced insignificant toxicity. Some species, however, prefer increased concentrations of TDS. Derry et al. (2003) found that *Brachionus plicatilis* (rotifer) and *Cletocamptus* sp. (harpacticoid copepod) showed population growth in Cl^- dominated water. *Leptodiptomus sicilis* and *Diaptomus nevadensis* (calanoid copepods) prevailed in SO_4^{2-} and CO_3^{2-} dominated water (Derry et al., 2003).

Weber-Scannell and Duffy (2007) categorized potential TDS water quality standards into three possible approaches: 1) Set the standard low enough to protect all species at all life stages exposed to the most toxic ions or combination of ions; 2) Set the standard to protect most species at most life stages for most ions and/or combination of ions; 3) Set different limits based on different categories of ions or combinations of ions, with a lower limit during fish spawning. They determined that the third approach would provide the least amount of unnecessary restriction to coal operators and provide the greatest protection to aquatic species (Weber-Scannell and Duffy, 2007).

Levels of EC in discharge water and standards established for effluent limits in surface mine permits continue to be very controversial subjects among the coal industry, federal and state regulatory agencies such as the USEPA and the West Virginia Division of Environmental Protection (WVDEP), and environmental groups. EC levels exceeding 0.5 dS m⁻¹ (500 μS cm⁻¹) can potentially have a negative effect on aquatic species, and therefore has become an upper limit in permitting by the USEPA. The Science Advisory Board (SAB) conducted evaluations of the science behind the 0.5 dS m⁻¹ threshold, and determined that although there is clear evidence that valley fills are associated with increased EC, EC should be used as a “coarse” indicator of

water quality because of confounding factors. The SAB concluded that the USEPA should not over-rely on EC for determining damage to streams, and advised that many other environmental factors and parameters must also be included in assessments (Copeland, 2013).

1.4. ARIES Initiative

A consortium of seven major research universities joined together to form the Appalachian Research Initiative for Environmental Science (ARIES). This initiative was formed to address the environmental impacts of the discovery, development, production, and use of energy resources in Appalachia. The universities involved are: West Virginia University, Virginia Tech, University of Kentucky, Ohio State University, University of Pittsburgh, Pennsylvania State University, and the University of Pennsylvania. ARIES is supported by numerous industrial affiliates including Alpha Natural Resources, Natural Resource Partners, TECO Coal Corporation, Patriot Coal Corporation, Cliffs Natural Resources, MEPCO, and Norfolk Southern (Craynon, 2013).

ARIES is focused on six areas. Area 1 is the assessment of mining impacts on ecosystem health and diversity. Area 2 focuses on the treatment and minimization of constituent discharges. Area 3 addresses an accurate prediction of constituent release (i.e. TDS) from overburden and refuse material. Area 4 focuses on overburden handling plans and designs to minimize release of constituents into the environment. Area 5 is the next-generation design for eco-friendly mining systems, and Area 6 evaluates and optimizes the impacts of mining on community well-being (Craynon, 2013). Our research explores Area 3, the release of constituents from overburden. The Appalachian coal industry has been very successful in developing technologies to identify, handle, treat and isolate potentially acid-forming overburden materials at coal mines in the region. However, the techniques used to predict acid mine drainage potential may not adequately predict the release of TDS. This often leads to handling plans that actually increase TDS release

due to the blending of net acid-forming and alkaline strata. The primary goal of research Area 3 is to develop new methods for characterizing and predicting constituent release potentials from coal overburden and refuse materials (Craynon, 2013).

1.5. Research Objective

The objective of this research was to determine a laboratory weathering method to determine an index for TDS release (high, moderate, and low) from overburden materials so that operators can properly treat, isolate and/or handle their overburden in a manner that will decrease TDS runoff from their site. Microwave-assisted digestion and a shaking/weathering technique using two extracting solutions (dilute nitric acid and Ethylenediaminetetraacetic acid) were utilized to obtain estimates of TDS release rates. These results were compared to ABA parameters such as MPA and NP, and discharge data from leaching columns.

1.6. Hypotheses

We hypothesized that there would be significant differences in TDS released from overburden materials using three different techniques. We predicted that overburden shaken in dilute HNO_3 would provide a lower limit on TDS release from overburden and that microwave digestion would provide the upper limit on TDS release. The EDTA extraction solution would provide an intermediate value between the other two.

- H_0 : There will be no significant difference in the mean concentration of TDS released among the three extraction techniques.
- H_a : There will be significant differences in mean concentrations of TDS released among the three extraction techniques.

We also hypothesized that different overburden types would be significantly different in terms of TDS release. For example, overburdens comprised of shales or sandstones with high sulfur contents or high carbonate (neutralization potential, NP) contents or a combination of the two would produce the most TDS. Rock units with medium TDS release potential would be shales or other rocks with low to moderate sulfur and/or carbonate content. And rock units with low TDS potential would be hard sandstones or oxidized/weathered sandstones or soil-like materials.

- H_0 : There will be no significant difference in mean TDS among varying rock types.
- H_a : There will be significant differences in mean TDS among overburden rock types.

2. Materials and Methods

2.1. Field Overburden Collection

Forty-one overburden samples were collected in 5-gallon buckets from surface coal mines in West Virginia, Virginia, and Kentucky (fifteen samples from WV, fifteen samples from VA, and eleven samples from KY). Emphasis was placed in collecting samples that represented a wide variety of rock type, such as mudstones, siltstones, and gray and brown sandstones. Rocks with high TDS may be those with high sulfur contents and/or high carbonate contents (neutralization potential). Rock units with medium TDS potential may be shales or other rocks with moderate sulfur and/or neutralization potential. Rocks with low TDS potential may be hard sandstones and/or oxidized/weathered sandstones. A preference was placed upon sampling rock units that would most likely be disposed of in valley fills or backfills instead of those strata that would be isolated as toxic strata or removed from the site.

Table 2.1: Acid-Base Accounts for fifteen overburden samples from West Virginia surface coal mines, provided by the coal company.

Sample #	Munsell Color	Rock Type	pH	% S	MPA	NP	NET	Se	Predicted TDS
WV 1	10YR 8/1	SS	6.4	0	2.5	5.0	2.5	ND	Low
WV 2	10YR 8/1	SS	6.4	0	2.5	5.0	2.5	ND	Low
WV 3	10YR 6/1	SH	8.3	0.018	0.44	17	16.66	0.85	Low
WV 4	10YR 8/1	SS	8.3	0.03	1.8	15	13.2	ND	Medium
WV 5	10YR 8/1	SS	8.3	0.006	0.25	10	9.75	ND	Low
WV 6	5Y 7/1	Gray SS	7.2	0.018	0.6	25	24.6	Not Listed	Medium
WV 7	2.5Y 6/1	Black Sh	6.0	0.15	30	30	0	Not Listed	High
WV 8	5Y 7/1	Gray Sh	8.1	0.001	0.25	60	59.75	Not Listed	Medium
WV 9	2.5Y 3/1	SS	5.0	0.1	4.0	3.0	-1.0	Not Listed	Low
WV 10	5Y 7/1	Sh	8.0	0.001	0.03	27	26.07	Not Listed	Medium
WV 11	2.5Y 6/1	Brown SS	6.1	0.02	0.47	23	22.53	<0.2	Medium
WV 12	N/2/0	Black Sh	7.0	2.0	65	5.0	60	0.3	High
WV 13	2.5Y 8/1	White SS	7.0	0.02	0.7	18	17.3	<0.2	Low
WV 14	2.5Y 7/1	SS	6.3	0.03	0.6	17	16.4	<0.2	Low
WV 15	2.5Y 7/1	SS	6.3	0.02	0.3	15	14.7	<0.2	Low

% S: percent sulfur; MPA: Maximum Potential Acidity; NP: Neutralization Potential; NET: Net Neutralizing Potential; Se: Selenium

2.2. Sample Processing

Samples were air-dried in the greenhouse at Virginia Tech and then the entire volume of each sample was crushed and passed through a 1.25 cm (0.5 in) sieve. Approximately 2000 g of each sample was sent to West Virginia University (WVU). The samples were halved, and then further ground at WVU using a BICO pulverizing mill (BICO, Inc. Burbank, CA) until roughly all of the sample could pass through a 2-mm (0.0787 in) sieve (the other half was archived at WVU). After preliminary weathering tests involving two overburden sieve sizes (250 μ m and 106 μ m), we found no statistical difference in the concentrations of constituents released between the two particle sizes. Therefore, we concluded that the current particle size (< 2mm) would suffice for our weathering experiments (Odenheimer et al., 2012).

2.3. Laboratory Analysis of Overburden Material

2.3.1. Dilute Nitric Acid Method

One microwave digestion technique and two extracting solutions: dilute nitric acid (HNO_3), and Ethylenediaminetetraacetic acid (EDTA), were utilized to determine TDS release potential from overburden material.

A solution of 0.0159 *M* dilute HNO_3 (pH of 2 and EC of 6.1 dS m^{-1}) was prepared in the lab by a 1/1000 dilution of trace metal grade HNO_3 (15.9 *M*). Approximately 200 mL ($\pm 2.0 \text{ mL}$) of dilute HNO_3 was combined with 1.00 g ($\pm 0.005 \text{ g}$) of 2-mm sized overburden material. The solution and overburden were placed in 250 mL plastic Nalgene bottles (twenty-four samples at a time) on a Wrist Action Shaker (Burrell, Model 75, Pittsburgh, PA) at approximately 200 shakes per minute for a total of 120 hours (five days). Aliquots of 20 mL were extracted from the bottles using disposable plastic pipette tips after 6, 24, 72, and 120 hours of shaking. Samples rested for one hour to let all solids settle prior to extraction. About 15 mL of the leachate were filtered and used for analysis of selected cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , P, Fe, Al^{3+} , Mn^{2+}) by inductively coupled plasma emission spectrometer, ICP-OES (Optima DV-2100, Perkin Elmer, Norwalk, CT). A volume of 3 mL was used to measure pH and EC using a Mettler Toledo SevenEasy pH meter, and Mettler Toledo SevenCompact conductivity meter, respectively. The remaining 2 mL were analyzed for anions (F^- , Cl^- , NO_2^- , Br^- , PO_4^{3-} , SO_4^{2-}) using Ion Chromatograph analysis (ICS-3000, Sunnydale, CA). Simulated weathering using dilute HNO_3 was replicated twice.

2.3.2 Ethylenediaminetetraacetic Acid Method

A solution of 0.5 M Ethylenediaminetetraacetic Acid (EDTA), pH of 8.0 and EC of 49.1 dS m⁻¹, was prepared by combining 372.2 g of EDTA disodium salt to a total of 2 L of deionized water in a volumetric flask. Sodium hydroxide (NaOH) pellets were added to the solution over a three-day period until the salt was completely dissolved (approximately 40 g of NaOH pellets). The final pH was brought to 8.0 with the addition of 1-4 mL of 10 M NaOH. A volume of 200 mL ($\pm$ 2.0 mL) of EDTA was combined with 1.00 g ($\pm$ 0.005 g) of 2-mm sized overburden. The solution and overburden samples were placed in 250 mL plastic Nalgene bottles (twenty-four samples at a time) on a Wrist Action Shaker (Burrell, Model 75) at approximately 200 shakes per minute for a total of 168 hours (one week). Aliquots of 20 mL were extracted from the bottles using disposable plastic pipettes after 6, 24, 72, and 168 hours of shaking. Samples sat for one hour to let all solids settle prior to extraction. About 15 mL of the leachate were filtered (Whatman 42) and analyzed for selected cations (Ca²⁺, Mg²⁺, Fe, Al³⁺, Mn²⁺) as described above. Prior to ICP analysis, the samples were diluted by one-fifth. A volume of 3 mL of the leachate were used for pH and EC analysis, as described above. Simulated weathering using EDTA was replicated twice.

2.3.3. pH and EC analysis

To determine overburden pH, 5 g of overburden were combined with 5 mL of de-ionized water. The mixture was placed on a reciprocating shaker table and mixed for 15 minutes, then allowed to equilibrate for an hour. A Mettler Toledo SevenEasy pH meter was used to take the pH readings. Overburden EC was determined by combining 5 g of overburden with 10 mL de-ionized water. The mixture was placed on a reciprocating shaker table and mixed for 15 minutes,

then allowed to equilibrate for an hour. A Mettler Toledo SevenCompact Conductivity meter was used to determine EC readings.

2.3.4. Microwave Digestion

Microwave-assisted acid dissolution using a modified USEPA Method 3051 procedure was used to provide an almost total elemental composition of each overburden sample. Microwave-assisted digestion is designed to be an alternative to conventional heating extraction with nitric acid (HNO_3) or alternatively, HNO_3 and hydrochloric acid (HCl) (USEPA, 1997). This method is not intended for analyzing total decomposition of a sample, but only what would be considered bioavailable under extreme conditions. Microwave-assisted digestion provides a rapid multi-element acid extraction so that decisions can be made about materials and site cleanup levels, the need for Toxicity Characteristic Leaching Procedure (TCLP) testing, and whether a Best Demonstrated Available Technology (BDAT) is providing acceptable performance. When “total” quantities of trace elements are required, the hydrofluoric (HF) method will be employed.

This procedure is an alternative to conventional extraction according to EPA Method 200.2 and EPA Method 3050. A mass of 0.500 g (± 0.005 g) of overburden (sieved to < 2 mm) was pre-weighed on weigh paper, and then transferred into a Teflon vessel. A volume of 9 mL of 16 M HNO_3 and 3 mL of 12 M hydrochloric acid (HCl) were added to each sample in Teflon vessels under the fume hood. The combination of these two acids (also known as aqua regia) achieves equivalent results with EPA Method 3050 for certain elements of concern: Fe^{total} , Al^{3+} , and Mg^{2+} (USEPA, 1997). Overburden samples and aqua regia were pre-digested under the fume hood overnight to allow any vigorous oxidation to vent. On the following day, the Teflon vessels were digested using microwave heating with a laboratory microwave unit (CEM, Mars 5,

Mathews, North Carolina). The sealed Teflon microwave vessels (seven at a time) were placed in the microwave and reached 175°C in the 5-min ramp time, and was held with constant temperature and pressure (350 psi) for fifteen minutes. After cooling, the vessel contents were diluted by 1/50, filtered (Fisherbrand grade P8) and analyzed for cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , P, Fe, Al^{3+} , Mn^{2+}), as described above. This microwave procedure was replicated twice.

2.4. Statistical Analysis

Software programs; R and JMP were used to perform statistical analyses to determine significant differences among samples and methods. The three methods were compared via regression to test for relationships among concentrations of constituents released at their respective endpoints. Analysis of variance (ANOVA) was also utilized to find significant differences between methods as well as the length of time the samples were left on the shaker. Principle Components Analysis (PCA) was used as an exploratory analysis to determine which factors were most correlated to TDS and to quickly discard factors that were not useful for TDS analysis. Regression was also used to examine relationships between TDS and other parameters.

3. Results and Discussion

3.1. Dilute Nitric Acid Method

Forty-one overburden samples were subjected to simulated weathering in a dilute nitric acid (HNO_3) solution. In general, elemental concentrations remained constant after 72 hours (three days) of shaking (Table 3.1). Figures 1A to 1E (Appendix 1) depict the release of elements over time. Aluminum concentrations ranged from 170 to 2,030 mg kg^{-1} (Table 3.2). Iron and calcium were released in the highest quantities from the overburden samples. Iron release ranged from 700 to 28,000 mg kg^{-1} . Calcium concentrations ranged from 250 to 1,870 mg kg^{-1} ; however the refuse sample (WV R) was an outlier, releasing 28,000 mg kg^{-1} . Magnesium concentrations ranged from 140 to 3,000 mg kg^{-1} with the refuse sample (WV R) releasing concentrations up to 6,000 mg kg^{-1} . Of the cations we measured, manganese was released from the overburden samples in the smallest quantities with a mean concentration from all forty-one samples ranging from 25 to 650 mg kg^{-1} at 72 hours of shaking.

Table 3.1: Means of elemental* release by time using the dilute HNO_3 method.

Time	Al	Fe	Mn	Mg	Ca	K	Na	P
hours	----- mg kg^{-1} -----							
6	707 ^A	3406 ^C	171 ^C	760 ^B	2455 ^A	208 ^B	47 ^A	148 ^A
24	523 ^B	6661 ^B	274 ^B	1023 ^{AB}	2651 ^A	229 ^{AB}	55 ^A	144 ^A
72	368 ^C	8624 ^A	338 ^A	1167 ^A	2725 ^A	281 ^A	52 ^A	142 ^A
120	824 ^A	8630 ^A	332 ^A	1138 ^A	2598 ^A	327 ^A	69 ^A	129 ^A

Means with different letters signify significant differences at $p=0.05$ level

*Only cations were utilized to determine shaking times

Table 3.2: Mean elemental release after 72 hours of shaking in dilute nitric acid.

ID [†]	Sample	EC		pH		Al		Fe		Ca		Mg	
		Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
1	VA 1	4.8	0.8	2.0	0.1	347	19	6268	956	3054	192	788	15
2	VA 2	4.1	0.7	2.0	0.0	441	6	15143	1387	3214	127	1894	167
3	VA 3	5.2	0.9	1.9	0.0	838	6	827	76	279	132	387	18
4	VA 4	5.0	0.8	1.9	0.0	1549	15	1168	85	440	120	697	18
5	VA 5	5.2	0.9	1.9	0.0	641	54	1273	129	710	174	444	23
6	VA 6	4.6	0.7	2.0	0.0	1379	172	4344	314	2985	341	1175	120
7	VA 7	4.7	0.8	2.0	0.0	1967	226	2086	212	1500	352	1186	187
8	VA 8	4.6	0.8	2.0	0.0	965	65	8913	494	1456	298	810	102
9	VA 9	4.2	0.7	2.0	0.0	681	34	12354	885	4775	448	1403	156
10	VA 10	4.3	0.7	2.0	0.0	1083	82	11576	882	3459	355	1659	238
11	VA 11	5.2	0.9	2.0	0.0	957	25	1105	13	632	40	457	31
12	VA 12	4.3	0.7	2.0	0.0	453	19	14151	646	1656	2156	1100	86
13	VA 13	5.0	0.9	1.9	0.0	405	0	3326	724	1874	91	903	70
14	VA 14	5.2	0.8	2.0	0.1	767	21	783	98	671	18	563	48
15	VA 15	3.2	0.6	2.2	0.0	978	31	21620	990	8237	448	3408	260
16	WV 1	5.3	0.9	1.9	0.0	199	15	2295	160	280	8	195	7
17	WV 2	4.0	0.5	2.1	0.0	643	15	21520	1442	2204	110	1973	73
18	WV 3	5.0	0.9	1.9	0.0	432	14	5552	130	1415	5	579	31
19	WV 4	4.6	0.8	2.0	0.0	535	43	10972	713	1110	85	771	80
20	WV 5	4.8	0.8	1.9	0.0	204	14	10939	279	468	56	493	35
21	WV 6	4.5	0.8	2.0	0.0	172	6	16457	1738	690	89	911	154
22	WV 7	3.1	0.6	2.2	0.0	2028	136	27870	3239	4371	782	2273	284
23	WV 8	5.6	0.0	2.0	0.0	385	131	8118	1066	760	213	614	78
24	WV 9	4.1	0.1	2.1	0.0	365	28	19376	430	6423	143	2580	229
25	WV 10	5.3	0.3	1.9	0.0	973	15	6628	755	1049	9	499	10
26	WV 11	5.5	0.1	2.0	0.1	684	14	8548	311	1474	49	753	17
27	WV 12	6.1	0.1	1.9	0.0	341	48	2615	205	952	54	307	21
28	WV 13	5.9	0.1	1.9	0.0	852	215	4604	102	447	1	390	6
29	WV 14	5.5	0.1	2.0	0.0	382	5	10191	273	2391	112	1046	15
30	WV R	3.1	0.5	2.3	0.3	605	3	3797	561	27700	3847	5946	297
31	KY 1	6.1	0.0	1.9	0.1	702	192	893	171	254	322	342	74
32	KY 2	5.4	0.1	2.1	0.1	190	14	7994	684	4616	653	1634	96
33	KY 3	4.9	0.2	2.0	0.0	365	22	10014	730	7446	453	2018	94
34	KY 4	5.4	0.9	2.0	0.0	1141	157	19657	2097	2233	21	1122	37
35	KY 5	6.1	0.0	1.7	0.2	916	34	720	27	496	54	140	13
36	KY 6	6.0	0.0	1.8	0.1	1153	49	945	45	465	27	547	14
37	KY 7	5.1	0.2	1.9	0.1	660	65	10468	1001	3685	129	1961	15
38	KY 8	4.5	0.6	1.9	0.1	500	9	14401	2185	2167	109	1344	111
39	KY 9	5.5	0.0	1.9	0.1	301	1	10243	593	1537	25	1097	90
40	KY 10	6.0	0.2	1.8	0.1	287	25	4122	1635	723	4	470	62
41	KY 11	5.4	0.0	1.9	0.1	528	4	9686	1213	1421	179	953	114

[†] ID corresponds to PCA figure

ID [†]	Sample	Mn		Cl ⁻		SO ₄ ⁻²		Ft		PO ₄ ⁻³		SumTDS	
		Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
		mg L ⁻¹											
1	VA 1	286	16	121	67	986	481	52	n.a.	219	29	61	
2	VA 2	525	98	155	155	2251	901	56	14	188	63	119	
3	VA 3	153	2	216	242	2243	2018	29	n.a.	n.a.	n.a.	25	
4	VA 4	387	12	168	173	1729	1372	33	n.a.	n.a.	n.a.	31	
5	VA 5	297	30	45	10	788	203	n.a.	n.a.	73	n.a.	21	
6	VA 6	452	103	47	11	1143	234	n.a.	n.a.	138	56	58	
7	VA 7	612	85	50	n.a.	644	n.a.	n.a.	n.a.	97	n.a.	41	
8	VA 8	185	20	44	7	1079	265	n.a.	n.a.	264	123	69	
9	VA 9	395	40	56	16	781	216	92	n.a.	327	155	104	
10	VA 10	422	48	70	42	749	228	n.a.	n.a.	221	19	96	
11	VA 11	378	16	59	17	690	209	n.a.	n.a.	89	n.a.	22	
12	VA 12	468	21	62	20	751	240	n.a.	n.a.	365	183	95	
13	VA 13	474	8	76	n.a.	883	n.a.	n.a.	n.a.	116	n.a.	40	
14	VA 14	373	31	66	7	731	137	n.a.	n.a.	47	n.a.	20	
15	VA 15	584	32	71	6	836	211	112	n.a.	304	46	181	
16	WV 1	26	1	76	8	749	90	n.a.	n.a.	n.a.	n.a.	19	
17	WV 2	520	16	70	n.a.	3123	n.a.	n.a.	n.a.	151	n.a.	151	
18	WV 3	71	5	111	60	1198	437	16	n.a.	n.a.	n.a.	47	
19	WV 4	222	18	213	197	2207	1928	43	n.a.	161	n.a.	81	
20	WV 5	365	13	56	n.a.	877	n.a.	n.a.	n.a.	n.a.	n.a.	67	
21	WV 6	501	50	55	n.a.	866	n.a.	n.a.	n.a.	115	n.a.	99	
22	WV 7	550	81	136	108	1459	930	40	n.a.	237	n.a.	195	
23	WV 8	174	11	51	5	652	35	n.a.	n.a.	290	85	55	
24	WV 9	520	40	126	n.a.	672	n.a.	n.a.	n.a.	116	n.a.	151	
25	WV 10	178	5	93	50	579	162	n.a.	n.a.	120	127	51	
26	WV 11	111	7	37	n.a.	412	n.a.	99	n.a.	n.a.	n.a.	61	
27	WV 12	31	2	91	53	653	140	n.a.	n.a.	139	95	26	
28	WV 13	121	2	112	89	637	236	n.a.	n.a.	79	76	36	
29	WV 14	222	2	57	4	571	147	n.a.	n.a.	141	124	75	
30	WV R	262	38	102	63	3576	1308	133	55	n.a.	n.a.	211	
31	KY 1	117	0	102	64	568	120	n.a.	n.a.	n.a.	n.a.	15	
32	KY 2	193	15	76	30	579	159	62	n.a.	125	118	77	
33	KY 3	333	16	5190	n.a.	9493	n.a.	893	n.a.	2551	n.a.	192	
34	KY 4	519	90	76	20	887	221	20	n.a.	67	54	129	
35	KY 5	603	30	124	19	644	50	n.a.	n.a.	n.a.	n.a.	18	
36	KY 6	301	29	114	51	610	70	14	n.a.	n.a.	n.a.	21	
37	KY 7	641	72	136	20	3181	39	n.a.	n.a.	469	175	106	
38	KY 8	371	51	135	27	950	51	n.a.	n.a.	190	9	100	
39	KY 9	336	27	73	3	1441	57	n.a.	n.a.	108	5	76	
40	KY 10	226	42	137	86	1684	1247	n.a.	n.a.	216	n.a.	385	
41	KY 11	349	9	137	28.7	773	100.8	n.a.	n.a.	141	69.9	70	

[†] ID corresponds to PCA figure

For the anions that were analyzed, chloride concentrations ranged from 35 to 5,200 mg kg⁻¹ (Table 3.2). The overburden samples released sulfate ranging in concentrations of 400 to 9,500 mg kg⁻¹. Fluoride was released in concentrations ranging from 10 to 900 mg kg⁻¹. Phosphate was also released from these samples ranging from 45 to 2,600 mg kg⁻¹. The forty-one samples used for this research were chosen based on the assumption that varying rock types and stratigraphic position in the geologic column would produce varying TDS potential, as well as data from acid-base accounts provided by the coal operators; hence a large range in elemental release was expected.

The average pH of the solutions for all forty-one samples stayed constant at 2.0 ± 0.05 at 72 hours of shaking (Figure 3.1). Electrical Conductivity (EC) did not change drastically over the duration of the shaking period (Figure 3.2). The average EC for all forty-one samples was 4.9 ± 0.5 dS m⁻¹ at 72 hours of shaking. The EC and pH of the background solution (2.0 and 6.1 dS m⁻¹, respectively) controlled the EC and pH of the solutions during shaking of all forty-one samples.

Figure 3.1: pH of all forty-one samples in dilute HNO₃ over time (Average of two replications).

Figure 3.2: EC of all forty-one samples in dilute HNO₃ over time (Average of two replications).

3.2. Ethylenediaminetetraacetic Acid Method

All forty-one overburden samples were also subjected to simulated weathering in 0.5 *M* Ethylenediaminetetraacetic Acid (EDTA) solution. The elements released by shaking with this solution resulted in different elemental concentrations than those released with the dilute HNO₃ solution; some were much less, while some were similar (Table 3.3). However, the proportion of elemental release was similar between EDTA and the dilute HNO₃ solution; i.e., iron and calcium were released in the greatest concentrations and manganese was released in the lowest concentrations. In general, elemental concentrations were constant after 168 hours (1 week of shaking) with EDTA as seen in Figures 1F to 1J (Appendix 1). Some samples continued to release high concentrations of elements even after a month of shaking, however due to time constraints, the shaking procedure was terminated at 168 hours.

In general, EDTA released lower amounts of elements during shaking compared to the dilute HNO₃ solution (Table 3.5). Aluminum concentrations ranged from 30 to 1,200 mg kg⁻¹

with EDTA, which were similar to aluminum concentrations released with the dilute HNO_3 solution. Also similar to the dilute HNO_3 solution, EDTA released a high concentration of iron and calcium. Average iron concentrations released from the overburden samples ranged from 180 to 7,000 mg kg^{-1} , which was essentially four times less than that from the dilute HNO_3 solution. Calcium concentrations, however, were greater with EDTA compared to dilute HNO_3 solution with concentrations ranging from 190 to 5,400 mg kg^{-1} , which was a similar finding in an EDTA-weathering study which found calcium to have the highest dissolution rate (Nowack and Sigg, 1996). The refuse sample (WV R) was an outlier, releasing 28,000 mg kg^{-1} of calcium after 168 hours of shaking. Magnesium concentrations ranged from 35 to 1,700 mg kg^{-1} with the refuse sample (WV R) releasing concentrations up to 4,600 mg kg^{-1} . Manganese was released from the overburden samples in the smallest quantities with average concentrations for all forty-one samples ranging from 4.0 to 1,200 mg kg^{-1} after 168 hours of shaking. Manganese release was not very different from the release of elements with the dilute HNO_3 solution. Anions were not analyzed due to the interference of EDTA with the seven anion standard solution.

Table 3.3: Mean elemental release at 168 hours of shaking in EDTA.

ID [†]	Sample	EC		pH		Al		Fe	
		Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
		dS m ⁻¹							
1	VA 1	47.2	1.3	8.1	0.1	44	95	1049	88
2	VA 2	47.2	1.1	8.1	0.1	145	10	3140	112
3	VA 3	47.2	1.0	8.2	0.1	529	36	1046	301
4	VA 4	47.4	0.8	8.2	0.1	413	73	563	88
5	VA 5	47.6	0.7	8.2	0.1	195	90	469	63
6	VA 6	47.6	0.5	8.3	0.1	350	24	1701	20
7	VA 7	47.6	0.3	8.2	0.1	384	61	799	47
8	VA 8	47.2	1.2	8.2	0.1	451	52	1109	30
9	VA 9	47.1	1.4	8.3	0.2	189	18	2899	273
10	VA 10	47.3	1.3	8.2	0.1	456	23	2255	8
11	VA 11	47.3	1.3	8.2	0.0	377	50	650	50
12	VA 12	47.4	1.3	8.2	0.0	109	12	1726	84
13	VA 13	47.3	1.2	8.2	0.1	81	15	825	43
14	VA 14	47.4	1.1	8.1	0.1	238	62	466	33
15	VA 15	47.5	0.8	8.1	0.1	323	37	6894	41
16	WV 1	49.0	0.7	8.2	0.1	36	63	726	82
17	WV 2	48.4	0.2	8.2	0.0	427	21	6251	1612
18	WV 3	48.6	0.1	8.2	0.1	492	249	2487	182
19	WV 4	46.8	1.3	8.3	0.2	443	2	5730	463
20	WV 5	46.5	2.2	8.2	0.1	121	83	2558	380
21	WV 6	46.7	2.2	8.2	0.1	84	52	1906	1501
22	WV 7	46.8	2.8	8.2	0.1	296	286	3353	1823
23	WV 8	46.6	2.5	8.2	0.0	371	315	4167	4187
24	WV 9	48.5	0.1	8.2	0.0	126	107	4623	339
25	WV 10	48.8	0.3	8.2	0.0	166	88	4840	704
26	WV 11	48.6	0.2	8.2	0.0	233	42	4922	412
27	WV 12	48.2	0.4	8.2	0.1	72	8	1557	34
28	WV 13	48.4	0.1	8.2	0.1	711	40	673	25
29	WV 14	48.3	0.2	8.1	0.0	88	40	2528	95
30	WVR	47.9	0.0	8.2	0.1	321	70	6937	1482
31	KY 1	45.5	2.5	8.2	0.2	54	62	188	658
32	KY 2	45.8	3.5	8.2	0.1	31	60	1692	838
33	KY 3	45.6	4.1	8.2	0.1	92	37	3036	625
34	KY 4	45.3	3.7	8.2	0.1	490	195	4196	409
35	KY 5	44.9	3.0	8.2	0.1	1196	482	1669	1731
36	KY 6	44.9	3.8	8.2	0.0	713	155	1665	64
37	KY 7	44.6	3.5	8.2	0.0	174	287	4001	1327
38	KY 8	45.3	6.1	8.2	0.0	211	86	1823	2081
39	KY 9	45.2	3.9	8.2	0.0	59	83	1585	1428
40	KY 10	45.3	3.5	8.2	0.0	50	51	782	1109
41	KY 11	45.9	2.9	8.2	0.1	127	11	1588	759

[†] ID corresponds to PCA figure Units in mg kg⁻¹

ID†	Sample	Ca		Mg		Mn	
		Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
1	VA 1	2112	154	428	12	126	7
2	VA 2	2274	30	943	12	181	6
3	VA 3	687	1764	329	112	138	32
4	VA 4	474	64	364	35	309	5
5	VA 5	590	90	243	13	217	4
6	VA 6	2152	166	607	11	289	11
7	VA 7	995	12	544	13	509	11
8	VA 8	827	108	349	31	37	11
9	VA 9	2879	198	531	35	145	9
10	VA 10	1812	83	762	18	143	1
11	VA 11	415	51	235	12	290	13
12	VA 12	1824	180	331	11	73	2
13	VA 13	982	84	514	25	306	15
14	VA 14	501	53	342	23	279	9
15	VA 15	5389	492	1661	34	227	3
16	WV 1	288	110	37	52	5	2
17	WV 2	977	66	544	192	156	57
18	WV 3	1252	17	284	90	24	1
19	WV 4	403	28	202	102	114	3
20	WV 5	2570	3275	477	644	106	22
21	WV 6	417	337	104	110	112	95
22	WV 7	1535	1410	369	193	92	11
23	WV 8	1517	1719	473	607	93	96
24	WV 9	4199	726	1306	380	130	21
25	WV 10	529	235	237	90	180	44
26	WV 11	1112	144	382	110	65	0
27	WV 12	393	1	134	89	15	1
28	WV 13	197	26	105	91	28	1
29	WV 14	1330	260	390	175	61	13
30	WV R	27745	7	4590	206	313	3
31	KY 1	430	119	184	22	103	42
32	KY 2	2363	953	746	318	62	45
33	KY 3	5641	1445	1165	149	177	61
34	KY 4	1303	3020	601	455	128	43
35	KY 5	694	617	151	321	1179	595
36	KY 6	592	296	420	137	671	290
37	KY 7	2912	1191	1187	441	452	281
38	KY 8	1481	1369	616	531	68	325
39	KY 9	916	588	447	227	79	35
40	KY 10	676	373	316	125	123	14
41	KY 11	809	10	449	107	209	65

† ID corresponds to PCA figure Units in mg kg⁻¹

For samples that were shaken in EDTA, the pH and EC of all overburden samples stayed relatively constant over the duration of the shaking period. Mean pH (Figure 3.3) for all forty-one samples was 8.2 ± 0.08 after 168 hours of shaking. Mean EC (Figure 3.4) for all overburden samples was $47.3 \pm 1.68 \text{ dS m}^{-1}$ after 168 hours of shaking. The background EDTA solution had a pH and EC of 8.0 and 49.1 dS m^{-1} , respectively, and controlled the pH and EC of all samples shaken in the solution.

Figure 3.3: pH from all forty-one samples in EDTA over time (Mean of two replications).

Figure 3.4: EC from all forty-one samples in EDTA over time (Mean of two replications).

3.3. Microwave Digestion Method

Microwave-assisted acid digestion is capable of breaking the mineral structure of the overburden samples and therefore released the largest quantity of elements compared to the two shaking methods (Table 3.3). This was expected due to the utilization of boiling concentrated nitric acid and hydrochloric acid. Table 3.4 displays the mean concentration of elements released via microwave digestion. In general, this method released constituent concentrations four to nine times more than the other two methods. Iron was released in the highest concentrations from the forty-one overburden samples. Mean iron concentrations ranged from 7,900 to 111,800 mg kg⁻¹. Aluminum concentrations ranged from 8,700 to 62,200 mg kg⁻¹. Calcium was also released in high concentrations, ranging from 600 to 41,800 mg kg⁻¹. Mean potassium concentrations for all forty-one samples ranged from 2,400 to 17,100 mg kg⁻¹. Magnesium ranged from 1,700 to 14,100 mg kg⁻¹, and sodium concentrations ranged from 440 to 2,800 mg kg⁻¹. Manganese and

Table 3.4: Mean elemental release from microwave digestion.

ID [†]	Sample	Al		Fe		Ca		Mg	
		Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
		mg kg ⁻¹							
1	VA 1	24106	5627	25944	1956	3871	307	4399	520
2	VA 2	48332	19370	46810	7878	6508	3006	9878	2041
3	VA 3	56243	8471	33669	1870	701	172	6191	765
4	VA 4	47985	3271	52945	1640	907	179	7119	559
5	VA 5	34590	3827	29075	2011	1139	143	3368	67
6	VA 6	53974	20620	53863	2767	4303	543	9493	1118
7	VA 7	48555	22098	53236	3134	2166	384	8594	1107
8	VA 8	58872	25721	38772	1937	2146	308	9153	1278
9	VA 9	37141	27965	41196	2271	6509	843	7904	857
10	VA 10	62279	21972	47387	2202	4453	507	11347	1353
11	VA 11	34522	11687	41273	1457	938	211	4137	540
12	VA 12	29657	14972	34271	2798	4320	578	6294	928
13	VA 13	34500	21584	44969	1058	2513	418	6733	859
14	VA 14	32355	17071	40740	2481	1006	210	3953	807
15	VA 15	52074	16450	60664	8505	11264	2364	14146	1669
16	WV 1	12770	1125	7906	1886	617	194	1773	262
17	WV 2	35321	4445	62930	11784	3252	339	7475	721
18	WV 3	51584	3069	19059	3911	2219	574	4837	483
19	WV 4	39289	18878	34342	8075	1861	427	4224	248
20	WV 5	24688	8347	40033	10022	945	290	2667	260
21	WV 6	8738	5442	30256	6576	1076	254	2822	511
22	WV 7	27367	491	79961	19684	6330	1759	10060	1582
23	WV 8	11688	5005	22029	4621	1587	370	3662	444
24	WV 9	12247	2075	37684	6243	10687	2861	6670	1122
25	WV 10	16759	1096	32779	7128	1830	470	4336	833
26	WV 11	27218	4349	30206	8154	2332	745	6525	1266
27	WV 12	11830	5891	16498	4516	1631	545	4057	1107
28	WV 13	9697	5524	20578	11197	962	378	2331	739
29	WV 14	16374	2762	26945	5541	3848	786	5147	1000
30	WV R	52043	19132	111879	22052	41850	12556	13339	2601
31	KY 1	15959	281	15246	4481	911	280	2209	404
32	KY 2	9712	6011	19443	4261	7028	1784	4612	770
33	KY 3	21415	12521	33319	8575	11038	3872	6679	1201
34	KY 4	34199	10715	52415	11346	3229	740	9020	1590
35	KY 5	31161	5629	33722	9057	1206	327	3363	535
36	KY 6	39271	7120	71920	17729	1005	318	8011	1044
37	KY 7	32798	3121	63668	11425	6698	1994	11437	1854
38	KY 8	38372	11653	43381	12565	3398	916	8957	1816
39	KY 9	22339	675	30237	7006	2604	696	5753	1000
40	KY 10	12770	2827	18588	7050	1398	438	2497	521
41	KY 11	35941	7865	47604	8645	2338	797	7457	1506

[†] ID corresponds to PCA figure

ID [†]	Sample	Mn		K		Na		P	
		Mean	Stnd Dev	Mean	Stnd Dev	Mean	Stnd Dev	Mean	Stnd Dev
		mg kg ⁻¹							
1	VA 1	477	52	8806	2154	602	362	465	78
2	VA 2	915	180	12646	4469	835	540	797	260
3	VA 3	376	53	13664	2148	704	538	599	297
4	VA 4	829	62	11039	385	838	287	677	98
5	VA 5	497	40	10426	1267	566	231	390	49
6	VA 6	801	91	14653	7100	748	283	991	214
7	VA 7	1031	154	13218	7722	655	354	1019	252
8	VA 8	439	49	14981	7429	639	533	913	526
9	VA 9	714	87	7866	3661	651	417	547	240
10	VA 10	832	93	17180	6835	1009	918	1012	294
11	VA 11	627	50	8766	4122	462	376	515	246
12	VA 12	737	116	9915	5725	449	281	574	131
13	VA 13	882	80	11238	8042	559	284	762	135
14	VA 14	725	93	7695	4908	455	460	468	307
15	VA 15	1035	183	15470	6110	1169	504	1164	195
16	WV 1	81	21	4099	208	497	61	75	16
17	WV 2	856	3	11463	1782	721	43	497	90
18	WV 3	189	44	14669	281	1007	21	222	53
19	WV 4	440	107	9545	3257	745	66	561	147
20	WV 5	650	193	6165	1214	833	193	256	55
21	WV 6	693	102	2521	1634	798	695	232	63
22	WV 7	1317	299	6031	99	860	614	683	200
23	WV 8	379	78	2597	1136	571	640	382	84
24	WV 9	909	137	4070	658	713	540	322	69
25	WV 10	364	92	4269	295	586	20	414	91
26	WV 11	338	99	7754	1171	653	235	252	81
27	WV 12	169	44	3033	1471	496	258	425	148
28	WV 13	372	156	2636	1431	508	242	236	63
29	WV 14	440	93	4844	671	620	163	311	63
30	WVR	700	160	14305	6215	2887	726	1742	506
31	KY 1	258	93	4166	105	571	165	274	110
32	KY 2	378	91	2440	1669	566	28	342	57
33	KY 3	631	169	5229	3104	726	73	483	126
34	KY 4	862	166	6549	2652	700	20	395	106
35	KY 5	1830	316	4485	673	599	63	562	162
36	KY 6	1800	162	8100	3015	731	123	1094	333
37	KY 7	1474	221	7549	1610	628	41	1333	394
38	KY 8	695	179	8039	2059	748	276	518	156
39	KY 9	564	166	6002	465	711	185	486	123
40	KY 10	388	139	3504	624	536	177	335	97
41	KY 11	748	163	7978	1635	727	348	613	127

[†] ID corresponds to PCA figure

phosphorus were released in the lowest concentrations ranging from 80 to 1,800 mg kg⁻¹ and 75 to 1,700 mg kg⁻¹, respectively.

Table 3.5: Mean of elemental release from the three different methods.

Method	Al	Fe	Mn	Mg	Ca
	----- mg kg ⁻¹ -----				
Dilute HNO ₃	707 ^B	8624 ^B	338 ^B	1167 ^B	2725 ^B
EDTA	223 ^B	1790 ^C	155 ^C	533 ^C	1968 ^C
Microwave Digestion	35034 ^A	40933 ^A	703 ^A	6702 ^A	4060 ^A

Different letters signify significant differences at p=0.05 level

3.4. Percent of Elements Released Compared to Microwave Digestion

Assuming that microwave digestion provided an almost total amount of each element that could be potentially released during weathering into the environment for each sample, the percentages released from the dilute HNO₃ and EDTA methods were calculated. For samples shaken in dilute HNO₃, low concentrations of aluminum (Figure 3.5) were release compared to the total amount available from microwave digestion, ranging from 0.5% to 9.0% for all forty-one samples. Iron concentrations released from the dilute HNO₃ solution ranged from 1.0% to 55% (Figure 3.6) of the total. Very high percentages of calcium were released with the dilute HNO₃ solution, ranging from 27% to 80% of the total (Figure 3.7). Magnesium concentrations ranged from 4.0% to 45% (Figure 3.8). Figure 3.9 displays the high percent of manganese released ranging from 16% to 73%.

Figure 3.5: Percent of aluminum released from the two shaking methods compared to “total” digestion.

Figure 3.6: Percent of iron released from the two shaking methods compared to “total” digestion.

Figure 3.7: Percent of calcium released from the two shaking methods compared to “total” digestion.

Figure 3.8: Percent of magnesium released from the two shaking methods compared to “total” digestion.

Figure 3.9: Percent of manganese released from the two shaking methods compared to “total” digestion.

Elements released from samples shaken in the EDTA solution were also compared to the microwave digestion concentrations to find percent release. Figures 3.5 through 3.9 present a visual representation of these percentages by element. Aluminum release ranged from 0.1% to 8.0% out of total microwave digestion concentrations for all forty-one samples. Iron release ranged from 1.0% to 20%. The percent of release for manganese ranged from 5.0% to 65%. Magnesium and calcium ranged from 2% to 35%, and 20% to 100%, respectively.

3.5. Comparison of the Three Methods

3.5.1. Regression

These three methods were compared via regression to test for relationships among concentrations of constituents released at their respective endpoints (i.e. 72 hours for the dilute HNO₃ samples, 168 hours for the samples shaken in EDTA, and concentrations obtained after microwave digestion.) Table 3.6 lists R² values for elements released using the dilute HNO₃ and

EDTA methods. The two shaking methods displayed strong relationships with respect to calcium, magnesium and manganese concentrations. Table 3.7 displays the relationship between microwave digestion and the dilute HNO₃ shaking method with respect to elements released. These two methods were strongly related in terms of calcium concentrations ($r^2 = 0.95$) released. Microwave digestion and shaking in dilute HNO₃ also showed a strong relationship with magnesium concentrations released from the overburden samples. Table 3.8 highlights R² values for elements released via microwave digestion and the EDTA method. As expected, calcium, magnesium, and manganese proved to be strongly correlated among all three methods.

Table 3.6: Relationship between dilute HNO₃ and EDTA in respect to elements released.

Element	R²	Trend
Aluminum	0.35****	Linear
Iron	0.60****	Linear
Manganese	0.34****	Linear
Magnesium	0.89****	Linear
Calcium	0.91****	Linear

**** Significant at the 0.0001 probability level.

Table 3.7: Relationship between microwave digestion and dilute HNO₃ in respect to elements released.

Element	R ²	Trend
Aluminum	0.19****	Linear
Iron	0.13*	Linear
Manganese	0.66*****	Linear
Magnesium	0.58*****	Linear
Calcium	0.95*****	Linear

*, ***, ***** Significant at the 0.05, 0.001 and 0.0001 probability levels, respectively.

Table 3.8: Relationship between microwave digestion and EDTA in respect to elements released.

Element	R ²	Trend
Aluminum	0.20*	Linear
Iron	0.19*	Linear
Manganese	0.67*****	Linear
Magnesium	0.59*****	Linear
Calcium	0.91*****	Linear

*, ***** Significant at the 0.05 and 0.0001 probability levels, respectively.

3.5.2. Elemental and Mineralogical Discussion

The earth's outer surface layer is primarily composed of oxygen (47%), silica (28%) aluminum (8%), iron (5%), calcium (4%), magnesium (2%), and sodium (3%) (Evangelou, 1998). Calcium from overburden samples in the Appalachian region is presumably in the form of calcite (CaCO₃) and is relatively soluble ($K_{sp} = 3.36 \times 10^{-9}$ at 25°C). In a mineralogical study conducted by the United States Geologic Service (USGS), they found that cores drilled in northern and southern coal fields of West Virginia were comprised of on average only 0.8% ± 3% calcite using X-ray Fluorescence (XRF) (Dulong et al., 2002). However, due to the relatively

high solubility of this mineral, strong relationships among these three methods were expected. Magnesium in the form of magnesium (II) carbonate is also relatively soluble ($K_{sp} = 3.5 \times 10^{-8}$ at 25°C). The USGS found that West Virginia strata were on average comprised of $0.3\% \pm 0.7\%$ dolomite ($\text{Ca,Mg}(\text{CO}_3)_2$) using XRF analysis. Magnesium could also be a by-product of weathered chlorite ($\text{Mg,Fe}_3(\text{Si,Al})_4\text{O}_{10}$), which makes up on average $2.0\% \pm 1.7\%$ of the coal bearing strata in West Virginia. Magnesium, however, may come from illite ($\text{(K,H}_3\text{O)}(\text{Al,Mg,Fe})_2(\text{Si,Al})$), which makes up $17.8\% \pm 12.4\%$ of the overburden strata in West Virginia coal fields (Dulong et al., 2002). Microwave digestion is capable of breaking the mineral structure, which could potentially release magnesium in 2:1 clays such as vermiculite ($\text{Mg,Fe}_2,\text{Al})_3(\text{Al,Si})_4\text{O}_{10}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$) and illite (Evangelou, 1998). Manganese ions in solution result from weathered manganese oxides and hydroxides. These three methods involve the submersion of overburden material in various solutions, which encouraged weathering of manganese oxides and hydroxides, thereby increasing solubility through the reduction of manganese (IV) to manganese (II) (Schwertmann, 1985).

Although iron release was not strongly correlated among the three methods, iron was released in the highest concentrations from all three methods. One reason may be that iron is commonly found in many minerals of the Appalachian region such as chlorite, siderite (FeCO_3), illite, hematite (Fe_2O_3), and pyrite (FeS_2), none of which are very soluble (FeCO_3 $K_{sp} = 3.13 \times 10^{-11}$, $\text{Fe}(\text{OH})_2$ $K_{sp} = 4.87 \times 10^{-17}$, FeS $K_{sp} = 8 \times 10^{-19}$, $\text{Fe}(\text{OH})_3$ $K_{sp} = 2.79 \times 10^{-39}$ at 25°C). Aluminum concentrations were also released in large amounts from the overburden samples due to the presence of aluminum in many minerals in this region. Planes of aluminum molecules are arranged hexagonally in dioctahedral sheets and these octahedral sheets combine with tetrahedral sheets to form layers that make up various minerals. Common minerals in the

Appalachian region which contain aluminum are chlorite, kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), illite, albite ($\text{NaAlSi}_3\text{O}_8$), and orthoclase (KAlSi_3O_8). Kaolinite and illite make up the largest proportions of the shale strata in this region ($15\% \pm 6.5\%$ and $17.8\% \pm 12.4\%$, respectively) (Dulong et al., 2002). Sulfate in the form of calcium sulfate is relatively soluble ($K_{\text{sp}} = 9.1 \times 10^{-6}$) and is a major ion of concern in contaminated mine drainage. Sulfate can contribute to as much as 50% of the TDS (Timpano et al., 2010), which was verified with some of the overburden samples in this study.

3.6. Determining the Best Method

When selecting a method to determine release of elements from overburden samples, several factors are important. Sample preparation, reproducibility, accurate correlation to field water quality measurements, time, the human health risk of exposure to chemicals, the amount of training needed for personnel to conduct analyses, and cost are all factors to consider. When considering four of these factors (time, risk, training, and cost), shaking with dilute HNO_3 proved to be a best method of the three alternatives (Table 3.9). Although shaking with dilute HNO_3 takes three days to get a maximum constituent release index, very little effort is needed to take the samples off of the shaker and to filter the samples prior to ICP-OES analysis. EDTA takes the same amount of effort, but at least five days are required to reach a maximum constituent release index, and aliquots from the samples must be diluted before ICP-OES analysis, unless special nebulizers are used. Microwave digestion only takes one day to run, but it takes more effort for sample preparation. Prior to microwave digestion, the samples are combined with hazardous concentrated acids and left in a fume hood for one day to let all emerging gases escape. For safety and risk, extreme caution should be taken when working with concentrated acids. The dilute HNO_3 solution is prepared by adding 2 mL of concentrated HNO_3 to 2 L of

water, so only a one-time exposure to a small volume of concentrated HNO_3 gave this method a moderate safety rating. EDTA is only slightly hazardous in case of skin and eye contact, as well as ingestion and inhalation, and was ranked a low safety risk. Microwave digestion had a high safety risk because it involved 12 mL of concentrated HNO_3 and HCl per sample. Extreme caution must be taken when working frequently with concentrated acids and in large quantities. No formal training is required for the dilute HNO_3 and EDTA methods, except for learning how to properly dilute and filter samples. Formal training is necessary for properly preparing samples and assembling digestion vessels for microwave digestion, and programming the microwave. The cost for the dilute HNO_3 method is relatively minimal. Very little acid is necessary for the preparation of dilute HNO_3 solution for a large number of samples. The preparation of EDTA requires a large mass of ethylenediaminetetraacetic acid disodium salt for 2 L of solution. Both of these methods also have costs associated with the Wrist-Action Shaker, the bottles used, filter paper, and ICP capabilities. The start-up cost associated with microwave digestion is very expensive if you do not have a laboratory-grade microwave and the appropriate vessels and associated equipment for preparation and operation. The use of two acids also increases the cost for this method. In terms of time, safety, training, and cost, the best method for determining elemental release from overburden material is the dilute HNO_3 method.

Table 3.9 Summary table of the three methods.

Method	Factors			
	Time	Safety Risk	Training	Cost
Dilute HNO ₃	3 days	Moderate	Low	\$
EDTA	5+ days	Low	Low	\$\$
Microwave	2 days	High	High	\$\$\$\$

Although dilute HNO₃ was the best method in terms of time, safety, training, and cost, it was imperative to test this method's (as well as the other two methods') ability to predict TDS release. We are assuming that EC is a preliminary indicator for TDS release potential. The sum of cations released from each method should give an approximate TDS concentration, and should ideally correlate with EC. The sum of cations released from all 41 samples from the microwave digestion technique was compared to the 2:1 EC obtained from all overburden samples (Figure 3.10). The R^2 of these two parameters was 0.31, however if you remove the refuse sample (WV R) from the dataset the relationship decreases to 0.07. The lack of relationship provided strong evidence that elements released from the microwave digestion method are not a useful tool for TDS release prediction. In a similar fashion, the sum of cations released from all 41 samples after 168 hours of shaking in the EDTA solution was compared to EC (Figure 3.11). No relationship ($R^2 = 0.55$, but decreases to 0.08 with the removal of WV R) existed between these two parameters, ruling out EDTA as a useful tool for TDS prediction. We had hoped that the cations released from the dilute HNO₃ method would have a strong relationship with EC, unfortunately this was not the case. The sum of cations released after 72 hours of shaking in dilute HNO₃ did not show a relationship with EC ($R^2 = 0.25$, but decreases to 0.09 with the

removal of WV R) (Figure 2.12). Although the dilute HNO_3 method was a relatively quick and easy method for weathering overburden material, it does not prove to be effective for TDS release prediction, and neither do the other two methods.

Figure 3.10: The sum of cations released from the microwave digestion method, compared to EC of the bulk sample.

Figure 3.11: The sum of cations released from the EDTA method, compared to EC of the bulk sample.

Figure 3.12: The sum of cations released from the dilute HNO₃ method, compared to EC of the bulk sample.

3.7. Determination of a TDS Release Index

Although the sum of cations from all three methods were ruled out as useful techniques for predicting TDS release, it was important to look at other parameters that may influence TDS. To do this, all further analysis was performed on concentrations acquired after three days of shaking using the dilute HNO₃ method. These samples had a charge balance error ranging from 41 to 97 percent. A positive charge balance error may indicate that one or more anions have been under-determined. We are making two assumptions that (1) bicarbonate is a prominent factor missing from this charge balance, and (2) carbonate is a by-product of weathering calcium carbonate. To validate these assumptions, the difference between the sum of cations (eq/L) and sum of anions (eq/L) was compared to calcium concentrations (eq/L). The resulting relationship suggested that bicarbonate was an essential component missing from the charge balance.

Principle Components Analysis (PCA) was first used as an exploratory analysis to determine which factors were most strongly related to TDS, and to quickly discard factors that

were not useful for TDS analysis. Figure 3.13 is a Scree Plot which is used as a visual representation of the appropriate number of principle components to use in a PCA. In this case, the first principle components accounted for about 64% of the variability within the original data set, and principle component 2 accounted for about 30% of the variation. Seventeen factors were analyzed for PCA: the cations - aluminum, iron, calcium, magnesium, manganese, potassium, phosphorus and sodium, and the sum of those cations; the anions - sulfate and chloride; chroma; paste pH; paste EC; calculated TDS from the paste EC; TDS measured as the sum of the cations and anions; and maximum potential acidity (MPA). Factor loadings are graphically demonstrated in Figure 3.14. The eigenvectors pointing in the lower left section of the plot showed strong similarities among paste EC (dS m^{-1}), maximum potential acidity (MPA) from the acid-base account analysis, and calculated TDS (mg L^{-1}). TDS was calculated using equations (1) and (2) provided by Evangelou, 1998.

$$\text{TDS} = 640 * \text{EC} (\text{dS m}^{-1}) \quad (1)$$

$$\text{TDS} = 640 * [\text{EC} (\text{dS m}^{-1})]^{1.087} \quad (2)$$

Since this TDS value was calculated from paste EC, this relationship was expected. However, it was not expected that a strong similarity existed between MPA and TDS. Paste pH, chroma, and cation eigenvectors point in opposite directions of calculated TDS, therefore we investigated this relationship further. Figure 3.15 examines the relationship between paste pH and calculated TDS. We expected to see an inverse relationship between pH and TDS because metals tend to go into solution at lower pH values, thus producing more dissolved solids, but this was not the case. Inspection of the relationship between chroma and calculated TDS produced an

apparent trend (Figure 3.16). Overburden samples with a chroma of 1 (gray) tended to produce high TDS (although with high variability), compared to samples with a chroma of 4 (brown), which produced very low TDS. The cation eigenvectors from PCA did not appear to influence TDS. R^2 values from linear regression verify PCA results that cation concentrations do not predict TDS release (Table 3.10).

Figure 3.13: Scree Plot for the determination of the appropriate number of principle components to use.

* Seventeen components were analyzed, but the variance after the ninth component was negligible and therefore not included in the figure.

Figure 3.14: Principle Components Analysis for the first two principle components. Numbers correspond to the sample ID described in figures 3.3 to 3.5.

Figure 3.15: The relationship between pH and TDS for all forty-one overburden samples.

Figure 3.16: The relationship between chroma and TDS for all forty-one overburden samples.

Table 3.10: The relationship between individual cations and calculated TDS for all samples, excluding outlier WV R.

Element	R^2	Trend
Aluminum	0.01	Linear
Iron	0.08	Linear
Manganese	0.13	Linear
Magnesium	0.12	Linear
Calcium	0.03	Linear

Neutralization potential (NP) (mt per 1000 mt of material) is an important parameter of the acid-base account that measures the alkalinity of overburden. We obtained NP data for the 14 West Virginia samples (not including the refuse sample WV R) from the coal company. NP versus TDS shows two outliers which happen to be WV 2 and WV 3 (Figure 3.17). These two samples had the highest NP (30 and 60 mt per 1000 mt of material) and also had the highest MPA (34 and 6.3 mt per 1000 mt of material) out of all of the West Virginia samples (Table 3.11). WV 2 is the only sample that produced more than 500 mg/L of TDS, and when looking more closely had the highest net acidity. WV 2 had almost equally high amounts of NP and MPA, which account for both the acidic and alkaline properties of the sample. When an acid and base react they produce water and a salt, which verifies the high TDS concentration of this particular sample. When removing these two outliers, NP and TDS have a relationship of $R^2 = 0.48$, which indicates that in general, as NP decreases, TDS increases (Figure 3.18).

Figure 3.17: Neutralization Potential (NP) versus TDS for all West Virginia samples.

Table 3.11: Neutralization potential provided from the coal company.

Sample	TDS [*] mg L ⁻¹	NP -mt per 1000 mt of material-	MPA	Net	pH
WV 1	53	25	0.7	-24	7.1
WV 2	1034	30	34	+ 4	4.1
WV 3	150	60	6.3	-54	7.2
WV 4	133	3	1.4	-2	6.4
WV 5	141	5	6.3	+ 1	6.3
WV 6	120	5	4.0	-1	6.6
WV 7	137	17	1.8	-15	8.0
WV 8	50	15	0.8	-14	7.3
WV 9	115	10	1.0	-9	8.1
WV 10	59	23	0.5	-23	7.3
WV 11	148	5	2.3	-3	7.6
WV 12	131	18	2.2	-16	7.2
WV 13	56	17	0.7	-16	6.9
WV 14	111	15	1.8	-13	7.8

^{*}TDS value is from the conversion of EC to TDS using Evangelou's equations.

NP: Neutralization Potential; MPA: Maximum Potential Acidity; Net: Net Neutralizing Potential

Figure 3.18: Neutralization potential versus TDS, excluding two outliers.

Percent sulfur was measured by another WVU student, Marianne Mannix, with a LECO CNS analyzer (TruSpec S, St. Joseph, MI). Percent sulfur, MPA, pH, and EC are shown in Table 3.11 for all overburden samples. MPA (mt per 1000 mt of material) was calculated by multiplying %S by 31.25. This conversion factor comes from the assumption that overburden containing 1% pyritic sulfur will yield an amount of sulfuric acid which would require 31.25 mt of calcium carbonate to neutralize 1000 mt of the material (Skousen et al., 1990). Figure 3.19 shows the relationship between MPA and TDS. When the y-axis is transformed to a log-scale, a strong relationship ($R^2 = 0.80$) is apparent with a power function. Based on this relationship, MPA ranging from 0.0 – 1.0 mt per 1000 mt of material will be categorized in the low TDS potential category because TDS did not exceed 150 mg L^{-1} . MPA roughly ranging from 1.0 to 3.0 mt per 1000 mt of material (Figure 3.17) produced a moderate amount of TDS (less than 300 mg L^{-1}), while MPA greater than 3.0 mt per 1000 mt of material produced concentrations of TDS that exceeded the USEPA's maximum contaminant limit of 500 mg L^{-1} . This high TDS limit is

not too distant from other literature where a value greater than 5.0 mt per 1000 mt in the Max Needed column of an acid-base account is flagged as likely to produce acid mine drainage, and samples below 5.0 are not likely to produce acid mine drainage (Skousen et al., 2002).

Table 3.12: Mean values for %S, MPA, paste pH, and paste EC

Sample	% S [†]	MPA	pH	EC [*]
VA 1	0.07	2.2	7.8	0.25
VA 2	0.26	8.0	7.2	1.01
VA 3	0.05	1.6	4.7	0.21
VA 4	0.02	0.8	5.1	0.10
VA 5	0.04	1.2	5.6	0.25
VA 6	0.12	3.7	7.1	0.61
VA 7	0.02	0.5	7.0	0.08
VA 8	0.16	5.0	6.7	0.44
VA 9	0.08	2.4	7.9	0.20
VA 10	0.08	2.6	7.8	0.25
VA 11	0.02	0.6	5.5	0.15
VA 12	0.04	1.4	8.0	0.14
VA 13	0.04	1.2	7.5	0.12
VA 14	0.02	0.7	6.0	0.09
VA 15	0.09	2.7	8.3	0.25
WV 1	0.02	0.7	7.1	0.08
WV 2	1.08	34	4.1	1.56
WV 3	0.20	6.3	7.2	0.24
WV 4	0.04	1.4	6.4	0.21
WV 5	0.20	6.3	6.3	0.22
WV 6	0.13	4.0	6.6	0.19
WV 7	0.06	1.8	8.0	0.21
WV 8	0.02	0.8	7.3	0.08
WV 9	0.03	1.0	8.1	0.18
WV 10	0.02	0.5	7.3	0.09
WV 11	0.07	2.3	7.6	0.23
WV 12	0.07	2.2	7.2	0.20
WV 13	0.02	0.7	6.9	0.09
WV 14	0.06	1.8	7.8	0.17
WV R	6.83	213	6.0	3.51
KY 1	0.02	0.6	6.8	0.08
KY 2	0.01	0.2	8.2	0.12
KY 3	0.09	2.8	7.8	0.39
KY 4	0.12	3.9	6.4	0.59
KY 5	0.01	0.4	5.3	0.10
KY 6	0.02	0.5	5.5	0.03
KY 7	0.90	28	5.4	2.42
KY 8	0.12	3.7	7.0	0.57
KY 9	0.23	7.3	5.4	1.16
KY 10	0.13	3.9	4.6	0.86
KY 11	0.05	1.5	6.8	0.25

*EC in dS m⁻¹

† Values obtained by Marianne Mannix

Figure 3.19: Maximum Potential Acidity versus TDS.

[†]MPA in units of mt per 1000 mt of material

Figure 3.20: MPA versus TDS with high, medium, and low release indices.

[†]MPA in units of mt per 1000 mt of material

This TDS release index is effective when comparing various elemental concentrations with TDS release from the forty-one overburden samples shaken in dilute nitric acid (Figures 1K to 1P, Appendix 1). Future research will be conducted to obtain NP values for all of these samples. Some particular samples have an MPA greater than 3.0 but do not produce TDS concentrations greater than 500 mg L^{-1} . This may be due to a high NP value, which can balance out the acidity, and potentially decrease TDS. Likewise, few samples have an MPA less than 3.0 but produce greater than 500 mg L^{-1} TDS and this may also be due to a high NP value.

3.8. Calculated TDS from WVU Compared to Virginia Tech's Leaching Columns

For this section, I will refer to the results of the shaking experiment with dilute HNO_3 as the “WVU study,” and the results of a leaching experiment conducted at Virginia Polytechnic Institute and State University as the “Virginia Tech study.” The TDS index obtained from the WVU study is only hypothetical unless it can be correlated and compared to other laboratory and field leaching studies. Virginia Tech has been conducting a similar weathering experiment using leaching columns with the same overburden samples used in the WVU study. Virginia Tech's data on elements leached from columns (Daniels et al., 2012) were compared to the results from the WVU study to determine how WVU's TDS release index relates to Virginia Tech's column leaching data. Figure 3.21 displays EC from Virginia Tech's leaching columns for fifteen overburden samples. The EC is high during the first few leachings and decreases drastically until it tails out for the remainder of the leachings. The peak provides a prediction for short-term EC release, and the tail provides a prediction for long-term EC release. To test if the index of low TDS potential (0.0 – 1.0 MPA), moderate TDS potential (1.0– 3.0 MPA), and high TDS potential (3.0 + MPA) fits Virginia Tech's leaching data; Virginia Tech's maximum, minimum, and average EC was first converted to calculated TDS (mg L^{-1}) using formulas (1) and (2), and

then compared to the MPA values obtained by WVU. Prior to correlating Virginia Tech's samples to MPA, the sum of cations released from the three WVU methods were first compared to Virginia Tech's calculated TDS, but still no relationship was found (Figures 1W-1Y, Appendix 1). Fortunately, The TDS of the WVU samples had a strong relationship with Virginia Tech's maximum, average, and minimum TDS with an R^2 of 0.85, 0.81, and 0.86, respectively (Figure 3.22).

Figure 3.21: A visual representation of Virginia Tech's column leaching data for EC.

Figure 3.22: Relationship between maximum, average, and minimum TDS calculated from EC at Virginia Tech versus TDS calculated from EC at WVU.

The relationship between MPA and average TDS obtained from Virginia Tech's leaching columns can be found in Figure 3.23. The y-axis does not need to be transformed for a strong relationship ($R^2 = 0.96$) to be apparent. Using the line of best fit, once MPA reaches 3.0, TDS is approximately 500 mg L^{-1} . This finding reflects the results inferred from Figures 3.19 and 3.20, where MPA ranging from 0.0 to 1.0 produced low TDS (less than 300 dS m^{-1}), MPA ranging from 1.0 to 3.0 produced a moderate amount of TDS (300 to $<500 \text{ dS m}^{-1}$), and MPA greater than 3.0 produced high TDS ($>500 \text{ dS m}^{-1}$) (Table 3.13). The minimum TDS value (long-term prediction of TDS release) was also compared to MPA (Figure 3.24), validating that an MPA of 3.0 will release approximately 500 mg L^{-1} TDS. Figure 3.25 shows the relationship between maximum EC (short-term prediction from Virginia Tech's columns) and MPA, which does not support the TDS release index.

Figures 1Q to 1V (Appendix 1) show the relationship between average elemental concentrations released from Virginia Tech's leaching columns versus their calculated TDS. It is apparent that some samples have MPA values of 3.0 mt per 1000 mt of material and produce over 500 mg L⁻¹ TDS. However, these samples may be high in NP, which may contribute to TD. They samples could also be very low in NP and not quite capable of neutralizing the acidic properties of the rock, which could contribute to TDS. NP data must be collected to fully understand this relationship.

Figure 3.23: Maximum Potential Acidity versus Average TDS from Virginia Tech
[†]MPA in units of mt per 1000 mt of material

Figure 3.24: Maximum Potential Acidity versus Minimum TDS from Virginia Tech
[†]MPA in units of mt per 1000 mt of material

Figure 3.25: Maximum Potential Acidity versus Maximum TDS from Virginia Tech
[†]MPA in units of mt per 1000 mt of material

Table 3.13: TDS release index using Maximum Potential Acidity.

TDS Release Index	TDS Concentration	MPA [*] Range
Low	< 300	0.0 – 1.0
Medium	300 - 500	1.0 – 3.0
High	> 500	3.0 +

^{*}MPA in units of mt per 1000 mt of material

To confidently use this TDS release index, a wider variety and number of overburden samples should be collected, and field studies must be conducted. If this release index holds true for future studies, than MPA and EC may be the only two factors necessary for a relatively quick and accurate prediction of TDS release. The dilute HNO₃ method is still useful for analyzing constituent release from overburden, but may not be necessary if MPA and EC are all that is needed for the development of a TDS index.

4. Conclusion

West Virginia is the largest coal-producing state in the Appalachian coal region (U.S. Energy Information Administration, 2012), and the coal industry has been at the forefront of controversy concerning human and environmental health and safety. To remove coal, overburden material must be blasted and moved. Overburden is then subjected to accelerated weathering, which promotes the release of soluble constituents into the environment. Depending on the chemical composition of the rock, weathering of these broken rocks can promote acid mine drainage, alkaline mine drainage (Berhhardst et al., 2012) as well as the release of heavy metals, and total dissolved solids. The Acid-Base Account has been a successful tool for predicting post-mining water quality, by focusing on the acidity (maximum potential acidity) and alkalinity of the rock (neutralization potential), but there is no current tool for predicting TDS related water quality issues.

The goal of this research was to determine a TDS release index for overburden material. Three weathering techniques were developed to determine which parameters are most strongly linked to TDS release. EC was converted to TDS using formulas (1) and (2) from Evangelou, 1998. TDS release was compared to cations, anions, pH, EC, %S, MPA, NP (partially provided from the coal operator), and chroma. There was a strong relationship between TDS and MPA ($R^2 = 0.80$), and provided evidence for a low, moderate, and high TDS release index using MPA ranging from 0.0 – 1.0, 1.0 – 3.0, and 3.0 +, respectively (Table 3.12).

To validate these preliminary results, Virginia Tech's column leaching data were used for comparison. Virginia Tech's average and minimum TDS values validated our TDS release index using MPA; however Virginia Tech's maximum TDS did not. With these results we can use MPA to determine a TDS release index, as listed in Table 3.12. MPA and EC can be used as a

quick test to determine which overburdens may need further analysis so that operators can properly treat, isolate and/or handle their overburden in a manner that will decrease TDS runoff from their site.

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APPENDIX 1

Figure 1A: Aluminum released from all forty-one samples in dilute nitric acid over time (mean of two replications).

Figure 1B: Iron released from all forty-one samples in dilute nitric acid over time (mean of two replications).

Figure 1C: Calcium released from all forty-one samples in dilute nitric acid over time (mean of two replications).

Figure 1D: Magnesium released from all forty-one samples in dilute nitric acid over time (mean of two replications).

Figure 1E: Manganese released from all forty-one samples in dilute nitric acid over time (mean of two replications).

Figure 1F: Aluminum released from all forty-one samples in EDTA over time (mean of two replications).

Figure 1G: Iron released from all forty-one samples in EDTA over time (mean of two replications).

Figure 1H: Calcium released from all forty-one samples in EDTA over time (mean of two replications).

Figure 1I: Magnesium released from all forty-one samples in EDTA over time (mean of two replications).

Figure 1J: Manganese released from all forty-one samples in EDTA over time (mean of two replications).

Figure 1P: Sulfate versus TDS from WVU with line indicating maximum contaminant limit of 500 mg L⁻¹, numbers indicate MPA values.

Figure 1Q: Aluminum versus TDS from Virginia Tech, with line indicating maximum contaminant limit of 500 mg L⁻¹, numbers indicate MPA values.

Figure 1T: Magnesium versus TDS from Virginia Tech, with line indicating maximum contaminant limit of 500 mg L⁻¹, numbers indicate MPA values.

Figure 1U: Manganese versus TDS from Virginia Tech, with line indicating maximum contaminant limit of 500 mg L^{-1} , numbers indicate MPA values.

Figure 1V: Sulfate versus TDS from Virginia Tech with line indicating maximum contaminant limit of 500 mg L^{-1} , numbers indicate MPA values.

Figure 1W: Virginia Tech's calculated TDS versus the sum of cations from the dilute nitric acid solution.

Figure 1X: Virginia Tech's calculated TDS versus the sum of cations from the EDTA solution.

1Y: Virginia Tech's calculated TDS versus the sum of cations from microwave digestion.