

**Assessment of Sustained Impacts from the
Kingston Fossil Plant Coal Ash Spill on Surface
Water and River Sediments in Eastern Tennessee**

A Thesis Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

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May 2018

ACKNOWLEDGEMENTS

First and foremost, I would like to thank the U.S. Department of Interior, the U.S. Geological Survey Grant (No. G16AP00084) and Dr. Anna Szyrkiewicz whose financial support made this project possible. A special thank you to my advisor, Dr. Anna Szyrkiewicz, for taking me on as a new graduate student two years ago and allowing me to work on a project that greatly interests me. Her expertise in geochemistry and stable isotopes were invaluable towards furthering my knowledge. I appreciate her insightful guidance and thought-provoking questions which challenged me to develop my ideas and complete this project. I would like to thank my committee members Dr. Jon Hathaway and Dr. Terry Hazen for their advice, discussions and continued interest in my work. Additionally, I could not have completed sampling, lab work, or successfully written this thesis without the assistance and validation of our lab manager, Dr. Anthony Faiia, and my lab mate, Jessi Ende. Many thanks to Diego Sanchez, Caleb Smith and the scuba divers Justin Coleman and Jared Malone for help during water and sediment sampling, and to Adrian Gonzalez for assistance with ICP-OES measurements. Finally, thank you to my family and friends for their continued encouragement in pursuing my career and enthusiasm towards my geology jokes and conversations about rocks.

ABSTRACT

In December 2008, the failure of a coal ash retention pond at the Kingston Fossil Plant contaminated the Emory River, Clinch River and Watts Bar Reservoir with toxic metals. Despite an extensive cleanup effort, further leaching of toxic metals from river sediments remains a cause of concern. In spring 2016, new water and sediment samples were collected from seven contaminated and three uncontaminated portions of the river systems for trace metal and H-C-O-S-N isotopic analyses. In the water column, the trace metals were below detection limit (<0.002 mg/L) and only Mn (0.11-0.29 mg/L) slightly exceeded the EPA human health guideline (0.05 mg/L) in two locations. However, the concentrations of As and Cd within the river sediments (3.5-10.9 and 0.7-2.2 mg/Kg, respectively) exceeded the sediment quality guidelines (8.2 mg/kg and 1.2 mg/kg, respectively). While no other trace metals (Cr, Cu, Ni, Pb, Zn) surpassed the established toxicity guideline levels, they were in highest concentrations further away from the spill location. This suggests important metal fluxes to the river sediments from other anthropogenic sources and/or bedrock dissolution. In the most contaminated sediment layers, the $\delta^{34}\text{S}$ [sulfur isotopic value] was the highest (+4 to +11‰ [per mil]) reflecting that of combusted coal (+9 to +12‰). Using sulfur isotopes, it was determined that the remaining coal ash is currently buried by at least ~5 cm thick layer of younger sediments. The measured low $\delta^{34}\text{S}$ values of elemental S (-3.5 to +1.1‰), acid-volatile sulfides (-2.7 to +1.1‰) and chromium-reducible sulfides (-6.9 to +1.3‰) in the uncontaminated sites suggest that microbial sulfate reduction is active in the studied rivers. However, the role of this process appears to be minor/negligible in the bio-immobilization of trace metals from coal ash spill. Other natural processes such as dilution, sedimentation, and dissolution of carbonate bedrock are more important in decreasing trace metal fluxes and burial of coal ash contaminants over time. It is evident that in addition to the 2008 coal ash spill these river systems continue to be negatively impacted by other metal contaminants from industry, mining, etc., thus continued research on the potential for toxicity in the Kingston region is necessary.

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CHAPTER ONE

INTRODUCTION

To date, the 2008 coal ash spill in Kingston, TN is the largest in U.S. history (Greeley et al., 2014; Ruhl et al. 2009) which caused contaminated waters to have elevated levels of toxic metals within seven miles of the main ash retention pond. These metals included As, Cu, Ba, Cd, Cr, Pb, Hg, Ni, and Tl (Stojak et al., 2015; Sherrard et al., 2015 Greeley et al., 2014; Stanley et al., 2013; Otter et al., 2013; Reash, 2012). Additionally, the spill killed hundreds of fish and contaminated many aquatic species within the river system (Greeley et al., 2014; Otter et al. 2013). This accident caused residents to question the quality of their drinking water and cease recreational activities within the seven-mile radius of the spill. In August of 2009, approximately nine months after the spill, the Environmental Protection Agency (EPA) officially closed the most contaminated sections of the Emory River around the spill site. The area was reopened to the public in the summer of 2010 after major remediation efforts were completed (TVA, 2016).

Since 1967, there have been roughly 24+ major coal ash spills in the U.S. (e.g., TVA Kingston Fossil Plant, Duke Energy Dan River Plant, Massey Energy Martin County Plant; Lemly, 2014). Over this period, ~\$3 billion have been spent on remediation efforts (Lemly, 2014). The Kingston spill was largely studied within three years after the accident. During this time, elevated concentrations of several trace metals (e.g. As and Hg) in river water and sediments were reported (Greeley et al., 2014; Ruhl et al., 2010, 2009). However, there is general disagreement on current water quality in the Kingston area. For example, Greeley et al. (2014) concluded that measured trace metal concentrations are not high enough to have a negative impact on human or aquatic life. In contrast, Sherrard et al. (2015) reported that trace metal concentrations remain elevated in the riverbed sediments and have the potential to harm existing aquatic ecosystems. These conflicting results indicate the necessity for continued research on the river systems surrounding the Kingston power plant and new estimates on what are the current metal concentrations roughly eight years after the spill.

Historically, some microbial processes have been effective in immobilization of toxic metals introduced to aquatic environments by various human activities. Research shows that microbial sulfate reduction (MSR) has been successful in remediating metal contamination from acid mine drainage (AMD) and other mining wastes by formation of insoluble metal sulfides (Herlihy and Mills, 1984). Since MSR has been observed in many freshwater sediments (Dvorak et al., 1992; Herlihy and Mills, 1984), this process has the potential to enhance natural remediation of toxic metals from coal ash spills. However, there are no studies evaluating whether MSR is sufficient in bio-immobilization of trace metals within river sediments contaminated by coal ash spills, thus, further research is necessary.

The long-term effects of coal ash spills can be studied with multiple chemical and stable isotope tracers. While trace metal concentrations provide useful information about existing toxicity levels, the stable isotope compositions of carbon ($\delta^{13}\text{C}$), nitrogen ($\delta^{15}\text{N}$), sulfur ($\delta^{34}\text{S}$), hydrogen ($\delta^2\text{H}$), and oxygen ($\delta^{18}\text{O}$) allow for studying biogeochemical cycling of these species and their flow paths in the environment (Peterson and Fry, 1987). This is mainly because the isotopic compositions of environmental materials change in predictable ways as they move through the biosphere, lithosphere, and hydrosphere, and can be measured with great precision using various mass spectrometry methods (Peterson and Fry, 1987). While coal typically shows similar isotopic compositions to modern organic materials (e.g. $\delta^{13}\text{C}$ of -27 to -21‰, $\delta^{15}\text{N}$ of $\sim +2$ ‰, $\delta^{34}\text{S}$ -4 to +14‰), after combustion, the isotopic composition of the coal combustion residuals (CCRs) are usually different (e.g. $\delta^{13}\text{C}$ of -31 to -29‰, $\delta^{15}\text{N}$ of +9.6 to +25.6‰, $\delta^{34}\text{S}$ +8 to +12‰; Warwick and Ruppert, 2016; Felix et al., 2012; Jiang et al., 2008; McRae et al., 1999). These changes in isotopic composition can be utilized as tracers for residual CCR contaminants remaining in the Emory River, Clinch River, and Watts Bar Reservoir.

CHAPTER TWO

RESEARCH OBJECTIVES AND HYPOTHESES

The goal of this study is to contribute to the knowledgebase as to the effectiveness of the clean-up efforts conducted by the Tennessee Valley Authority (TVA) and EPA in removing trace metal contaminants of the coal ash spill from the Emory River, Clinch River, and Watts Bar Reservoir. Specifically, the major objectives of this research project that will aid in this understanding are:

- 1) To characterize which trace metals, if any, in the river water and sediments are sourced from the remaining coal ash contaminants.
- 2) To delineate if microbial sulfate reduction was involved in the bio-immobilization of trace metals induced by coal ash spilling into the riverbed sediments.

My first null hypothesis is that the remediation efforts put forth by the TVA and EPA were successful in removing major contaminants (e.g., coal ash particles, trace metals) from the water bodies and river bottom sediments, thus, leaving no future threat of contamination to the aquatic ecosystem. The alternative hypothesis is that the remaining heavy metals from the coal ash spill are in higher concentrations in contaminated sites compared to uncontaminated river sediments. Additionally, I propose a second null hypothesis that microbial sulfate reduction has been a successful aid in the bio-immobilization of toxic trace metals in the river bottom sediments through the formation of insoluble metal sulfides.

These hypotheses will be tested through six approaches; (1) the measurement of major ion and trace metal concentrations of both water and riverbed sediment samples, (2) dissolved inorganic and organic carbon (DIC and DOC) concentrations, (3) determination of water isotope composition, (4) sulfur (S) and oxygen (O) isotope compositions of sulfate (SO_4^{2-}), (5) nitrogen (N) and O isotope compositions of nitrate (NO_3^-) in the water column, and (6) quantitative and isotope analyses of reduced sulfur species (S^0 , S^- , S^{2-}) in the anoxic riverbed sediments.

CHAPTER THREE

BACKGROUND

3.1. Contaminants from coal power plants

Coal-fired power plants produce over 130 million tons of industrial waste each year in the United States in the form of coal combustion residuals (CCRs), also known as coal ash (Wang et al., 2009). CCRs include fly ash, bottom ash, and flue gas desulfurization waste (Harkness et al., 2016; Schwartz et al., 2013). While CCRs can be reused to create concrete, drywall, and other construction materials, over 56% of CCRs are disposed in long-term surface impoundments and landfills (Harkness et al., 2016, Ruhl et al., 2012; Luther, 2011). CCRs are majorly a fine particulate that is mixed with water for storage so that it does not escape into the atmosphere with produced S and N gases (Luther, 2011). Nationwide, there are over 300 landfills and 600 retaining ponds for CCR disposal (Schwartz et al., 2013). Coal ash is enriched in trace metals (e.g. As, B, Cr, Hg, Mo, Pb, Sb, Se, V, and Zn) that, while found naturally in the environment, can be toxic to all organisms at elevated levels (Harkness et al., 2016, Sherrard et al., 2015; Stojak et al., 2015; Otter et al., 2013; Reash, 2012; Luther, 2011). Unfortunately, 42% of coal ash retention ponds found within the United States are unlined and open to leaching into the subsurface, allowing for potential environmental contamination (Luther, 2011). Since 1955, the United States EPA CCR Management Rule has reported 40 coal ash spills and 113 potential contamination cases related to the disposal of coal ash in long-term retention ponds (US EPA, 2016).

In 1955, the TVA built the Kingston Fossil Plant, once the world's largest coal-fired power plant (TVA, 2016). Located 40 miles southwest of Knoxville, TN, the Kingston Fossil Plant lies on a peninsula at the intersection of the Emory River, Clinch River and Watts Bar Reservoir on the Tennessee River. The plant is capable of powering over 700,000 homes which equates to about 10 billion kilowatt/hours of electricity per year (TVA, 2016). To reduce gas emission into the atmosphere, the plant utilizes low S coal, reduced catalytic converters, and scrubbers (TVA, 2016). Consequently, in recent years the plant has reduced its emissions of SO₂ and NO into the atmosphere by 90 and 95 %, respectively (TVA, 2016). However, the Kingston plant still produces as much as 300,000 tons of coal ash waste each year that was stored in its onsite retention pond constructed in 1955 (Luther, 2011). The retention pond was unlined allowing for leaching of trace metals into the subsurface and located on the confluence of three river systems, thus, increasing the chance of contaminating these rivers (TVA, 2016; Luther 2011).

On December 22, 2008, the TVA Kingston Fossil Plant retention pond ruptured allowing 4.1 million cubic meters of coal ash to flow four miles upstream into the Emory and Clinch Rivers and seven miles downstream into the Watts Bar Reservoir (Stojak et al., 2015; Greeley et al., 2014; Stanley et al., 2013). In total, 300 acres of land was affected by this accident (Bednar et al., 2010). The wave of coal ash sludge washed out one road, ruptured a major gas line, destroyed power lines, and inundated a rail line (Bednar et al., 2010). Twelve homes were flooded with the sludge, including one pushed off its foundation into a nearby road (Bednar et al., 2010). Although 54 properties were damaged, no persons were reported injured in the spill (Bednar et al., 2010).

3.2. Remediation of Kingston coal-ash spill

After the spill in Kingston, major remediation efforts were required to reduce contamination in the Emory River, Clinch River and Watts Bar Reservoir. Most remediation efforts included the physical removal of coal ash from the bottom of the Emory and Clinch Rivers (TVA, 2016; Bednar et al., 2010). From the winter of 2009 through spring of 2010, high intensity dredging projects were implemented, utilizing as many as five hydraulic dredges capable of removing simultaneously 8,000 cubic meters of ash per day. The dredged ash was pumped through a pipeline into an ash recovery ditch, allowing heavy particles to settle. Afterward, the heavier particles were mechanically excavated, dewatered, and transported to an approved landfill in Alabama (TVA, 2016; Bednar et al., 2010). The lighter particles were mixed with the plant cooling water and left in a stilling pond before releasing the water back into the Emory River. Additional remediation efforts included: (1) capturing of cenospheres (e.g., hollow glass spheres formed during coal combustion) on the water surface using floating orange booms until they could be pumped from the water and properly disposed, (2) construction of a 13-foot cement containment wall (the largest of its kind), (3) lining and closing the original coal ash retention pond, and (4) mechanical excavation of coal ash from the impacted land area (TVA, 2016; Bednar et al., 2010). Additionally, EPA and TVA repaired some homes, pipelines, and rail lines impacted by the spill, and many of the damaged properties were purchased by the TVA outright (TVA, 2016). All remediation efforts cost over \$1.1 billion and took nearly 6 years to complete (TVA, 2016).

3.3. Impacts of Kingston coal-ash spill

Multiple studies have been conducted in the Kingston area to evaluate the impact of the toxic metals released by the coal ash spill on the water column and benthic and fish ecosystems (Greeley et al., 2014; Bartov et al., 2013; Ruhl et al., 2010, 2009). Immediately following the spill, in January through March of 2009,

Ruhl et al. (2009) conducted a study on water column and riverbed sediments collected near the shoreline of the Emory and Clinch rivers, beginning at the spill site and extending about four miles upstream of each river. River water samples, on average, did not show concentrations above the EPA maximum contamination level (MCL) guidelines for aquatic life, except for concentrations of As. However, in almost all water samples, concentrations of As (0.0001-0.0856 mg/L) exceeded the EPA human health MCL of 0.000018 mg/L as well. Unfortunately, water samples were collected near the banks of the rivers, and may be an underestimate of true dissolved trace metal concentrations. The follow-up study, in January 2009 to June 2010 by Ruhl et al. (2010), showed similar trace metal concentrations as the ones found in Ruhl et al. (2009). For example, the pore water of sediment cores collected from similar locations showed increasing concentrations of trace metals with depth (Ruhl et al., 2010). However, only As exceeded the EPA MCLs (OW US EPA, 2015a; Ruhl et al., 2010). In the next study, Greeley et al. (2014) collected sediment samples at the spill site and roughly one mile upstream. These sediments ranged in coal ash concentration from 46 to 78 wt.% and had elevated concentrations of As, Se, and Hg compared to uncontaminated upstream sediments (Greeley et al., 2014). Through lab tests on embryonic fathead minnows, Greeley et al. (2014) concluded that there are no negative effects on larval development of the fish. Therefore, they suggested that the coal ash remaining in the Watts Bar reservoir does not pose any risk to the developing fish populations. In contrast, other studies (Stojak et al., 2015; Sherrard et al., 2014) proposed that high concentrations of As, Se, B, Sr, and Ba in the Emory and Clinch river bottom sediments, containing up to 40% of coal ash, pose a threat to microbial communities within sediments and can be leached back into the water column, or concentrated through bioaccumulation, causing future harm to the local aquatic ecosystem.

Generally, current trace metal concentrations (about eight years after the spill) are unknown for the Emory River, Clinch River, and Watts Bar Reservoir. Therefore, this study will aim to provide new results on trace metal concentrations, within both the river water column and bottom sediments, that can be compared to previous studies completed shortly after the ash spill.

3.4. Isotope Tracers

As C, N, and S cycle through the biosphere, lithosphere and hydrosphere their isotopic compositions will change in predictable ways through various fractionation processes which have become relatively well known over last few decades (Chen et al., 2009; Knöller et al., 2005; Peterson and Fry, 1987). This study aims to utilize the $\delta^{13}\text{C}$ values of DIC, DOC and sediment to better understand the major carbon sources for each of these pools in three river systems of the Kingston area. The $\delta^{13}\text{C}$ values of organic matter can be used to determine sources of organic carbon in the studied river sediments. Due to the unique carbon

isotopic compositions of terrestrial and aquatic organic materials, it is often possible to determine if these materials constitute a significant portion of the river and lake sediments. The major sources of terrestrial detritus include C_3 and C_4 plants which are known to have average $\delta^{13}C$ values of -27 and -13‰, respectively, in a temperate forest (Kohn, 2010; Kendall et al., 2001). Aquatic sources usually include phytoplankton, algae and macrophytes with average $\delta^{13}C$ values of -30, -23, and -24‰, respectively. It has been found that phytoplankton account for almost 50% of the particulate organic matter (POM) within freshwater sediments due to large plankton blooms that occur in the summer (Kendall et al., 2001). Given the large proportion of phytoplankton (-30‰) in river sediments and the dominance of C_3 (-27‰) flora in eastern Tennessee, the expected $\delta^{13}C$ of the studied river sediments should be similar to these two endmembers.

Like with C, understanding the sources of N and its cycling has gained attention due to the impact of NO_3^- on water contamination and N gases such as N_2O on global warming (Chen et al., 2009). N isotopes will be utilized to determine major NO_3^- sources and nutrient cycling in the Emory River, Clinch River, and Watts Bar Reservoir. By plotting $\delta^{15}N$ values vs. $\delta^{18}O$ values of NO_3^- , sources like precipitation (-10 to +1‰), fertilizer (-10 to +6‰), soil organics (+1 to +8‰), and manure/septic waste (-1 to +24‰) can be differentiated.

In a similar fashion, the $\delta^{34}S$ and $\delta^{18}O$ from dissolved SO_4^{2-} can be plotted to differentiate between major SO_4 sources. These include S oxidation (-10 to -3‰), soils (0 to +10‰), evaporite dissolution (+8 to +15‰) and anthropogenic inputs such as acid rain (0 to +11‰). While SO_4^{2-} is not a major concern for contamination, it is often linked to the degradation of water quality. Additionally, processes like sulfide oxidation can result in the production of H_2SO_4 , reducing the pH and DO concentration of water and potentially harming local ecosystems (Knöller et al., 2005).

3.5. Microbial Processes

Coal combustion produces a waste that is highly toxic to the environment (Wang et al., 2009) as it contains elevated concentrations of trace metals, which are highly mobile in acidic and alkaline waters (Gomes et al., 2015). When coal ash spills occur, mitigating the contaminants before they spread across large areas and contaminate drinking water becomes important. However, there are natural processes that may aid in this remediation and lessen the extent of contamination (Herlihy and Mills, 1984). One such process is microbial sulfate reduction (MSR) (Dvorak et al., 1992; Herlihy and Mills, 1984). Sulfate reducers utilize sulfate and organic carbon from surface and pore waters to produce H_2S gas, which reacts with trace metals. As a result, various insoluble sulfides are formed. Frequently, this process is referred to as bio-immobilization. Examples of trace metals that often form insoluble sulfides, and are also abundant in coal ash, include As^{6+} , Cr^{6+} , Fe^{3+} , Se^{6+} , and U^{6+} (Muyzer and Stams, 2008).

Acid mine drainage is a good example of a pollutant that has been effectively remediated through MSR (Herlihy and Mills, 1984). In addition to elevated metal concentrations, AMD contains high concentrations of SO_4^{2-} which, in turn, stimulates sulfate reduction in the presence of organic material (Herlihy and Mills, 1984). This process ultimately reduces acidity and causes the precipitation of trace metals as metal sulfides, which are relatively insoluble in natural waters (Herlihy and Mills, 1984). It has been shown that up to 95% of trace metals can be efficiently removed from the AMD via controlled microbial sulfate reduction (Dvorak et al., 1992).

While there have been studies evaluating the effects of the coal ash on methylmercury producing bacteria (Deonarine et al., 2013), no studies examine the direct effects on sulfate reducing microbial communities in anoxic river bottom sediments in response to the Kingston ash spill. Generally, major limitations for microbial sulfate reduction include insufficient sulfate and organic carbon concentrations, and/or sulfate reducing bacteria (Herlihy and Mills, 1984). It is unknown whether the coal ash contains enough labile organic carbon that can be utilized by the bacteria to allow this process to occur. Further, temperate river systems show relatively small concentrations of sulfate in the water column. To better assess the bioremediation potential of microbial sulfate reduction in the freshwater system, more field studies are needed to determine if microbial processes are able to immobilize trace metals from coal ash spill contamination.

3.6. Environmental Setting

3.6.1. Geology of Kingston

The Emory River, Clinch River, and Watts Bar Reservoir encompass four unique geologic groups. Interbedded rocks of the Conasauga group, Rome formation, and Knox group characterize the northwest portion of this region, while the southeast portion is comprised solely by the upper Chickamauga group (Hardeman et al., 1966). The portion of the Conasauga group that runs through this region is called the Central Phase, which is made up of the Cambrian Maynardville Limestone, Nolichucky Shale, Maryville Limestone, Rogersville Shale, and Rutledge Limestone (Rodgers, 1953). Both shale and limestone in this region are silty near their boundaries, with interbedded dolomite found within the limestone units (Rodgers, 1953). The Rome formation is of Cambrian age and is the lowest formation with surface exposures found in the eastern Tennessee Valley (Rodgers, 1953). This unit is an interbedded sandstone, siltstone, shale, dolomite, and limestone (Rodgers, 1953). The Knox group is composed of interbedded siliceous dolomite and Magnesian limestone and is Ordovician in age. This group is dominated by a light-colored dolomite in most regions (Rodgers, 1953). The Chickamauga group is composed of Ordovician limestone and shale (Rodgers, 1953). In the northwest region of Kingston/Harriman, TN, this group is dominated by limestone with thin shaley tops (Rodgers, 1953).

Generally, limestone, dolomite, and shale dominate the studied region with thin, interbedded siltstone and sandstone (Rodgers, 1953). These types of rocks are largely composed of calcite, aragonite, Ca-Mg calcite, clay minerals, quartz, feldspars, iron oxides, and organic matter (Tucker, 2001). Through both physical and chemical weathering processes, these rocks break down and release major ions and trace metals (e.g. Ca, CO₃, SO₄, Fe, Mn, Ba, Sr, V, B, Zn, Cr) into the river systems (Appelo and Postma, 2013). Waters influenced by carbonate dissolution will be dominated by Ca, CO₃, Mg, and HCO₃ composition, while waters influenced by shale and clay weathering would contain higher concentrations of trace metals (e.g. Mn, Ba, Sr, V; Forstner and Wittmann, 1979). Turekian and Wedepohl (1961) analyzed the concentrations of minor and trace elements and their relative concentrations from chemical weathering of granite, deep sea clay, shale, sandstone, and carbonate. According to this study, contents of Ba, V, Zn, Cr, Li, and Cu from shale leaching can be 3 to 9 times higher compared to carbonate catchments (Turekian and Wedepohl, 1961).

Because trace metals can be naturally occurring in the environment, it is important to distinguish between natural and human-induced (e.g., coal ash spill) metal fluxes. In this study, the comparison of metal concentrations in samples collected within and outside the zone of coal ash contamination in the Emory River, Clinch River, and Watts Bar Reservoir will be used to differentiate between natural and anthropogenic metal sources.

Globally, the Cambrian and Ordovician limestones, dolomites, and shales show unique carbon and sulfur isotopic compositions. In the studied area, the river and lake sediments are composed of detritus that comes from erosion of these rock types. Therefore, the bulk $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ values of detrital sediment fraction should reflect their average isotopic compositions. This is mainly because physical and chemical (dissolution/oxidation) weathering does not involve significant carbon and sulfur isotope fractionations (Gill et al., 2007). Marine carbonate rocks formed during the Cambrian and Ordovician typically have $\delta^{13}\text{C}$ values of about -0 to +1‰, and $\delta^{34}\text{S}$ values of +15 to +35‰ (Gill et al., 2007; Longstaffe, 1978). Dolomites have also a very similar carbon isotope composition to limestone with an average $\delta^{13}\text{C}$ of -1.5‰ and $\delta^{34}\text{S}$ of +25‰ (Gill et al., 2007; Hoefs, 1997). Shales/siltstones vary a little more from that of limestone and dolomite due to their higher content of organic matter resulting in $\delta^{13}\text{C}$ of +2 to +4‰ and $\delta^{34}\text{S}$ -sulfide of -14 to -9‰ (Gill et al., 2007; Steiner et al., 2001; Longstaffe, 1978).

3.6.2. Sedimentation rates

In the early 1940s, the Watts Bar Dam and Fort Loudoun Dam were constructed, enclosing the portion of the Tennessee River now referred to as the Watts Bar Reservoir (DOE, 1995). Twenty years later, the Melton Hill Dam was constructed on the Clinch River, 12 miles upstream from the Watts Bar Reservoir. The presence of upstream dams, like the Melton Hill Dam and Fort Loudoun Dam, aid in decreasing sediment accumulation rates downstream by trapping sediment from passing through. According to Brenkert et al. (1992) and DOE (1995), the sedimentation rates in Watts Bar Reservoir range from 0.3 to 2.8 cm/year.

Because this estimate was conducted over 20 years ago, the current sedimentation rates might have increased due to less vegetation cover resulted from increased construction of homes and other commercial developments. This could increase the amount of leaf litter and sediment flowing into the rivers and reservoirs, increasing sedimentation rates. If present sedimentation rates have remained at least on average 1.6 cm/year, the coal ash contaminants deposited in 2008 are likely present at depth of 13 cm below the sediment-water interface.

3.6.3. Lake stratification and climate

The Kingston area is characterized by a temperate climate with warm, humid summers, and cool, wet winters (DOE, 1995). Seasonal variations of temperature and water releases from surrounding dams cause a weak thermal stratification in the Watts Bar Reservoir that occurs from late spring to early autumn (Thevenon et al., 2011; DOE, 1995). This stratification of water in lakes is referred to as being monomictic (Thevenon et al., 2011). During the summer, the upper water layer (epilimnion) becomes warmer and more enriched in dissolved oxygen (DO) than the lower water layer (hypolimnion). Because of decreasing DO concentration with depth; the hypolimnion often turns into a reducing environment in the summer, with lower pH than the epilimnion. Consequently, these two factors can lead to leaching of trace metals from sediments into the water column as reduced forms of trace metals are more mobile (Thevenon et al., 2011; Jain et al., 2007, DOE, 1995). Thus, there is an increased potential for the leaching of trace metals from late summer through early fall than during the winter in the monomictic lakes such as Watts Bar Reservoir.

Consequently, the seasonal changes in DO concentration create varied redox conditions in warm monomictic lakes (Eckert et al., 2002). The diurnal cycling of nutrients moves dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) from the productive warmer waters of the epilimnion to the depths of the hypolimnion (Eckert et al., 2002). In the warm summer months, the DOC is primarily in the productive upper oxygenated waters of the epilimnion, and when the temperature shifts, the DOC and DIC move down into the hypolimnion. Water below the thermocline is oxygen deficient and the concentration of CO₂ is higher than the concentration of DO creating a reducing, low pH environment. These hypolimnetic waters are known to contain high concentrations of SO₄²⁻ and hydrogen sulfide (H₂S) produced during the process of anaerobic decomposition of organic matter, and elevated levels of metals such as iron and manganese brought into water column from the bottom sediments because of the strong reducing conditions (Song et al., 2011; Wan et al., 2001; Canavan et al., 2000; Petts, 1984). In aqueous, reducing environments, metals are released into the surrounding water from the sediment-water interface (Santschi et al., 1990). Under these conditions, the high sulfide content of the Kingston coal ash would likely add H₂S to the bottom river waters as has been documented to occur in sulfur-rich sediments within deep anoxic reducing conditions (Chen et al., 2015). Additionally, within these oxygen poor environments, atmospheric sources do not contribute

much C into the water system, resulting in negative $\delta^{13}\text{C}$ values of DIC from organic matter decomposition in the sediments (Ishikawa et al., 2015).

CHAPTER FOUR

FIELD AND LABORATORY METHODOLOGY

4.1. Field Sampling

To allow for comparison with previous studies, water and sediment samples from the Emory River, Clinch River, and Watts Bar Reservoir were collected in spring of 2016 from similar locations as in Ruhl et al., 2010 (Fig. 1, all figures are presented in appendix A). Additional samples were also collected further downstream (4 miles into Watts Bar Reservoir) to analyze the contamination levels where little remediation efforts were undertaken in 2008-2010. By evaluating current water quality of the Emory River, Clinch River, and Watts Bar Reservoir, this research project will better establish (1) how effective the clean-up efforts conducted by the TVA and EPA were, (2) what type and quantities of toxic metals may be sourced from the remaining coal ash in the river bottom sediments, and (3) whether microbial sulfate reduction might have been involved in immobilization of toxic metals from the coal ash spill.

For collecting water and sediment samples, a pontoon boat was rented from the Caney Creek Marina located off Watts Bar Reservoir. Three sites located furthest upstream (2, 6, and 9) were chosen to measure the chemical and isotope compositions of the water column in sites not contaminated by coal ash (Fig. 1). Additionally, seven sampling sites (1, 3, 4, 5, 7, 8, and 10) were selected near the Kingston plant to determine current water quality of previously contaminated sites. Uncontaminated site 2 on the Watts Bar Reservoir was also used for the collection of sediment cores along with five sites at locations 1, 3, 4, 8, and 10 on the Emory River, Clinch River, and Watts Bar Reservoir. Unlike samples collected by Ruhl et al. (2009) and Stojak et al. (2015), all sediments and water samples were collected near the midpoint of the rivers rather than near the river banks. This method was chosen to improve the understanding of the changes in trace metal concentrations along the water column and any changes resulted from dredging and sedimentation over the last eight years.

Water sample collection took place on April 28, 2016. Using a Wildco Van Dorn type water sampler, the surface water samples were obtained at all locations and water column (at 0, 4 and 6 m depth) was sampled at six sites (Locations 2, 6, 7, 8, 9, and 10). In-situ measurements included: temperature, pH, specific conductance, and DO using a YSI ProDSS multiparameter meter. Additionally, alkalinity was determined using a Lamotte titration kit. Water samples for major ion, trace metal and isotope analyses were filtered using 0.45 μm nylon filters, stored in Nalgene bottles, and kept on ice until frozen at the end of the day. Water samples for S and O isotope analysis of dissolved SO_4^{2-} were filtered using Whatman glass microfiber filters. All collected water samples included:

- 1 L of water for S and O isotope analysis of dissolved SO_4^{2-}
- 60 mL of water for major anion and isotope composition of NO_3^- analyses
- 60 mL of water acidified with 2% HNO_3 for major cation and trace metal analyses
- 1 mL of water injected into a GasBench vial, with He gas headspace and 100 μL phosphoric acid, for C isotope analysis of DIC and DOC.

The sediment sampling of riverbeds took place on June 15 and 16, 2016. The sediment samples consisted of 26-30 cm long cores, which accounted for ~16 cm natural sediment accumulation in the past 8 years (see chapter 3.6.2). To obtain the cores, two scuba divers hammered a 30 cm PVC pipe into the riverbed sediment, capped off the cores immediately to preserve anoxia, and brought them back to the surface. These cores were stored on ice until frozen at the end of each day.

4.2. Laboratory Analysis

Major ions, trace metals and stable isotope compositions of water and sediment samples were analyzed using modified methods previously described by Barbooti (2015) and de Groot (2004, 2008). In the following chapters, a summary of the major methods and instruments used is presented, and the obtained analytical precision is reported.

4.2.1. Water Column

Ion analysis

Major cation and anion concentrations were measured using a Dionex ICS-2100 and Dionex ICS-2000 ion chromatographs (IC) located in the Stable Isotope Laboratory of the Department of Earth and Planetary Sciences, The University of Tennessee. The Inorganic Ventures standards IV-STOCK-7 and IV-STOCK-59 were used for determining cation and anion concentrations, respectively. These standards were diluted to generate the necessary calibration curve. The analytical precision was ± 0.001 mg/L.

Trace metal concentrations of water (Al, Cu, Fe, Mn, Mo, Zn, Cd, Ge, Ni, Pb, As, Ba, Be, Cr, Li, Se, Sr, V, and Tl) were analyzed using a Thermo Scientific iCAP 7000 Series ICP spectrometer in the Water Quality Research Laboratory located in the Department of Civil and Environmental Engineering, The University of Tennessee. Acidified water samples were transferred into 50 mL Fisher Scientific plastic tubes. Prior to sample analysis, blank tests were performed on the Fisher tubes and Nalgene bottles used for water storage to determine what metals, if any, could be leached out from those containers. Standards were prepared using the Claritas PPT multi-element solution 4 and 2A at 10mg/L,

5mg/L, 1 mg/L, 0.7 mg/L, 0.5 mg/L, 0.1 mg/L, and 0.05 mg/L to obtain the calibration curve. The analytical precision was ± 0.002 mg/L.

Isotope analysis

Hydrogen and oxygen isotope composition of water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively) was measured using a Los Gatos Research DLT-100 located in the Stable Isotope Laboratory. The Los Gatos DLT-100 was calibrated using in house standards, which were calibrated against international standards. Un-acidified water samples (1.5 mL) were used for this analysis. The analytical precision for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water was $\pm 0.2\text{‰}$ and 0.7‰ , respectively.

Concentrations and isotope compositions ($\delta^{13}\text{C}$) of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) were measured using the Thermo-Scientific Gas Bench II coupled with a Delta Plus XL isotope ratio mass spectrometer (IRMS) located in the Stable Isotope Laboratory. The Gas Bench was calibrated using in house standards, which were previously calibrated against international standards. In first step, CO_2 gas headspace liberated by phosphoric acid was measured to determine concentration and $\delta^{13}\text{C}$ of DIC. In second step, the remaining water was bubbled with He gas for 5 minutes at the rate of 100 mL/min to remove any remaining DIC/ CO_2 . Afterward, the water was oxidized to convert DOC into CO_2 using 0.8 ml of 1 N sodium persulfate. The water was heated in metal sleeves up to $90\text{--}100^\circ\text{C}$ for 1 hour, let cool, and concentration and $\delta^{13}\text{C}$ of DOC was determined. The analytical precision for $\delta^{13}\text{C}$ and wt. % of DIC and DOC were $\pm 0.08\text{‰}$ and 1.4% , and 0.35‰ and 2.0% , respectively.

The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- were analyzed using a bacterial denitrifying method (Casciotti et al., 2002, Sigman et al., 2001). These bacteria lack N_2O reductases thus convert all NO_3^- ions dissolved in water to N_2O gas, which was analyzed for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ using a Thermo Finnigan Gas Bench II coupled with a Delta Plus XL IRMS in the Stable Isotope Laboratory. The analytical precision for $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of dissolved NO_3^- was $<0.5\text{‰}$.

The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of dissolved SO_4^{2-} was measured using a Costech elemental analyzer (EA) coupled with a Delta Plus XL IRMS, and $\delta^{18}\text{O}$ of dissolved SO_4^{2-} was measured using a Thermo Finnigan TC/EA in the Stable Isotope Laboratory. Prior to isotope analysis, dissolved SO_4^{2-} was precipitated to BaSO_4 in a reaction with a 10% solution of BaCl_2 . In order to obtain enough BaSO_4 for isotope analysis, 1 L of river water was used. For $\delta^{34}\text{S}$ analysis, 0.4-0.5 mg of BaSO_4 was packed into a tin capsule with 1-5 mg of V_2O_5 to allow for a complete combustion of the sample inside the EA. For $\delta^{18}\text{O}$ analysis, 0.15-0.25 mg of BaSO_4 was enclosed in silver capsules with 0.2 mg of NaF for reaction in the TC/EA. The analytical precision for both $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ of dissolved SO_4^{2-} was $<0.3\text{‰}$.

4.2.2. Sediment

Prior to lab analysis, the sediment cores were thawed on a lab counter until they could be removed from the PVC pipe. The frozen cores were then cut using a porcelain knife every 2-3 cm. Afterward, the sediment was freeze-dried using a

Labconco FreeZone 6 Freeze Dry System before utilized for metal and bulk C-N-S isotope analyses. Freeze-dried sediment samples, first, were homogenized in the 50-mL falcon tube using a glass rod. Sediments composed of grains and/or organic matter larger than sand size were ground using a ceramic Spex Certiprep Series 8000 mixer mill. Leachable ions and stable isotope compositions of the leachate and sediment were analyzed using modified methods previously described by Clark et al. (2014) and de Groot (2004, 2009).

Trace metal analysis

The core sediments were analyzed in two steps to leach out metals that were present in “pore water” (e.g., water soluble metals) and adsorbed (e.g., acid mobile metals) on the sediment particles. Firstly, 1 g of sediment was weighed into a 50 mL Fisher Scientific plastic tubes. Next, 35 mL of ultra-pure DI water was added to the tube and shaken for an hour. Afterward, the leachate was separated from the sediment with a centrifuge and filtered with a 0.2 μm nylon filter into a 15-mL plastic tube which was acidified with 2% HCl for trace metal analysis. Secondly, the same portion of sediment used for water leaching were freeze-dried using a Labconco FreeZone 6 Freeze Dry System. Afterward, acid mobile metals were leached out from the sediments using 35 mL of 2% HCl, following the same methodology as with DI water. TraceMetal Grade HCl (<5 ppb) was used in this step due to expected low concentrations of trace metals in the studied river sediments. The metal concentrations (Al, Cu, Fe, Mn, Zn, Cd, Ni, Pb, As, Ba, Be, Cr, Li, Se, Sr, V, and Tl) were analyzed using a Thermo Scientific iCAP 7000 Series ICP spectrometer in the Water Quality Research Laboratory. The analytical precision was ± 0.002 mg/L.

Isotope analysis

Bulk $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$ of sediments were measured using a Costech elemental analyzer (EA) coupled with a Delta Plus XL IRMS in the Stable Isotope Laboratory. For both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analyses, the sediment was packed into tin cups to allow for a complete combustion of the sample inside the EA. The sediment for $\delta^{34}\text{S}$ analysis was packed into tin capsules with V_2O_5 to facilitate complete combustion inside the EA. Analytical precision for bulk wt. % C and $\delta^{13}\text{C}$ were 1.4% and 0.16 ‰, respectively. Analytical precision for bulk wt. % N and $\delta^{15}\text{N}$ of sediment was 2.0% and 0.16‰, respectively. Finally, analytical precision for bulk wt. % S and $\delta^{34}\text{S}$ was 2.3% and 0.5‰, respectively.

The content and S isotope composition of oxidized (S^{6+}) and reduced sulfur species (S^0 , S^- , S^{2-}) from river sediments were analyzed using a sulfur sequential extraction (SSE) method. This method allows for separation of various sulfur species (acid-soluble SO_4^{2-} , elemental sulfur, acid-volatile and chromium-reducible sulfides) for quantitative and $\delta^{34}\text{S}$ analyses (e.g., Szyrkiewicz et al. 2009). SSE was completed in 3 major steps. The first step was the extraction of elemental S from the sediment in a Soxhlet apparatus. At a constant temperature of 40°C, dichloromethane was dripped into a glass thimble containing the sediment to allow

for dissolution of elemental sulfur. The bottom flask contained activated copper granules which reacted with dissolved elemental S and resulted in precipitation of copper sulfides (CuS). Afterward, in a separate extraction apparatus, copper granules were treated with 20 ml of 6 N HCl in oxygen-free atmosphere using N₂ gas flowing through the extraction apparatus. The evolved H₂S was then precipitated as silver sulfide (Ag₂S). The second step of SSE was the extraction of the acid-volatile sulfide and acid-soluble SO₄²⁻ phases. The sediment processed through step 1 was treated with 30 ml of 6 N HCl generating H₂S gas from decomposition of acid volatile sulfides which was then precipitated as Ag₂S. The acid leachate with dissolved SO₄²⁻ was then separated from the sediment using a centrifuge. This leachate was treated with NaOH pellets to raise pH up to 9-10 in order to facilitate the precipitation of Fe hydroxides. After removal of Fe precipitates and acidification with 12N HCl, the acid-soluble SO₄²⁻ was precipitated as BaSO₄ by adding 2 ml of 10% BaCl₂ Solution. The final third step of SSE was the extraction of chromium-reducible sulfides. Sediment from step 2 was freeze-dried and treated with a mixture of 20 ml 12 N HCl and 20 ml of 1 M CrCl₂. Evolved H₂S gas generated from decomposition of chromium-reducible sulfides was recovered as Ag₂S. The amount of sulfur species within a sample was calculated based on the air-dried masses of BaSO₄ and Ag₂S compared to the freeze-dried mass of the initial sample used. The $\delta^{34}\text{S}$ of generated Ag₂S (no measurable quantity of BaSO₄ was obtained during step 2) was measured after being packed into tin capsules with V₂O₅ using a Costech elemental analyzer (EA) coupled with a Delta Plus XL IRMS in the Stable Isotope Laboratory. The analytical precision for $\delta^{34}\text{S}$ was <0.2‰ and for S weight content was <0.01%.

CHAPTER FIVE

RESULTS

All field in-situ measurements, water chemistry, and isotope compositions of the Kingston water column and sediments are presented on Figures 2-7 in Appendix A and Tables 1-9 in Appendix B. The figures and tables summarize the obtained chemical and isotope results relative to the depth of water column and sediment, and in some cases the comparisons to previous studies (Stojak, Bonnevie, and Jones 2015; Ruhl et al. 2010, 2009; Bednar et al. 2010) are made as well.

5.1. Analysis of River Waters

5.1.1. Water chemistry

In April 2016, the water temperature varied between 14 and 24°C and showed a consistent decrease with increasing depth at all sites (Fig. 2, Tab. 1; all tables can be found in appendix B). Conversely, pH and alkalinity showed variations between 6.37 to 8.71 and 20 to 116 mEq/L respectively, with no significant difference between the surface and the bottom of water column. The dissolved oxygen (DO) concentrations ranged from 4.98 to 13.10 mg/L. Most sites showed a decrease in DO concentration with depth, except for site 8 (closest to the spill) in the Emory River. Specific conductance ranged from 73 to 277 $\mu\text{S}/\text{cm}^3$. Sites 9 and 10 (Emory River) and Site 6 (Clinch River) did not show significant changes of specific conductance with depth. However, Sites 7 and 8 (Emory River) and Site 2 (Watts Bar Reservoir) showed increases in specific conductance with increasing depth. Overall, the Emory River had the lowest temperature, pH, alkalinity, DO, and specific conductance.

The reported concentrations of major ions are in mg/L and presented in Table 2. Using these data, a piper diagram was constructed by plotting the normalized abundances, in meq/L, of Na, K, Ca, Mg, Cl, HCO_3 , CO_3 and SO_4 . This analysis allowed for the classification of the studied waters as Ca- HCO_3 type (Fig. 3).

Trace metal concentrations are reported in ppm and presented in Table 3. Concentrations of Al, As, Cd, Cu, Cr, Be, Li, Ni, and Pb were below the detection limit of <0.002 mg/L. Concentrations of B, Fe, Se, and Zn were <0.040 mg/L and randomly detected along the water column in the uncontaminated portions of the Clinch River (Site 6) and Emory River (Site 9). The concentrations of Mn varied between 0.111 and 0.292 mg/L and were detected in two water samples at depth of 10 m and 6 m depth (e.g., near the sediment-water interface) in the uncontaminated portion of the Clinch River (Site 6) and contaminated portion of the Emory River (Site 7), respectively. Sr was detected in all analyzed samples at

concentration between 0.029 and 0.088 mg/L. There were no correlations between metal concentration and depth or distance from the spill site (Fig. 8).

5.1.2. Isotope composition

Hydrogen and oxygen isotope composition of water for the Emory River, Clinch River and Watts Bar Reservoir had $\delta^{18}\text{O}$ values ranging from -6.4 to -5.6‰ and $\delta^2\text{H}$ values between -37.4 to -32.4‰. Most of water samples plotted above the global meteoric water line (GMWL; White 2015) and below the Knoxville meteoric water line (KMWL; unpublished data) (Fig. 4, Tab. 4).

Carbon isotope composition ($\delta^{13}\text{C}$) of DIC varied from -7.3 to -13.7‰ (Fig. 5, Tab. 4). All rivers had similar $\delta^{13}\text{C}$ values, however, the $\delta^{13}\text{C}$ of Emory River showed larger variation with depth (by 6.4 ‰) compared to the Clinch River and Watts Bar Reservoir (<3.1‰). The Clinch River had the highest concentration of DIC (34.0 to 91.5 mg/L) compared to smaller concentrations in Emory River (7.7 to 54.9 mg/L) and the Watts Bar Reservoir (20.1 to 37.9 mg/L). With increasing depth, the $\delta^{13}\text{C}$ of DIC showed a negative correlation. The $\delta^{13}\text{C}$ value of DOC varied from -35.2 to -29.0‰ in the Emory River. In contrast, the Watts Bar Reservoir and Clinch River showed smaller variation of $\delta^{13}\text{C}$ in DOC, -33.1 to -29.6‰ and -31.5 to -29.7‰, respectively. As with DIC, the Clinch River had the highest concentration of DOC (42.9 to 50.0 mg/L) compared to smaller concentrations in the Emory River (7.5 to 15.2 mg/L) and Watts Bar Reservoir (7.1 to 10.4 mg/L). There were no important correlations between $\delta^{13}\text{C}$ of DOC concentration with depth.

The $\delta^{15}\text{N}$ of NO_3^- ranged from +4.4 to +10.8‰ and $\delta^{18}\text{O}$ from -2.7 to +5.7‰ (Fig. 6, Tab. 4). Like other isotope results, the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ showed larger variations for the Emory River compared to the Clinch River and Watts Bar Reservoir. However, concentrations of NO_3^- were similar in all studied river systems and ranged between 0.0 and 1.3 mg/L.

$\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of dissolved SO_4^{2-} ranged from +2.7 to +5.8‰ and +3.3 to +6.7‰, respectively (Fig. 7, Tab. 4). The highest $\delta^{34}\text{S}$ values were observed in the Watts Bar Reservoir (+3.9‰ to +5.8‰) with lower values in the Emory River (+2.7 to +4.3‰) and Clinch River (+4.6 to +4.8‰). Similarly, the most positive $\delta^{18}\text{O}$ values were determined for the Watts Bar Reservoir (+3.9 to +6.7‰) and the lowest values in the Emory River (+3.2 to +5.9‰) and Clinch River (+3.6 to +4.6‰).

5.2. Analysis of River Sediment and Bedrock

5.2.1. Trace metals

Trace metal concentrations for the sediment are reported in mg/kg of sediment separately for DI- and acid-leachates, and are presented in Tables 5 and 6. The initial concentrations of trace metals determined by ICP-OES analysis were reported in mg/L, however these values have been converted to dry weights and

reported in mg/kg in order to make comparisons with previous studies by Ruhl et al. (2009, 2010) and Stojak et al. (2014).

For water leachable metals, the concentrations of B, Be, Cd, Cr, Mo, Pb, and Zn were below the instrument detection limit (<0.002 mg/L). Additionally, for acid leachable metals, the concentrations of B, Fe, and Mo were also below detection limit. Elevated concentrations of As, B, Ba, Be, Cr, Cu, Fe, Ge, Li, Mn, Ni, Pb, Se, Sr, Tl, V, and Zn were measured in both the water and acid leachable fractions. The concentrations of water-soluble trace metals were as follows: Fe $\leq 1,650$ mg/kg; V ≤ 200 mg/kg; Mn, Zn ≤ 100 mg/kg; Cr, Cu, Tl ≤ 40 mg/kg; As, B, Se, Ba, Pb, Sr, Ge ≤ 20 mg/kg; Cd, Li, Ni ≤ 4 mg/kg; Be ≤ 0.2 mg/kg; and Mo below detection limit (0.002 mg/L). The acid soluble trace metals were as follows: Fe $\leq 12,200$ mg/Kg; Al, Mn $\leq 5,000$ mg/Kg; V $\leq 1,000$ mg/Kg; Ba, Tl ≤ 200 mg/Kg; As, Sr, Zn, Ge ≤ 65 mg/Kg; Cu, Ni ≤ 30 mg/Kg; B, Cr, Pb ≤ 20 mg/kg; Be, Cd, Se ≤ 10 mg/kg; and Mo below detection limit (0.002 mg/L). However, there were no significant correlation with depth or distance from the spill site (Fig. 9) according to visual analysis and multiple linear regression analysis utilizing SAS analytical software (Tab. 7). The procedure used in SAS analysis included the utilization of the PROC REG command to discern the significant relationships that may exist between variables in the dataset based on calculated p values compared to a significance p of 0.05.

Representative bedrock samples were also analyzed for trace metal concentrations with the same method that was used for the core sediment analysis. The concentrations of water-soluble trace metals observed were as follows: Pb ≤ 35 mg/Kg; Al ≤ 20 mg/Kg; As, Fe, Mn, Se, Tl ≤ 4 mg/Kg; Sr ≤ 2.5 mg/Kg; Ba, Cr, Cu, Li, Zn ≤ 0.02 mg/Kg; and Be, Cd, Ni below detection limit (0.002 mg/L). The concentrations of acid-soluble trace metals were usually significantly higher than in water soluble fraction, however the concentrations of Cd and Ni remained below detection limit. The acid soluble trace metals were as follows: Fe $\leq 2,000$ mg/Kg; Al $\leq 1,000$ mg/Kg; Mn, Sr ≤ 425 mg/Kg; Ba, V ≤ 100 mg/Kg; As, Cr, Cu, Li, Pb, Se, Zn ≤ 15 mg/Kg; and Be, Tl ≤ 1.5 mg/Kg.

5.2.2. Bulk isotope composition

Bulk $\delta^{13}\text{C}$ values of sediment ranged from -27.8 to -24.0‰ (Fig. 10, Tab. 8). The largest variation and the most negative $\delta^{13}\text{C}$ values were observed in the Watts Bar Reservoir and Clinch River (-27.8 to -24.4‰). Conversely, the Emory River had the most positive $\delta^{13}\text{C}$ values (-25.2 to -23.9‰).

Bulk $\delta^{15}\text{N}$ values ranged from $+1.1$ to $+8.8\text{‰}$ with the highest values in the Watts Bar Reservoir ($+4.3$ to $+8.8\text{‰}$) and the lowest ($+1.1$ to $+6.8\text{‰}$) in the Emory River (Fig. 10, Tab. 8). The $\delta^{15}\text{N}$ values do appear to correlate with the wt. % N, with Watts Bar Reservoir showing the highest concentrations (0.06 - 0.26%) and the Emory River with the lowest concentrations (0.01 to 0.13%).

Bulk $\delta^{34}\text{S}$ ranged from -5.4 to $+6.2\text{‰}$. At depth of 11 to 18 cm the Clinch River had the most negative $\delta^{34}\text{S}$ values (-3.8 to -2.1‰) and the Emory River the most positive $\delta^{34}\text{S}$ values ($+4.7$ to $+6.2\text{‰}$) (Fig. 10, Tab. 8). At these depths, the

Clinch River had the highest wt. % of S (0.11 to 0.16%) and Emory the lowest (0.02 to 0.03%). Bulk S concentrations ranged from 0.02 to 0.15 wt.%.

5.2.3. Sulfur sequential extraction

Sulfur sequential extraction allowed for detailed chemical and isotope analyses of elemental S, acid-volatile sulfides, acid-soluble SO_4 , and chromium-reducible sulfides present in the studied sediments. The obtained results are presented in Table 9. Generally, acid-soluble SO_4 , representative of pore-water sulfate and sulfate minerals soluble in both water and acid, was not present in the analyzed river sediments. Additionally, the concentrations of elemental S and acid-volatile sulfides were relatively low (<0.05 wt.S%) compared to higher concentrations of chromium-reducible sulfides (between <0.05 and 0.2 wt.S%).

The $\delta^{34}\text{S}$ values of elemental S ranged from -3.6 to +0.8‰ and did not show significant variation with depth (Sites 1, 2, 3, 4, and 10), except for Site 8 (contaminated by coal ash spill) which showed a significant increase of $\delta^{34}\text{S}$ value with depth, +10.8‰ (Fig. 11). Note that Site 8 also had the lowest concentration of elemental S. The $\delta^{34}\text{S}$ of acid-volatile sulfides (e.g., mainly monosulfides) showed no significant trends with depth and ranged from -2.7 to +1.1‰. Overall, $\delta^{34}\text{S}$ values of chromium-reducible S (e.g., mainly polysulfides such as pyrite) ranged from -7.1 to +0.2‰ and showed increasing $\delta^{34}\text{S}$ value with depth in the uncontaminated sites of Clinch River and Watts Bar Reservoir (Fig. 7). Conversely, the $\delta^{34}\text{S}$ value was higher in the contaminated sediments of Emory River (0 to +4.8‰) without any correlation between the concentration of chromium-reducible sulfides or $\delta^{34}\text{S}$ and depth.

CHAPTER SIX

DISCUSSION

6.1. Current Water Quality

To minimize environmental impacts of the coal ash spill, the EPA and TVA implemented expensive remediation efforts focused on physical removal of ash particles from the Emory River within the first year following the spill (e.g., TVA, 2016; Bednar et al., 2010). It has been estimated that approximately 60% of coal ash was removed from the river (R. 04 US EPA, 2016). It has been eight years since the Kingston Fossil Plant coal ash spill occurred. Previous studies on the Emory River, Clinch River, and Watts Bar Reservoir were conducted within the first 1 to 2 years following the spill to assess the contamination levels of trace metals due to the coal ash (e.g. As, B, Cr, Hg, Mo, Pb, Sb, Se, V, and Zn; Ruhl et al., 2009, 2010; Bednar et al., 2010). The effectiveness of the remediation efforts were initially evaluated by both Ruhl et al. (2009 & 2010) and Bednar et al. (2010) showing that surface water did not have significant increases of trace metal concentrations, except for As which showed elevated concentrations (up to 0.950 mg/L) exceeding the EPA guideline for Human Health (0.00002 mg/L for clean water). This suggested that the remaining ~40% of the coal ash is a potential health risk to Kingston residents.

Current trace metal concentrations of the water column (including As) remain unknown for the Emory River, Clinch River, and Watts Bar Reservoir. Residents question water quality of the river systems near the Kingston Plant as numerous warning signs (e.g., “do not consume fish”) remain near or within recreational areas, implying continued health risks. Therefore, this study aimed to provide new results on the trace metal concentrations, within both the river water column (10 m) and bottom sediments (30 cm) that can be compared to previous studies completed shortly after the coal ash spill. Under current conditions, the coal ash contaminants should be mainly present in the river sediments due to natural sedimentation that has taken place over last eight years. Therefore, it was necessary to evaluate changes of trace metal concentrations through the water column to better evaluate the risks of metal releases through sediment disturbance via bottom currents or aquatic organisms (Clark et al., 2014). In contrast, the studies by Ruhl et al. (2009, 2010) and Bednar et al. (2010) mainly focused on studying the top of the water column near the shorelines using grab sampling techniques.

To determine current potential for toxic side effects in the water column of the Emory River, Clinch River, and Watts Bar Reservoir, the obtained chemical results have been compared to three sets of water quality guidelines established by the EPA (OW US EPA 2015a, 2015b, 2015c). The utilized guidelines include

maximum contamination levels (MCLs) for aquatic life, drinking water, and human health (Table 10). The same aquatic life MCLs for trace metals were used by studies assessing water quality immediately after the coal ash spill (e.g., Ruhl et al., 2010, 2009; Bednar et al., 2010) and are, therefore, a good means for comparison of past and present water quality. The aquatic life MCLs are used to aid in the determination of the health of a river system and potential toxicity towards aquatic organisms. In addition, this study utilized the drinking water and human health guidelines for toxicity analysis due to the frequent use of these rivers for recreation, and as a source for fish and drinking water.

The water samples collected in April 2016 showed significantly lower concentrations of dissolved trace metals than those observed in 2009, shortly after the coal ash spill (Ruhl et al., 2009). The 2016 concentrations of Al, As, Be, Br, Cd, Cr, Cu, Li, Ni, and Pb were below the detection limit of 0.002 mg/L (Fig. 12). However, in Site 6 (uncontaminated site on Clinch River; depth 10 m) and Site 7 (contaminated site at the convergence of Emory River and Clinch River; depth 6 m) the concentrations of Mn were 0.292 and 0.111 mg/L, respectively, which exceeded the EPA human health MCL of 0.05 mg/L. Generally, the EPA human health criteria for Mn establishes the point above which consumption of water and aquatic organisms results in unpleasant qualities like laundry stains and bad tastes (OW. US EPA, 2015b). However, it was recently shown elevated concentrations of Mn can be especially harmful to children at concentrations above 0.1 mg/L (Ying et al., 2017). As a result of ingestion, Mn can cause intellectual impairment, muscle weakness, and infertility. Given that higher concentrations of Mn were mainly detected further away from the coal ash spill, with the highest concentration in the uncontaminated portion of the Clinch River, it is implied that Mn might come from another upstream source (e.g. industrial activities). In April 2016, other detectable trace metals in the water column included B, Fe, Se, Sr, and Zn (<0.100 mg/L). However, these concentrations were below any established EPA MCL guidelines, thus they do not appear to pose any significant health risks. It can be concluded that at present the contamination of the water column with respect to the trace metals from the Kingston coal ash spill is minor/negligible.

While the concentrations of As remained elevated during the first 2 years following the ash spill (<0.950 mg/L; Ruhl et al., 2009, 2010; Bednar et al., 2010), the low concentrations observed in 2016 (<0.002 mg/L) suggest that even incomplete physical removal of the coal ash was likely important in minimizing the continued release of As and other trace metals into the studied rivers. However, it is recognized that there are several natural processes that have aided in the lowering of trace metal concentrations in the water column. For example, the active hydrological system and regional wet climate may lead to constant dilution and downstream transport of contaminants adsorbed on the river sediments.

Water isotope composition ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) is usually a good indicator of water sources (e.g. precipitation, groundwater) and subsequent processes affecting its cycling through the environment (e.g. evaporation, water-rock interaction; Hoefs, 1987). The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of surface water and shallow

groundwater in the watersheds such as in the Kingston area typically show similar isotope composition of local precipitation that has fallen relatively recently within a given recharge area (Sharpe, 2007). In contrast, evaporation of surface water leads to significant increases of both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values (Hoefs, 1987). In April 2016, the measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of the Emory River, Clinch River, and Watts Bar Reservoir were closely aligned with the Local and Global Meteoric Water Lines and did not show any significant changes toward higher values (White, 2015; Fig. 4). This suggests that the studied surface waters are representative of typical meteoric origin and do not experience significant evaporation (Fig. 4), indicating a quick exchange of water in the studied rivers. Most likely, the high precipitation rates and wet climate of eastern Tennessee significantly increase water flows and dilution, reducing ponding and potential increases of trace metal concentrations due to evaporation effect.

Generally, under neutral pH (~ 7), trace metals are insoluble and largely found adsorbed onto the surfaces of sediment particles (Clark et al., 2014). It has been shown that carbonate dissolution can increase buffering capacity in large rivers (Spry and Wiener, 1991). In April 2016, the studied rivers showed neutral pH within the range of 6-9 (Fig. 2E). Therefore, this can explain the low concentrations of dissolved trace metals measured within the water column (Fig. 8, 12). The bedrock of the Kingston region is dominated by limestone and dolomite (Spry and Wiener, 1991; Rodgers, 1953) and can explain higher pH and alkalinity measured (Fig. 2D-E). According to the Piper diagram (Fig. 3), the studied waters can be classified as mainly Ca-HCO_3 type, which is likely the result of carbonate dissolution of local bedrock (Figs. 2D-E, 3). Carbonate bedrock usually shows distinctive $\delta^{13}\text{C}$ values of $\sim 0\text{‰}$ ($\pm 2\text{‰}$) (Gill et al., 2007) and given that carbonate dissolution is not accompanied by significant carbon isotope fractionation (Mackenzie and Lerman, 2006), the $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) in the water column should reflect the $\delta^{13}\text{C}$ value of carbonate if this is the main DIC source. Nevertheless, the $\delta^{13}\text{C}$ of DIC in the Kingston rivers showed more negative values (-13.7 to -7.4‰) than typical carbonate bedrock (Fig. 5B). This suggests that there is likely an additional source of isotopically light carbon in these water systems such as organic matter which has negative $\delta^{13}\text{C}$ values (-23 to -40‰ ; Kohn, 2010; Kendall et al., 2001). In freshwater settings, decomposition of organic matter, particularly on the river bottom, leads to releases of isotopically light CO_2 which causes significant decreases of $\delta^{13}\text{C}$ of DIC (Mackenzie and Lerman, 2006). The bulk $\delta^{13}\text{C}$ of river sediments in the Kingston area was more negative (-27.8 to -24.0‰) compared to carbonate bedrock, and it was consistent with the organic matter source. Therefore, decomposition of organic matter is likely responsible for the observed decrease of $\delta^{13}\text{C}$ of DIC with depth in the water column (Fig. 5B).

The following isotope mass balance equation can be used to determine the approximate contributions of bedrock dissolution and decomposition of organic matter into DIC pool:

$$\delta^{13}\text{C}_{\text{Sample}} = X \cdot \delta^{13}\text{C}_{\text{Organic matter}} + (1-X) \cdot \delta^{13}\text{C}_{\text{bedrock}}$$

where x is the proportion of organic matter endmember (Raymond and Bauer, 2001). In this calculation, the average $\delta^{13}\text{C}$ of dissolved organic carbon (DOC) measured in the water column was used (-30.8‰) because the bulk $\delta^{13}\text{C}$ of river sediments might be affected by some contributions of carbonates from physical erosion of bedrock in the watershed. The latter would increase the bulk $\delta^{13}\text{C}$ of river sediments because of considerably higher $\delta^{13}\text{C}$ of carbonates ($\sim 0\text{‰}$) compared to organic matter. The carbon isotope mass balance calculation indicates that in the studied surficial waters (top of water column) bedrock dissolution constitutes $\sim 72\%$ of DIC and at the base (sediment-water interface) is $\sim 62\%$. This implies that bedrock carbonate dissolution is likely a major contributor of DIC through the entire water column, which is in a good agreement with major water chemistry indicative of Ca-HCO_3 type (Fig. 3). Conversely, the contributions of DIC from decomposition of organic matter appear to be smaller ($< \sim 38\%$). However, in addition to decomposition of organic matter in the river sediments there can also be some addition of light carbon from similar processes in soil interacting with meteoric water. Given that $\delta^{13}\text{C}$ of DIC in soil and river sediments usually overlaps (Ishikawa et al., 2015), the obtained results do not allow for better differentiation of DIC inputs from these two organic sources.

Alternatively, higher $\delta^{13}\text{C}$ of DIC in the studied surficial waters (-11 to -7‰ ; Fig. 5B) might be largely influenced by dissolution of atmospheric CO_2 (-6.5‰ ; Ishikawa et al., 2015; Mackenzie and Lerman, 2006). According to the carbon isotope mass balance calculation, 91% of atmospheric-derived DIC in surficial waters and 78% in basal waters would be needed to explain the observed variations of $\delta^{13}\text{C}$ DIC value in the water column due to mixing with DIC sourced by organic processes in the sediments (Fig. 5B). However, this is an unlikely scenario as it is not supported by water chemistry that suggests significant dissolution of carbonate bedrock present in the watershed (Fig. 3).

The studied rivers in Kingston area drain surrounding watersheds of different sizes. This, in turn, might be reflective of different physicochemical properties which were noted in April 2016 (Fig. 2). The Emory River is relatively small and showed consistently lower temperature, pH, DO, specific conductance, and alkalinity than the Clinch River and Watts Bar Reservoir that receive recharge from larger areas (Fig. 2). This implies the importance of local processes in controlling water chemistry of Emory River. According to the results of this study, carbonate dissolution and organic processes are important in increasing alkalinity and water pH, which keeps the trace metals insoluble in the water column. However, it is necessary to evaluate how the smaller Emory River might respond to subsequent acidification by rain and pyrite oxidation. For example, acid rains have high impact on forested watersheds in eastern Tennessee (Neff et al. 2009) and the presence of shale bedrock (Rodgers, 1953) has the potential to release sulfuric acid due to pyrite oxidation (Evangelou, 1995).

The Emory River was most impacted by coal ash spill contaminants and showed the lowest pH of 6.6 to 8.0 and alkalinity of 15 to 60 mg/L (Fig. 2D-E); therefore, it is at a higher risk to release trace metals from river sediments due to

seasonal changes of water pH. The approximate 40% of coal ash remaining in the Emory River may contain some sulfidic minerals which are common in coals (Evangelou, 1995; Vassilev, et al. 1995) and when oxidized would produce sulfuric acid and cause a decrease in pH. Additionally, because the Emory River drains a relatively small watershed it can be more affected by local processes of shale sulfide oxidation and less influenced by dissolution of bedrock carbonates, which are dominant on a regional scale. In April 2016, the pH and concentration of DO showed decreasing trends with depth in all locations (Fig. 2B, E). This could be the result of oxidation of organic matter to CO₂ during microbial respiration at the sediment-water interface and along water column, and it is in good agreement with negative $\delta^{13}\text{C}$ of DIC along the water column (Fig. 5B). Further, oxidation of pyrite present in the bedrock (e.g., soils, shale rock) and coal ash contaminants might be an additional factor withdrawing oxygen with depth. Generally, both organic matter and sulfide oxidation have the potential to cause more acidic conditions at the sediment-water interface and along the water column (Mackenzie and Lerman, 2006; Evangelou, 1995), thus leading to the subsequent releases of trace metals remaining in the river sediments.

Isotope composition of dissolved sulfate (SO₄²⁻) is a good environmental tracer because $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulfate sourced by pyrite oxidation have distinctively lower values ($\delta^{34}\text{S}$: -30 to 0‰, $\delta^{18}\text{O}$: -5 to +6‰) compared to atmospheric deposition ($\delta^{34}\text{S}$: 0 to +10‰, $\delta^{18}\text{O}$: +6 to +12‰), dissolution of bedrock evaporites ($\delta^{34}\text{S}$ +8 to +15‰, $\delta^{18}\text{O}$: +6.5 to +12‰), and soil processes ($\delta^{34}\text{S}$: 0 to +10‰; $\delta^{18}\text{O}$: 0 to +5.5‰) (Szynkiewicz et al., 2015; Knöller et al., 2005). In April 2016, the measured $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of dissolved SO₄²⁻ ($\delta^{34}\text{S}$: +2.7 to +5.8‰, $\delta^{18}\text{O}$: +3.2 to +6.7‰) suggest some inputs from atmospheric deposition (e.g. industrial emission, acid rain) and soil processes rather than the direct oxidation of pyrite or evaporite dissolution in the watershed bedrock (Fig.13). While some acidification of the Emory River may be sourced by acid rain, the $\delta^{18}\text{O}$ of SO₄²⁻ were lower than what would be expected for direct sulfate input from atmospheric deposition, +6 to +12‰ (Peterson and Fry, 1987). Interestingly, the $\delta^{34}\text{S}$ of Emory River was always lower (+2.7 to +4.0‰) compared to the Clinch River and Watts Bar Reservoir (+4.0 to +5.8‰), suggesting plausible inputs of sulfide-derived SO₄²⁻ with lower $\delta^{34}\text{S}$ from the bedrock and/or coal ash remaining in the sediments. Note that the lowest pH and most significant decreases of pH with depth of water column were also observed in the Emory River (Fig. 2E), supporting the importance of local acidification factor such as sulfide oxidation in the river sediments.

In summary, the obtained isotope results (Figs. 7B-C) suggest multiple processes that may lead to acidification of water column in the studied rivers such as acid rain, oxidation of organic matter and/or sulfide minerals. It appears, however, that even in the presence of varied local acidification factors, the water pH of the studied rivers generally remained higher than 6.6 and did not become acidic in April 2016 (Fig. 2E). This implies that dissolution of bedrock carbonates results in effective buffering of the acidity from anthropogenic and geologic sources. It is also proposed that higher water pH driven by carbonate dissolution

allows the trace metals to remain adsorbed onto sediment particles. In this case, the presence of carbonate bedrock is likely important factor in decreasing trace metal fluxes into the water column from the remaining coal ash and other contaminants present in the river sediments.

6.2. Trace Metal Contamination of Riverine Sediments

Current methodology for assessing trace metal contamination of riverine sediments by anthropogenic activities utilizes a simple comparison of trace metal concentrations in the contaminated sites to the concentrations present naturally in the bedrock and/or in uncontaminated sites (MacDonald et al., 2000). This method is believed to represent a good measure of contamination levels and potential for toxicity. Sediment quality guidelines (SQGs) for some trace metals (As, Cd, Cr, Cu, Ni, Pb, and Al) consider two types of toxicity potentials such as effect range low (ERL; low potential for inducing toxic side effects) and effect range median (ERM; medium potential for inducing toxic side effects; Tab. 11; MacDonald et al., 2000). These guidelines are based on studies predicting thresholds for the toxic side effects that freshwater organisms would experience when exposed to various concentrations of toxic trace metals (MacDonald et al., 2000). While these guidelines are not intended to determine whether cleanup or remediation must occur, they provide a means to predict and evaluate the potential environmental risks.

Shortly after the spill accident in 2008, Ruhl et al. (2009) analyzed the trace metal concentrations of the spilled Kingston Fossil Plant coal ash relative to the uncontaminated riverbed sediments within Emory River, Clinch River, and Watts Bar Reservoir. The coal ash samples were collected from an embayment formed near the spill location and the uncontaminated river sediments were collected from upstream locations. These samples were then analyzed for trace metal composition by the Tennessee Department of Environment and Conservation (TDEC) and the Tennessee Department of Health. The coal ash showed enrichments of trace metals relative to the uncontaminated sediments, for As (21x, x means times), Al (1.5x), Sr (30x), Li (5x), Ba (5x), Ni (5x), V(4x), Cu (3x), Hg (8x) and Cr (2x) (Ruhl et al., 2009). Consequently, these enrichments represent the potential for contamination within riverine sediments after an event like the Kingston coal ash spill. In a later study, Stojak et al. (2015) analyzed trace metal concentrations of the riverbed sediment in samples collected 2 years (winter and spring of 2011) after the coal ash spill occurred. These sediment samples consisted of the upper 16 cm of riverine sediment collected near the banks of the river channels, which were homogenized into one sample. The metal concentrations were determined through nitric acid digestion (OSWER US EPA, 2015). The reported concentrations of As (9-78 mg/Kg), Cu (19-61 mg/Kg), and Ni (18-32 mg/Kg) surpassed both ERL and ERM consensus based on sediment quality guidelines (Fig. 14., Tab. 11). In summary, Stojak et al. (2015) showed that

the concentrations of trace metals 2 years after the Kingston coal ash spill were still at levels when toxic effects could occur, thus more detailed investigation was needed to better assess the existing environmental risks.

Eight years after the coal ash spill, it can be expected that remaining coal ash contaminants have undergone burial by younger sediments. According to the previously estimated sedimentation rate of ~1.6 cm/year (DOE, 1995; Brenkert et al., 1992), they would reside at ~13 cm below the sediment-water interface. Therefore, the sediments sampled in June 2016 consisted of the top ~30 cm of sediment collected from the center of the Emory River, Clinch River, and Watts Bar Reservoir channels. Each sediment core was divided into 2-3 cm layers which were homogenized before analysis. This approach allowed for a more precise determination of changes of trace metal concentrations with depth compared to Stojak et al. (2015) that analyzed the bulk 16 cm thick top layer. In order to better understand potential releases of metals by changing environmental conditions (e.g., dilution by rain, fluctuations of pH), the analysis of trace metal concentrations involved a 2-step leaching process instead of complete acid digestion as in Stojak et al. (2015). The first step included leaching with DI water to demonstrate what trace metals might potentially be released as a result of natural groundwater discharge to the river channels through the sediments and/or when sediments are disturbed by erosion and/or infiltration of water due to river currents and aquatic organisms. The second step included leaching with 2% HCl, allowing for assessment of trace metals insoluble in DI water that were mostly adsorbed on mineral surfaces and/or present as individual minerals (e.g. metal sulfides). Consequently, leaching with acid provided some insight to the concentrations and types of trace metals that could be released by local acidification factors (e.g., acid rain, sulfide oxidation). Ultimately, the determined trace metal concentrations are likely underestimated compared to Stojak et al. (2015) that used complete acid digestion.

Accordingly, the 2016 sediments showed lower concentrations of trace metals compared to the 2011 sediments analyzed by Stojak et al. (2015), both for DI water- and acid-leachable trace metals (Fig. 14). However, note that when the DI water- and acid-soluble fractions are added together, some of the analyzed trace metals (e.g., As, Cu, Ni, Zn) were found in concentrations very similar to those reported by Stojak et al. (2015). On the other hand, some metals such as Cr, Mn, Tl, and V had increased by ≤ 1.5 , ≤ 2 , ≤ 60 , and ≤ 14 times, respectively (Fig. 15). The concentrations of As appear to exceed the ERL SQG (8.2 mg/Kg; Tab. 11) by ≤ 2 times for DI water-leachates and by ≤ 7 times for acid-leachates (Fig. 14). The measured As increases were particularly significant in Site 8, closest to the spill, suggesting that the remaining coal ash contaminants might still be a major source of As in the Emory River sediments. Additionally, it is noted that the concentrations of Cd likely increased (0.740-2.200 mg/kg for water-soluble, 0-0.350 mg/kg for acid-soluble fractions) since the Stojak et al. (2015) study (0.130-0.300 mg/kg) and currently exceed the ERL SQG of 1.2 mg/kg by ≤ 2 times (Fig. 14, Tab. 11). However, note that in addition to Site 8 (closest to the spill), the

concentrations of Cd were similarly elevated at Site 2 located in the uncontaminated portion of the Watts Bar Reservoir (Fig. 9F). This indicates that Cd might also be sourced by local contaminants from industrial and mining activities. No other trace metals (Cr, Cu, Ni, Pb, or Zn) surpassed the established ERL and ERM toxicity potential levels for the water-soluble and acid-soluble trace metal analysis. While it is impossible to better evaluate whether the trace metal concentrations have significantly decreased since 2011 (Stojak et al. 2015), the concentrations of As and Cd remain above the sediment quality guidelines suggesting the continued environmental risks. Further research would be needed to better characterize the locations and potential for release of these metals into the water column in the Kingston area.

Following a one-time contamination event like the Kingston Fossil Plant coal ash spill, it can be expected that over time major contaminants would settle at the bottom of the river channel and form a distinct layer eventually buried by younger, uncontaminated sediments. Assuming an average sedimentation rate of ~1.6 cm/yr in the Watts Bar Reservoir (Brenkert et al. 1992; DOE 1995), the coal ash contaminant layer would have been buried by at least 13 cm of fresh sediment in 2016 (See Chapter 3 section 6.2). By this principle, the highest trace metal concentrations (e.g. As, Be, Li, Sr, and V present in coal ash) should be present in the middle of the 30 cm long sediment cores that were collected in June 2016. Given that there only was one major event releasing contaminants into the studied rivers, it would be expected to see a sudden increase (spike) in trace metal concentration at the sediment depth of ~13 cm corresponding with that point in time. However, there were no obvious relationships between trace metal concentrations and depth (Fig. 9). In some locations (e.g., Site 8 near the spill location), several trace metals such as Al, As, Cr, Cu, and V showed smaller concentrations at shallower depths (5 to 10 cm) compared to significantly higher concentrations at a depth of ~15 cm (Fig. 9A, B, G, H, P, R). Note that this depth is in good agreement with the predicted depth of ~13 cm with expected greatest contamination. On the other hand, these metals were also relatively high in the top sediment layer (0-5 cm), suggesting more recent metal loads. Generally, no clear relationships of trace metals with depth close to the spill location could be distinguished using the results of this study. This might be the result of dredging between 2009 and 2010 that involved multiple cycles of sedimentation and disturbance during first two years of remediation efforts by EPA and TVA. Additionally, it should be kept in mind that seasonal processes may affect metal loads into the studied rivers. For example, the variations of metal loads have been previously linked to changes of sediment transport and runoff due to climate. In river systems, increases in metal fluxes are typical during the spring when discharges and sediment transport are high (e.g., Frederick et al. 2017). Most of the metal contaminants from mining activities, roads, or urban areas are usually transported on suspended sediment particles because of higher pH in runoff, which keeps the trace metals insoluble in water. Ultimately, the results of the 2016 study in the Kingston area do not allow for better characterization of seasonal metal

fluxes compared to coal ash spill. But a lack of distinctive relationships of metal concentrations with depth implies multiple natural and anthropogenic processes affecting their contents in the studied river sediments.

An additional process that might lead to the observed various distribution of trace metals in the analyzed sediment cores from the Kingston area (Fig. 9) is a natural heterogeneity of metals in the local bedrock that undergoes erosion by active hydrological cycle. In September 2017, the representative bedrock samples of the Knox Group dolomite; Upper and Lower Chickamauga Group Limestone and shale; and Rome Formation limestone, sandstone, and shale were analyzed for DI- and acid-soluble trace metals (Tab. 12). The analyzed bedrock samples were collected near the Knoxville area (~66 km from the coal ash spill location) and were representative of the main geologic units comprising the watersheds of Emory River, Clinch River and Watts Batt Reservoir (Hardeman et al., 1966; Rodgers, 1953). Most of the analyzed trace metals were found in the acid-soluble fraction ($\leq 2,000$ mg/kg) rather than the DI water-soluble fraction (≤ 35 mg/kg) (Tab. 12). In contrast, the elevated concentrations of trace metals (e.g., As, Cr, Cu, Mn, Se, V, Zn) were found as DI water-soluble fraction in the studied river sediments (Fig. 9, 14). This implies that there is a significant portion of these metals adsorbed on the sediment grains that must originate from outside (anthropogenic) sources. The concentrations of Cd and Ni were below detection (Tab. 12), thus their elevated concentrations in the studied river sediments must be mainly controlled by anthropogenic inputs. The total concentrations (sum of water- and acid- leaching) of certain trace metals such as Li, Pb, and Sr were found significantly higher in the bedrock than those observed in the river sediments, suggesting multiple sources and processes controlling their variations in the studied rivers (Fig. 16). However, in the case of Al, As, Cr, Cu, Mn, Ni, Ti, V, and Zn the observed total concentrations in the river sediments are significantly higher than those determined for the bedrock but were similar to those observed in coal ash (Ruhl et al., 2009) and/or in 2011 sediment (Stojak et al., 2015). This indicates that these trace metals might be sourced by remaining coal ash contaminants in the riverine sediments (Fig. 16, 19).

There is no established method for tracing coal ash contaminants in river sediments. Usually, a general comparison of trace metal concentrations between contaminated and uncontaminated sites is used. Some previous methods also included isotopic composition of B and Pb in the water column (Davidson and Bassett, 1993; Ault et al., 1970) and/or ratios of As/Fe in the sediments (Schreiber et al. 2017). In this study, bulk C and S isotopic compositions were used to evaluate whether these tracers are useful in determining the coal ash contaminants in river sediments because of distinctive isotope compositions in coal ash and major endmembers participating in C and S cycling in the studied area. In this study, the $\delta^{13}\text{C}$ of organic matter and $\delta^{34}\text{S}$ of chromium-reducible sulfides show distinctive negative values of -35.2 to -29.0‰ and -6.9 to +4.8‰, respectively (Tab. 3, 8, 9; Fig. 5, 10, 11), which are consistent with isotope composition of temperate biomass and biogenic pyrite formed naturally via microbial sulfate reduction in

freshwater settings (e.g., Warwick and Ruppert, 2016; Ishikawa et al., 2015; Jiang et al., 2008; Knöller et al., 2005; Peterson and Fry, 1987). Additionally, Warwick and Ruppert (2016) and Jiang et al. (2008) showed that $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ of coal (-27 to -21‰ and -4 to +11‰, respectively) gets enriched in lighter ^{12}C and heavier ^{34}S isotopes during combustion leading to distinctive isotope compositions (-31 to -29‰ and +9 to +11‰, respectively). Given that mixing of different C and S sources does not involve significant isotope fractionations (e.g., Sharp 2007), the bulk $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ should show different variations in the uncontaminated and contaminated sites, if coal ash still remains in the river sediments, particularly in the Emory River located in close proximity to the Kingston Fossil Plant. Accordingly, the sediments collected in Sites 8 and 10, the most impacted by the coal ash spill, showed higher $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ (-25.8 to -24.0‰ and -1.7 to +6.2‰, respectively) compared to the uncontaminated sites (-27.8 to -25.4‰ and -5.4 to +3.3‰, respectively) in June 2016 (Fig. 5, 10, 11). While the increases of bulk $\delta^{34}\text{S}$ were the most significant at depth of ~15 cm, consistent with the current residence of coal ash using sedimentation rates determined by Brenkert et al. (1992) and DOE (1995), the $\delta^{13}\text{C}$ values more reflected that of non-combusted coal (-26 to -24‰) along the entire core (Fig. 10B). In fact, it was possible to distinguish visually larger coal fragments in the sediments of contaminated sites (Fig. 17), with similar $\delta^{13}\text{C}$ values to non-combusted coal (-25.6 to -24.2‰), that were likely deposited at the time of the coal ash spill. The results of S sequential extraction also revealed significant increases of the $\delta^{34}\text{S}$ values of chromium-reducible sulfides (likely pyrite) and elemental S in the Emory River sediments (+0.7 to +4.8‰ at depth of ~15 cm), which were more positive and corresponded to the $\delta^{34}\text{S}$ of combusted coal (-2 to +11‰) (Jiang et al., 2008). Interestingly, the highest $\delta^{34}\text{S}$ values are in good agreement with the estimated depth of remaining coal ash contaminants that was determined using the previously estimated sedimentation rates (Fig. 10F, 11). Conversely, the $\delta^{34}\text{S}$ of uncontaminated sediments (-6.9 to +1.3‰) and in the top layers (0-5 cm) of contaminated sites was considerably lower (Fig. 11), consistent with isotope composition of biogenic pyrite formed via microbial sulfate reduction (Souza et al., 2016; Utgikar et al., 2002; Canfield, 2001; Detmers et al., 2001; Holmer and Storkholm, 2001; Berner, 1981). This suggests that under current condition the top layer of river sediments are least affected by the coal ash spill and the observed high concentrations of Al, As, Cr, Cu, Sr, and V in the younger layers (Fig. 9A, B, G, H, P, R) must be sourced by a post-coal ash spill event(s) and/or naturally by bedrock composition. Generally, it is unclear why the bulk $\delta^{13}\text{C}$ did not follow the same pattern as $\delta^{34}\text{S}$ in the contaminated sediments of Sites 8 and 10 when both bulk C and S contents were significantly lower (0.00 to 0.03 wt. % and 0.03 to 0.07 wt. %, respectively). It is likely that different sedimentation rates of non-combusted coal (big fragments) and coal ash (fine grains) led to different $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ variations with depth in the studied sediment cores.

Due to the efforts put forth by the EPA and TVA (removal of ~60% coal ash and floating cenospheres), a significant portion of trace metals was likely removed from the river sediments of the Kingston area. However, it is recognized that like

the water column, there are various natural processes also aiding in the decrease and removal of trace metals from riverbed sediments over time. One such process is dilution through the inflow of groundwater and surface runoff. However, higher pH of the water column (e.g., 6-9; Fig. 2E) suggests that dilution might be limited due to low solubility of metals under this condition. Another important process might be constant erosion and transport of sediment by river currents. As noted by the scuba diving team during the sediment core collection in June 2016, very strong currents are present at the base of the studied rivers and could be responsible for the transport of sediment and adsorbed trace metals downstream. To some extent, this might be a cause for metal increases observed downstream in Site 3, further away from the spill (Fig. 18). However, the burial of older sediments through sedimentation appears to also be important and was evident by considerable decreases of $\delta^{34}\text{S}$ in the top layer of contaminated sites (0-5 cm), implying microbial sulfate reduction with typical isotope signatures of the uncontaminated sites (Fig. 11). This shows that the new sediment deposited in the studied rivers, likely buried remaining coal ash contaminants and now separates them from the active river currents, thus preventing further erosion and downstream transport. Due to less vegetation and continuous construction of impervious surfaces (e.g. roofs, concrete) in the Kingston area, meteoric water is less able to infiltrate into the ground resulting in rapid runoff and soil erosion (Clark et al., 2014). Ultimately, the increasing urbanization of the studied area may increase sedimentation rates and overall burial of coal ash contaminants with time.

Of the trace metals analyzed and detected in the studied river sediments, the concentrations of Al, B, Ba, Cd, Cr, Cu, Fe, Ge, Mn, Pb, Se, Tl, and Zn were usually higher in the uncontaminated Site 2, located in the Watts Bar Reservoir farthest away from the Kingston coal plant (Fig. 18). This suggests that there is also a significant metal load from other sources than coal ash. In Tennessee, only 70% of reservoirs and 52% of streams and rivers meet guidelines established by the Tennessee Department of Environment and Conservation (TDEC) for both fish and aquatic life and recreation ("Water Quality Reports & Publications - TN.Gov"). The most common pollutants in reservoirs, rivers and streams include sediment/silt, pesticides, urban waste, pathogens, metals, organic pollutants, and nutrients. Although it is impossible to trace these all pollutants with chemical and isotope tracers used in this study, in Apr 2016 the measured $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3 in water column was indicative of significant nutrient-rich inputs from waste/septic effluents and fertilizers (Fig. 6). This, in turn, suggests potential contamination of the Kingston rivers by local urban and agricultural sources. Additionally, in Tennessee Rivers (e.g., part of Watts Batt Reservoir) major trace metal pollutants include; Al, As, Cr, Cu, Fe, Mn, Pb, and Zn, which are consistent with the chemical analysis of rivers sediments analyzed in this study (Fig. 9). While many of the pollutant sources are due to ongoing industrial, agricultural, construction, mining, and municipal activities, these water bodies have been also greatly affected by legacy activities. In addition to the 2009 Kingston coal ash spill, the legacy activities include strip mining and industrial waste Hg spills from Oak Ridge Y-12 (Clinch

River), which continue to be sources of metals and decreases of pH in the Tennessee surface waters (“Water Quality Reports & Publications - TN.Gov”).

6.3. Critical Assessment of EPA and TVA Cleanup Efforts

The assessment of the success of the clean-up efforts put forth by the EPA and TVA in 2009 remains complicated. In some ways, the clean-up did remove significant amounts of the toxic coal ash contaminants by dredging and physical removal of the river sediments. This likely helped to reduce subsequent fluxes of trace metals into the water column since current concentrations are below detection limit and the contents of most trace metals in sediments are usually lower than established sediment quality guidelines. However, the concentrations of As and Cd in the riverine sediments continue to be elevated, above the low toxicity potential sediment quality guideline within the previously contaminated regions of the rivers. This indicates continued environmental risk and the need for more detailed analysis of the sediments in the studied rivers in the future. Currently, it is unclear to what degree the remediation efforts aided in the lowering of trace metal concentrations in the contaminated portions of the studied river systems versus what has been a result of natural processes such as dilution, adsorption, erosion, and sedimentation.

Because the sediments containing coal ash contaminants appear to have undergone some degree of burial by new sediments (up to ~5 cm or so as inferred using $\delta^{34}\text{S}$), it is concluded that natural sedimentation and neutral water pH, driven by carbonate dissolution, might be important factors preventing these trace metals from being released back into the water column. Most likely, a disturbance of the top 15 cm of sediment would need to occur, in conjunction with some acidification, for a significant metal release to take place. The results of this study suggest that natural sedimentation over time may be important for ensuring safety of aquatic organisms and human beings and protecting from high concentrations of trace metals induced by the 2008 coal ash spill. Given that the coal ash contaminants still remain near the sediment-water interface (within 0-5 cm), regular analysis of water chemistry and riverbed sediments should continue to ensure trace metals are not being released to the water column by seasonal processes (acidification, river currents) and/or biological activity.

6.4. Presence of Microbial Sulfate Reduction (MSR)

MSR is a natural process that may remediate trace metals via formation of insoluble sulfides. It has been commonly used to mitigate high metal loads from acid mine drainage (Utgikar et al., 2002; Evangelou, 1995). Reducing microbes utilize sulfate and organic carbon from surface and pore waters to produce H_2S

gas, which reacts with trace metals (Souza et al., 2016; Utgikar et al., 2002; Canfield, 2001; Detmers et al., 2001; Holmer and Storkholm, 2001; Berner, 1981). As a result, various insoluble sulfides are formed. However, MSR necessitates labile carbon, abundant SO_4^{2-} reservoir, and anoxic conditions (Souza et al., 2016; Canfield, 2001; Detmers et al., 2001; Holmer and Storkholm, 2001; Berner, 1981). While MSR is one of the main metabolic pathways in marine sediments due to elevated SO_4^{2-} concentration in seawater, this process has also been observed in freshwater sediments (e.g., lakes, rivers) with smaller SO_4^{2-} availability. Generally, MSR leads to increases of the $\delta^{34}\text{S}$ of dissolved sulfate and significant decreases of $\delta^{34}\text{S}$ in the formed H_2S /sulfides (Souza et al., 2016; Canfield, 2001; Detmers et al., 2001; Holmer and Storkholm, 2001; Berner, 1981). Sulfur isotope fractionations between SO_4^{2-} and H_2S /sulfide can widely vary (by 4 to 46‰), depending on microbial activity rates and the size of SO_4^{2-} pool. These distinctive isotope fractionations allow for studying the effects of MSR on sediments of marine and freshwater origin and evaluation of remediation potential related to formation of biogenic metal sulfides (Souza et al., 2016; Detmers et al., 2001; Canfield, 2001).

In this study, S sequential extraction method was used to evaluate whether MSR might have been important in the remediation of toxic metals from coal ash spill in the Kingston area. For example, toxic metals present in coal ash (e.g. As, Cu Fe, Zn) are known to react with H_2S to form insoluble sulfide minerals such as orpiment, realgar, covellite, pyrite, mackinawite, and sphalerite (Rodriguez-Freire et al., 2016; Meier et al., 2012; Church et al., 2007). Therefore, $\delta^{34}\text{S}$ of acid-volatile sulfides (AVS) and chromium-reducible sulfides (CRS) was analyzed in the core sediments collected in June 2016. Additionally, $\delta^{34}\text{S}$ of elemental S was determined because it is a common product of MSR accompanying microbially-mediated formation of AVS and CRS. Generally, microbial processes lead to formation of sulfides and elemental S with negative $\delta^{34}\text{S}$ values (-40 to <0 ‰; Canfield, 2001) compared to significantly higher bulk $\delta^{34}\text{S}$ reported for coal ash (+8.8 to 12.6‰; Jiang et al. 2008). Accordingly, the sediments of Clinch River and Watts Bar Reservoir showed relatively low $\delta^{34}\text{S}$ values of elemental S (-3.5 to +1.1‰), AVS (-2.7 to +1.1‰) and CRS (-6.9 to +1.3‰) suggesting that MSR takes place in the studied rivers (Fig. 11). The observed S isotope fractionations between elemental S, AVS, CRS and SO_4^{2-} dissolved in water column varied in a range of 5 to 14‰ (Fig. 7B, 11B, 11F) and were reflective of those frequently observed in the anoxic sediments undergoing MSR (Souza et al., 2016; Canfield, 2001; Detmers et al., 2001; Holmer and Storkholm, 2001; Berner, 1981). Isotope fractionations between aqueous SO_4^{2-} and H_2S /sulfides are generally known to be smaller under stressed conditions, lacking a sufficient SO_4^{2-} source (Werne et al., 2004; Canfield, 2001). As a result of small SO_4^{2-} pool and closed condition, the SO_4^{2-} can be quickly exhausted due to microbial consumption and converted to H_2S , leaving minor/negligible S isotope signature in the sediment. It is observed that $\delta^{34}\text{S}$ values of CRS and elemental S in the studied sediments showed increasing $\delta^{34}\text{S}$ value with depth (Fig. 11b, F). This usually occurs due to the utilization of available SO_4^{2-} with depth, resulting in $\delta^{34}\text{S}$ values more similar to the

initial SO_4^{2-} pool present in the water column or delivered by groundwater. In the Kingston area, the $\delta^{34}\text{S}$ of water column SO_4^{2-} varied in a narrow range (+2.7 to +5.8‰) but it was higher compared to the $\delta^{34}\text{S}$ of sediments (Fig. 11). Additionally, the older sediments get enriched in heavier ^{34}S isotopes over time because microbial processes preferentially remove lighter ^{32}S isotopes. Overall, the observed variations of $\delta^{34}\text{S}$ with depth in the Kingston sediments are consistent with other studies in similar freshwater settings (Werne et al., 2004; Holmer and Storkholm, 2001). Note that the analyzed sediments did not contain any acid-soluble SO_4^{2-} phases (e.g., pore water sulfate and sulfate minerals). This suggests that MSR is limited by a small SO_4^{2-} pool in the studied river systems. Consequently, the contents of elemental S, AVS, and CRS were also relatively low, varying from <0.01 to 0.22 wt. S% (Tab. 9, Fig. 11).

In contrast, the highly contaminated sediments of Emory River (Sites 8 and 10) showed more positive $\delta^{34}\text{S}$ values of elemental S and CRS (+0.3 to +10.8‰) and were closely related to the higher $\delta^{34}\text{S}$ of coal ash (+8.8 to +12.6‰) previously reported by Jiang et al. (2008) (Fig. 11B, F). Additionally, the $\delta^{34}\text{S}$ demonstrated a clear increase at depth of ~5-15 cm (0 to +10.8‰; Fig. 11B, F), consistent with a depth of residing coal ash from the 2008 spill event, and did not reflect the same isotope fractionations between various S forms (SO_4^{2-} , elemental S, AVS, CRS) as observed in the Clinch River and Watts Bar Reservoir sites (Fig. 5B, 11B, 11F). While there are multiple processes affecting S isotopic composition of river sediments (e.g. microbial oxidation-reduction, bedrock dissolution), the high $\delta^{34}\text{S}$ of the studied contaminated sediments, followed by decreases of bulk and elemental S contents (<0.2 wt. %), and to some degree CRS, strongly supports the effect on coal ash spill and plausible inhibition of the MSR process during the 2008 spill event. Sulfate reducing bacteria are known to be inhibited under the presence of oxygen and an excess of trace metals (Utgikar et al., 2002; Holmer and Storkholm, 2001). Under oxygenated conditions, several enzymes and proteins necessary for the reduction of SO_4^{2-} are inhibited/inactivated (Holmer and Storkholm, 2001). Similarly, many trace metals can be toxic to sulfate reducers at elevated concentrations, usually from a few mg/L to as much as 100 mg/L (Holmer and Storkholm, 2001). This toxicity has the potential to inhibit enzymes and proteins like oxygen does, or result in death of the microorganisms (Holmer and Storkholm, 2001). It is proposed that both conditions (oxygenation and high metal load) are likely to have occurred as a result of the Kingston coal ash spill in 2008. The sediments directly contaminated by coal ash likely became oxygenated by dredging activities and significant mixing with oxygenated water column, while increases of trace metal concentrations were induced by the high quantities of spilled coal ash into Emory River. The inhibition or even death of microbial sulfate reducers would have ceased the production of biogenic sulfides (CRS) and elemental S with negative $\delta^{34}\text{S}$ in the Emory River sediments. This would result in a significantly more positive $\delta^{34}\text{S}$ values induced by the coal ash contaminants. Alternatively, the observed higher $\delta^{34}\text{S}$ of the Emory River sediments could be a result of detrital sulfides and elemental S sourced from erosion of local bedrock

enriched in heavier ^{34}S isotopes (Fig. 11B, F). While similar S isotope analyses were not done on the local bedrock samples, this is unlikely scenario because of the observed negative $\delta^{34}\text{S}$ in the top sediment layers of the Emory River (Fig. 11B, F) more typical for MSR naturally occurring in the studied areas. Note that negative $\delta^{34}\text{S}$ of elemental S (-3.6 ‰) and CRS (-7.1‰) in the youngest (top) sediment layers of Site 8 were similar to $\delta^{34}\text{S}$ of the uncontaminated sites (Fig. 11b, F). Therefore, the observed depth trend, with distinctive decrease of $\delta^{34}\text{S}$ toward the surface, is more consistent with a restoration of the inhibited/lost MSR community and return to natural conditions over time, reflected in the similar, negative $\delta^{34}\text{S}$ values observed in the uncontaminated river sediments within the ~5 cm thick top layer (Fig. 11).

Sediment and bedrock erosion are sources of dissolved ions in freshwater systems. Sulfides are common in shale rocks but are less abundant in carbonate sedimentary formations (Tucker, 2001). Therefore, it is important to consider that some of the studied sulfide phases (AVS, CRS) in the core sediments might have come from physical erosion of the bedrock. Unfortunately, the S mineral content was too low for more detailed analysis using XRD methods to describe what metal sulfides were naturally present from bedrock erosion and which might have been formed due to MSR occurring in the river sediments. Generally, sulfide concentrations between 0.5-1 wt.% are necessary to characterize mineralogical composition using XRD. In contrast, the studied sediments had significantly lower concentrations of <0.05 wt.S%. While it is impossible to definitely distinguish between geo- and biogenic sulfides using the results of this study, it is inferred that some trace metals from coal ash might have been bio-immobilized by MSR through the formation of insoluble sulfides. The MSR process appears to be active and isotopically distinctive in the uncontaminated Clinch River and Watts Barr, and in the younger layers of contaminated Emory River (Fig. 11). However, the influence of MSR might be relatively small because the elevated concentrations of many trace metals (e.g. As, Be, Cd, Zn) were mostly found in the DI water-soluble fraction. Given that the biogenic metal sulfides are insoluble in water, it is expected that these metals would have been more abundant in acid-soluble fraction, if MSR was dominant immobilizing process.

Because of relatively low S content in the Kingston river sediments, future studies using Scanning Electron Microscope (SEM) techniques would have to be applied in order to better characterize the type of sulfide mineralization associated with MSR and describe the distribution of trace metals within the contaminated versus uncontaminated river sediments. This type of study could also help in better understanding how metals from various anthropogenic activities are stored in the riverine sediments and assessing their potential releases into the water column.

CHAPTER SEVEN

CONCLUSIONS

The results of multiple chemical and isotope analyses indicate that the surface waters of the Emory River, Clinch River, and Watts Bar Reservoir show negligible concentrations of trace metals (e.g., Al, As, Be, Br, Cd, Cr, Cu, Li, Ni, and Pb) eight years after the Kingston coal ash spill. In April 2016, these metals did not exceed the EPA guideline for aquatic life, human health or drinking water, suggesting that the combination of remediation efforts put forth by the TVA and EPA to remove ~60% of coal ash and natural processes such as dilution, adsorption, etc., were helpful in mitigating the elevated trace metals present in the water column shortly after the spill. Additionally, it is recognized that local dissolution of carbonate bedrock increases the buffering capacity of the studied rivers, which allows for pH to remain at neutral levels (6-9) where trace metals are most likely to be found adsorbed onto sediment particles. Conversely, the elevated concentrations of various trace metals were measured in the ~30 cm top layer of river sediments. While many of the trace metals were in concentrations lower than the established sediment quality guidelines, the concentrations of As and Cd (≤ 71.015 mg/kg and ≤ 2.381 mg/kg, respectively) appeared to exceed the low toxic potential sediment quality guideline in the Emory River sediments. Given that Cd concentrations were similarly high both close to the spill and in the uncontaminated portion of the Watts Bar Reservoir, Cd might be sourced by other anthropogenic activities (e.g., industry, mining). This was also the case for other metals such as Al, B, Ba, Cd, Cr, Cu, Fe, Ge, Mn, Pb, Se, Tl, and Zn which generally showed highest concentrations further away from the coal ash spill location.

Changes of metal concentrations with depth of the river sediments were not useful to determine the current residence (burial) depth of coal ash contaminants. However, bulk $\delta^{34}\text{S}$ of river sediments, elemental S, and chromium-reducible sulfides was a better tracer, suggesting that the remaining coal ash contaminants are currently buried by ~10-15 cm younger sediments in the Emory River, close to the 2008 spill location. In the most contaminated layers, the $\delta^{34}\text{S}$ was the highest (+4 to +11‰), reflecting the $\delta^{34}\text{S}$ of combusted coal (+9 to +12‰; Jiang et al. 2008).

The process of microbial sulfate reduction does appear to be occurring in the studied river sediments of Clinch River and Watts Bar Reservoir and to some extent in Emory River. Consequently, this process has the potential to aid naturally in the mitigation of trace metals from various anthropogenic sources (e.g., coal ash spill, industry, mining). However, in the presence of small SO_4^{2-} pool and increased toxicity by trace metals from coal ash spill that lowered (or inhibited) the activity of sulfate reducing bacteria, the bio-immobilization via this process appears to be insignificant. This conclusion is supported by the high solubility of many sediment trace metals in DI water used for leaching experiments, implying that many of the toxic metals analyzed in this study (e.g. As, Cr, Cu, Mn, Se, V, Zn) are adsorbed

on grain surfaces. It appears that microbial sulfate reduction in freshwater sediments is not likely to form enough insoluble sulfides to eliminate the necessity for other remediation efforts.

In summary, the results of this study suggest that the Kingston rivers are dominated by normal meteoric waters that are being impacted by various local contaminants in addition to coal ash spill. Tennessee rivers are known to have high levels of contaminants sourced from industry, agriculture, urbanization, municipal activities, and legacy events, to name a few. Given that elevated metal concentrations are present in the studied river systems, there is a necessity of continued analysis and monitoring to better characterize the contaminant sources and potential environmental impacts (e.g., subsequent releases) in this region.

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APPENDICES

Appendix A: Figures

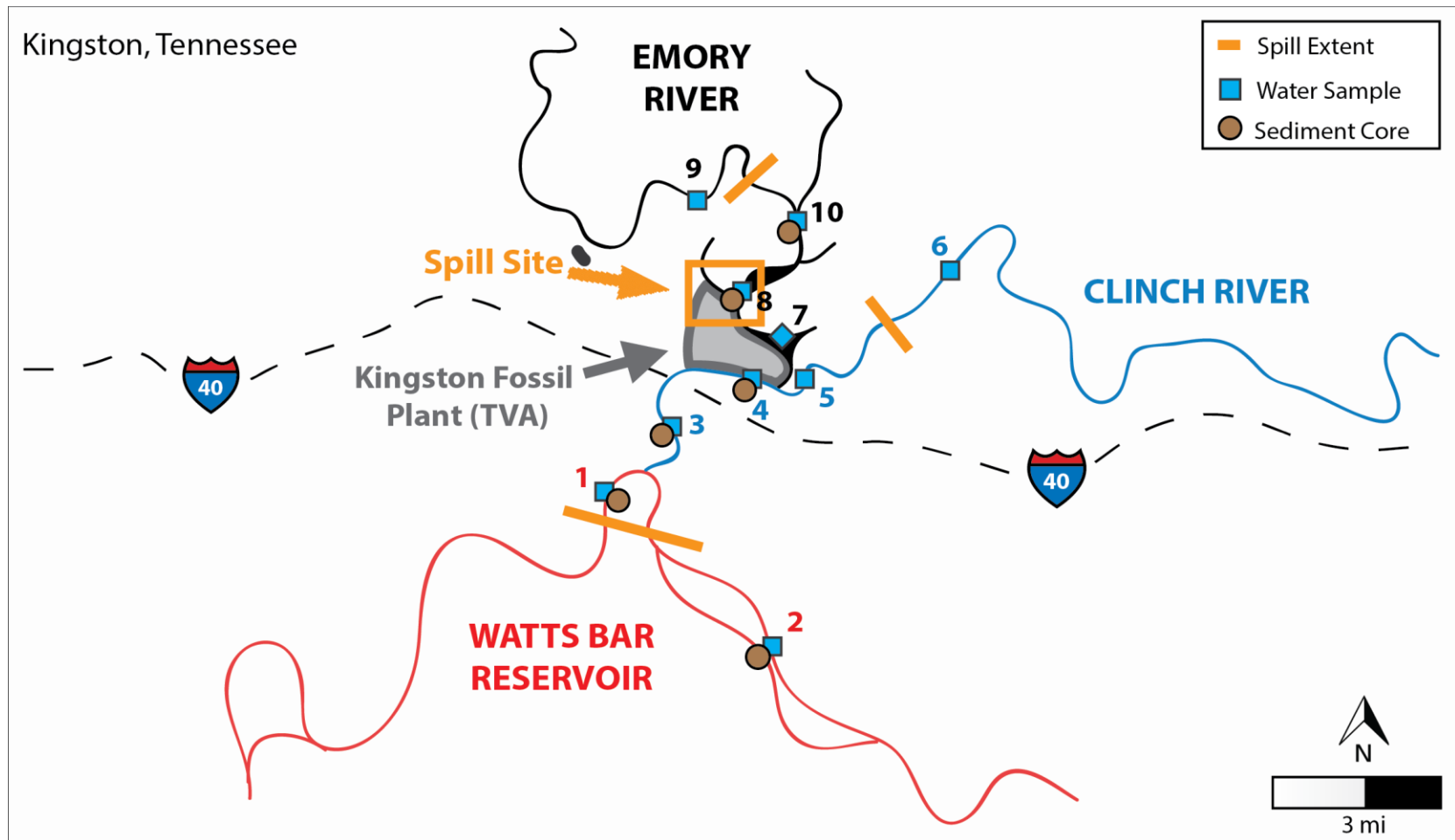


Figure 1: A simplified map showing the location of the coal ash spill and its contamination extent (orange box and bars), and the sampling locations of water (blue squares) and sediment cores (brown circles) collected in Apr-Jun 2016. Dotted gray line indicates Interstate Highway No. 40.

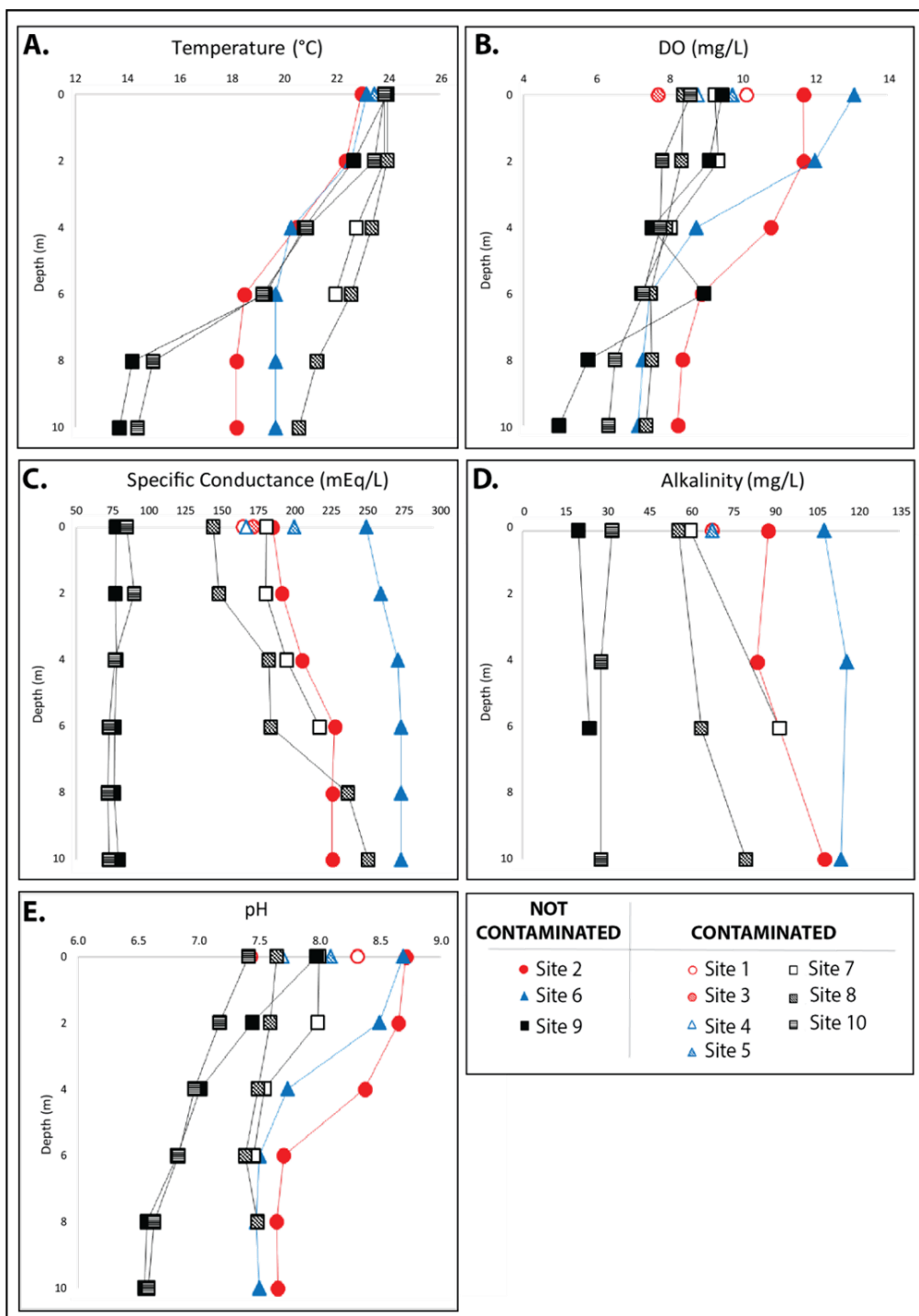


Figure 2: Variations of (A) Temperature, (B) DO, (C) Specific conductance, (D) Alkalinity, and (E) pH with depth of the water column. Note that water samples in Sites No. 3, 4, and 5 were only collected at the surface (0 m).

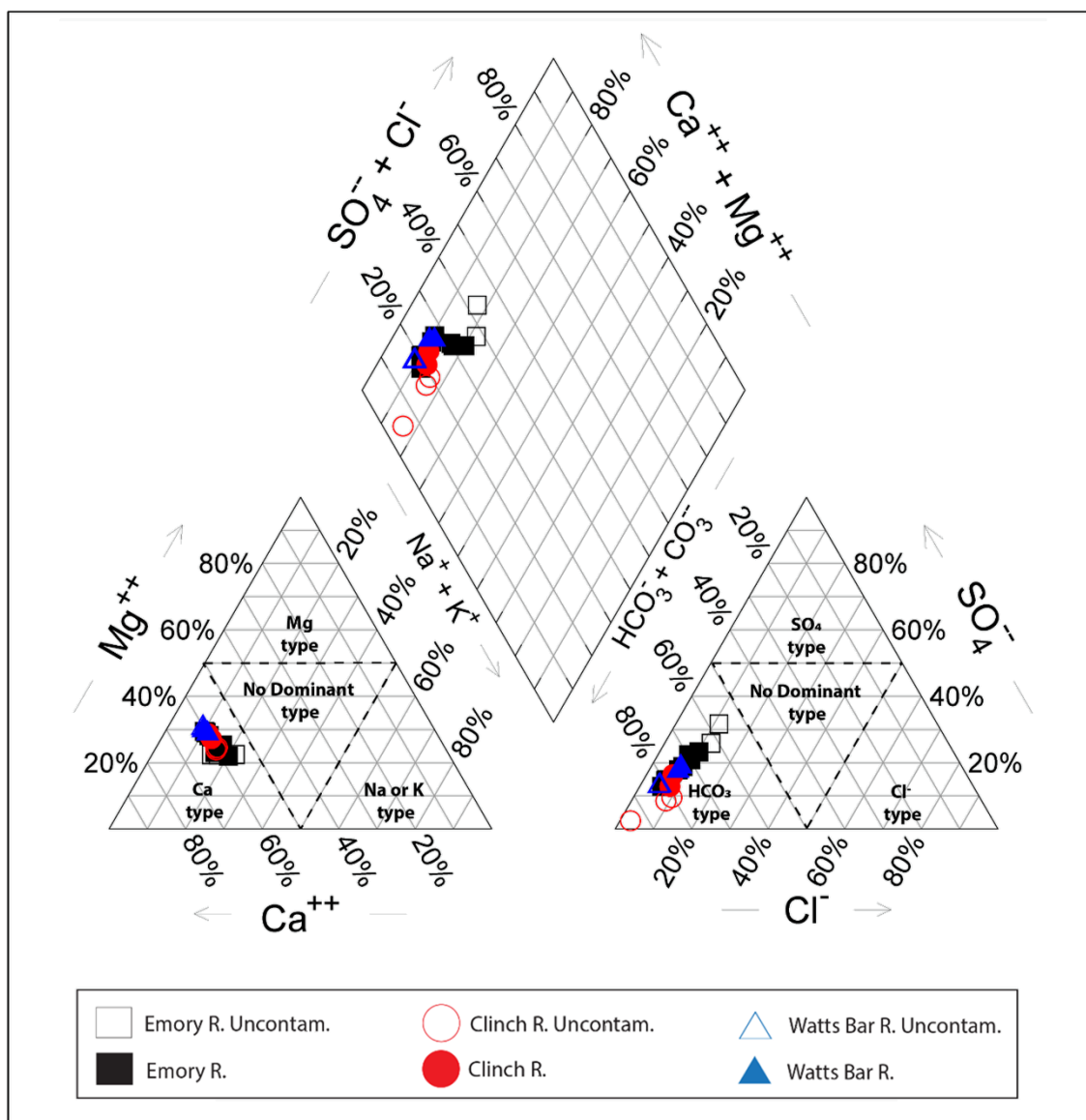


Figure 3: Piper diagram showing a major Ca-HCO_3 water type in the Emory River (black squares), Clinch River (red circles), and Watts Bar Reservoir (blue triangles). Samples collected from uncontaminated sites (outside of the coal ash spill) are indicated by hollow shapes. Classification of water type is based on Sadashivaiah et al. (2008).

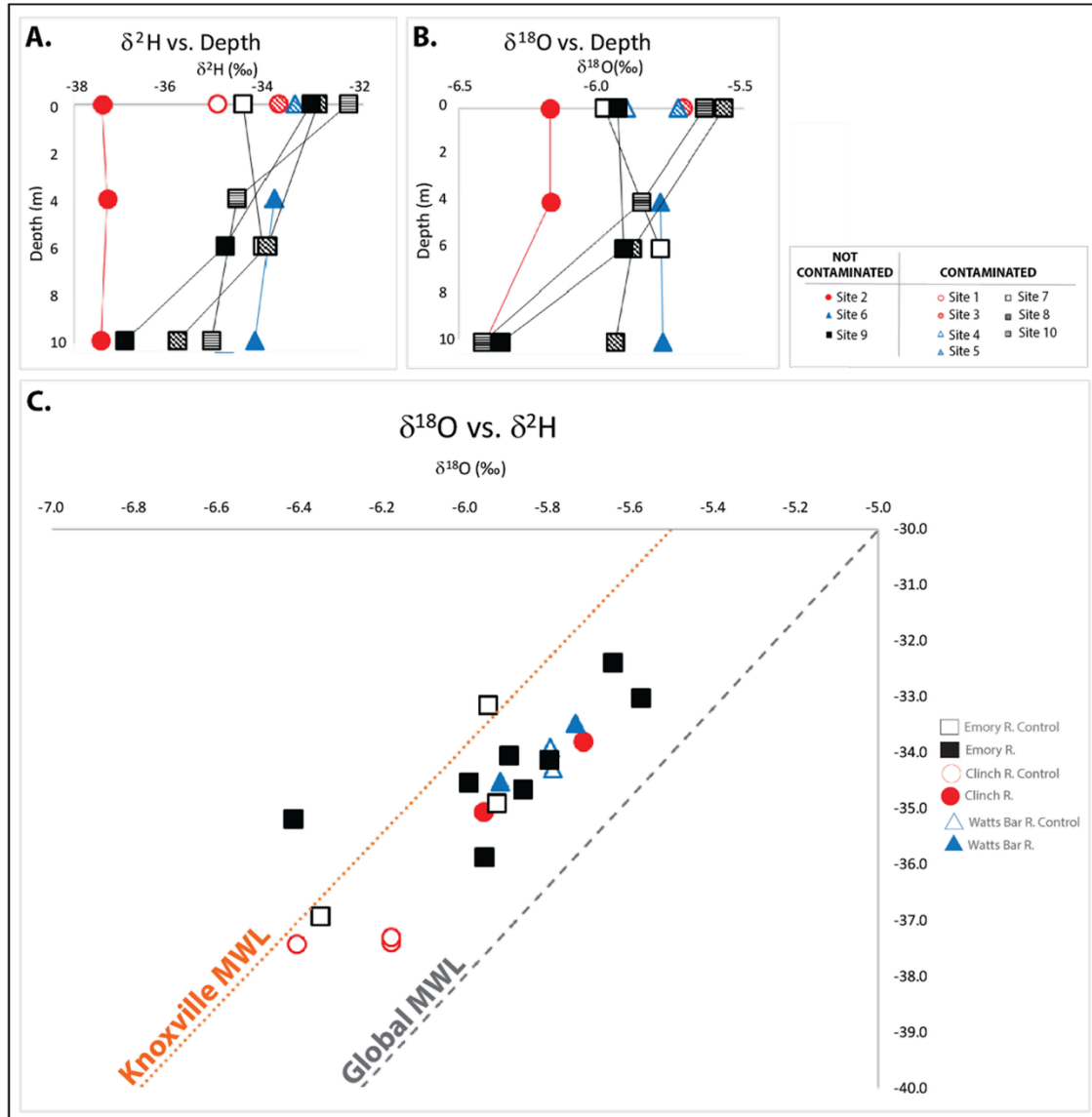


Figure 4: Variations of (A) $\delta^2\text{H}$ and (B) $\delta^{18}\text{O}$ of water with depth, and changes of (C) $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ relative to the Global Meteoric Water Line (grey) and Knoxville Meteoric Water Line (White, 2015; Unpublished data for City of Knoxville). The Emory River samples are in black, Clinch River samples are blue, and Watts Bar Reservoir samples are red. On (C), the samples collected outside the zone of contamination are shown as open symbols and in the contaminated sites as closed symbols.

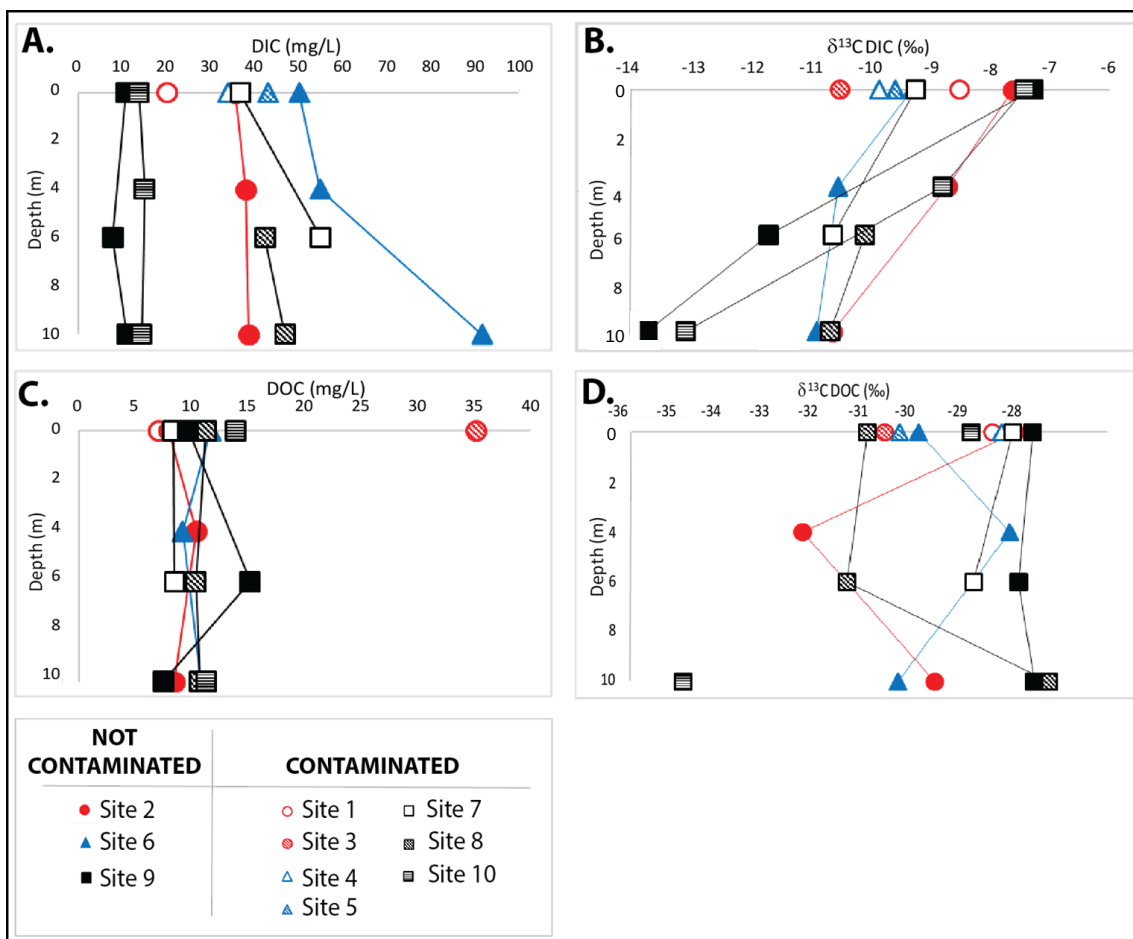


Figure 5: Variations of DIC concentration (A), and its $\delta^{13}\text{C}$ value (B), DOC concentration (C) and its $\delta^{13}\text{C}$ value (D) with depth of water column. The Emory River samples are in black, Clinch River samples are blue, and Watts Bar Reservoir samples are red.

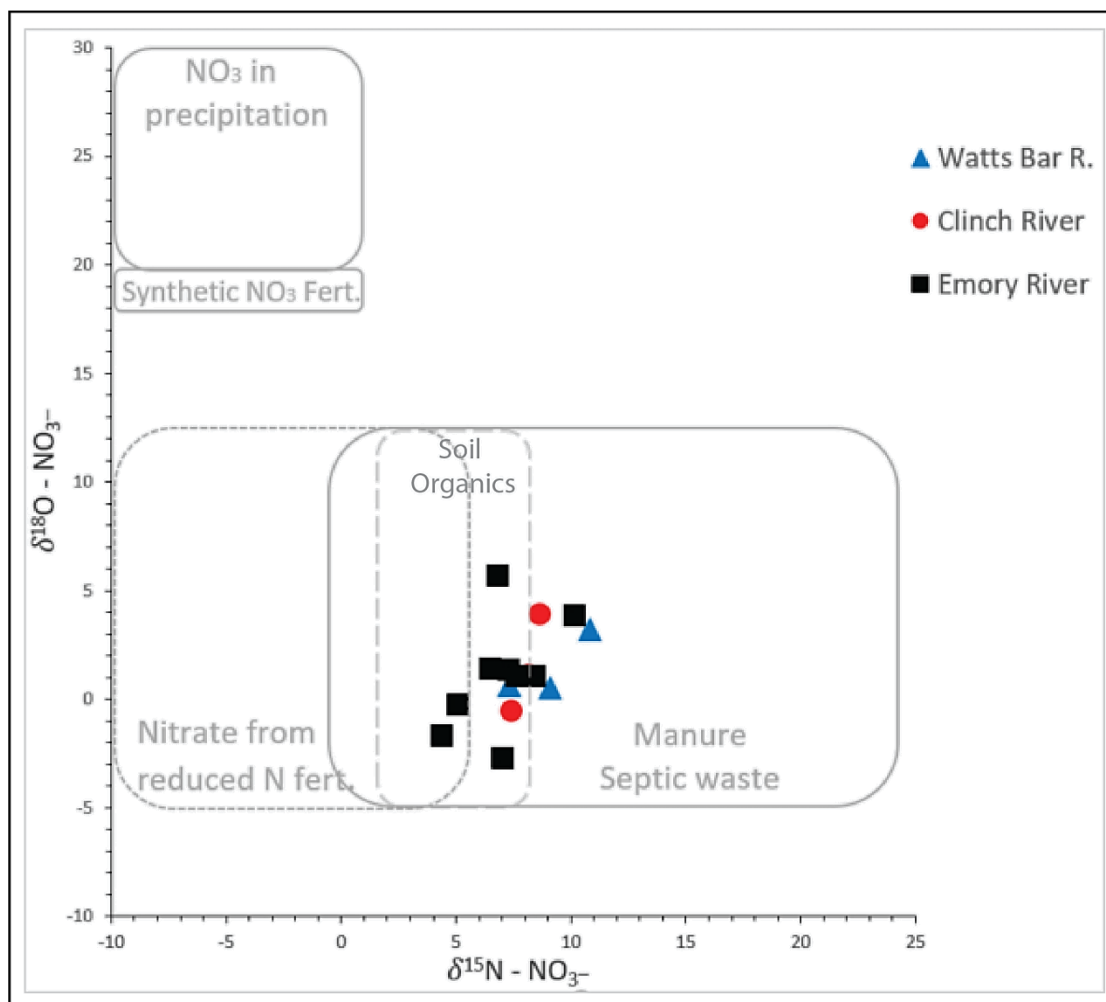


Figure 6: Variations of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of dissolved NO_3^- in the water column. Boxes represent typical isotope compositions of NO_3^- derived from different sources (after Chen et al. 2009). The Emory River samples are shown as black squares, Clinch River samples as blue triangles, and Watts Bar Reservoir samples as red circles.

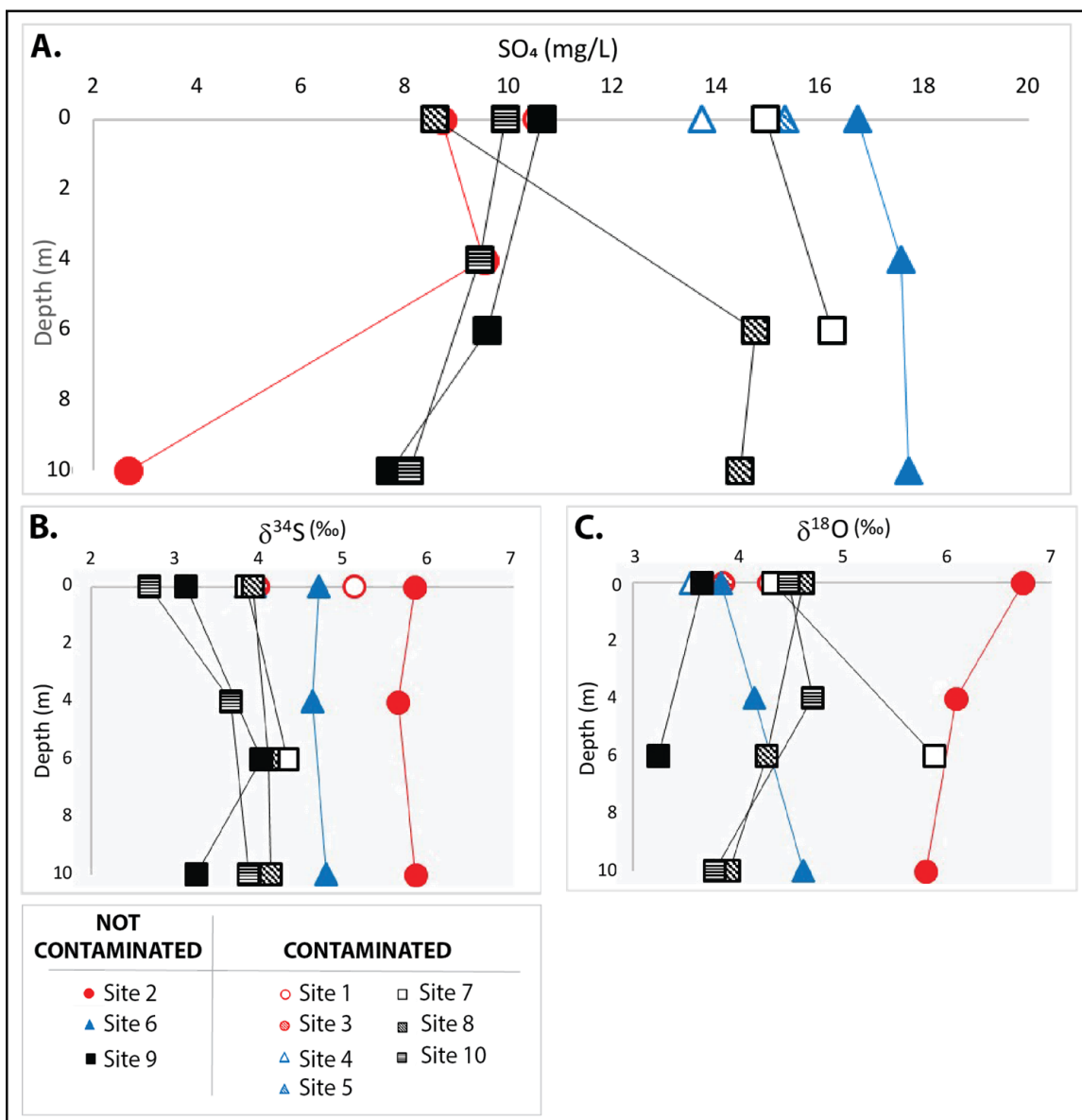


Figure 7: Variations of dissolved SO_4^{2-} concentration (A), $\delta^{34}\text{S}$ (B), and $\delta^{18}\text{O}$ (C) with depth of water column. The Emory River samples are shown in black, Clinch River samples in blue, and Watts Bar Reservoir samples in red.

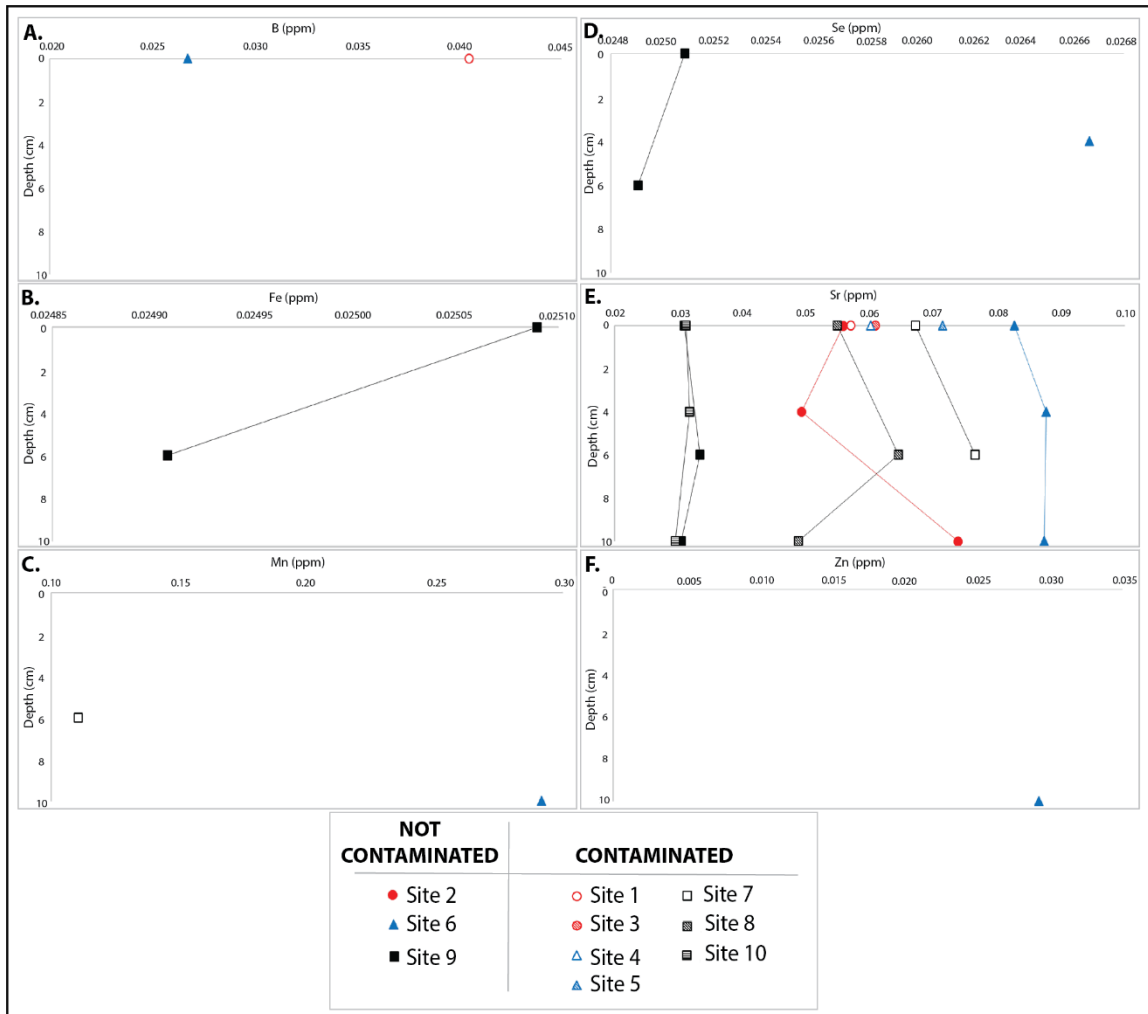


Figure 8: Variations of detectable trace metals with depth of the water column. The Emory River samples are shown in black, Clinch River samples in blue, and Watts Bar Reservoir samples in red.

Figure 9: Variations of detectable trace metals in the sediment cores. Water-soluble trace metals are depicted by open symbols and acid-soluble trace metals by solid symbols. The Emory River samples are shown in black, Clinch River samples in blue, and Watts Bar Reservoir samples in red. Site 2 (red circles) represents the sediment core collected outside the zone of contamination by coal ash spill.

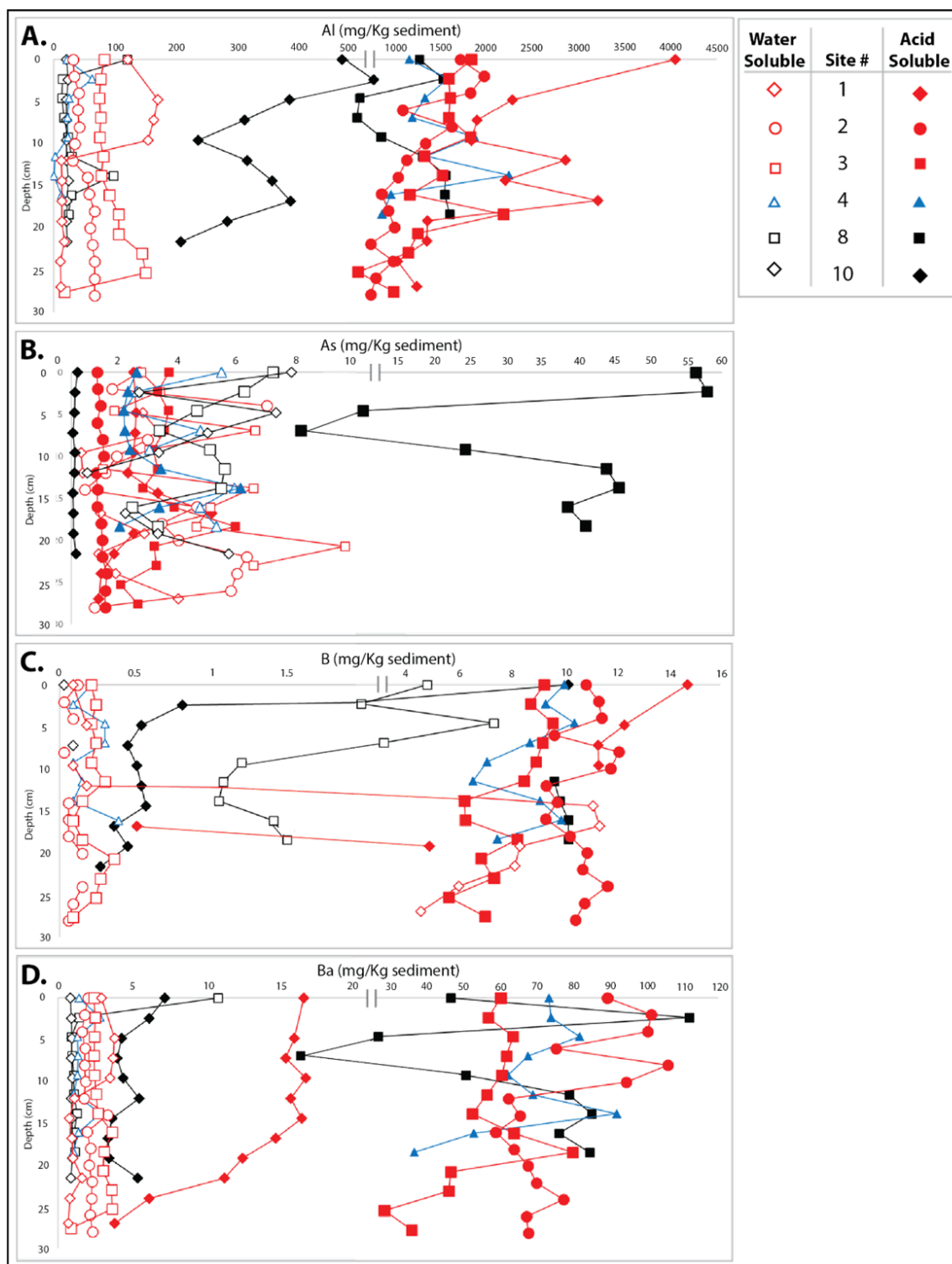


Figure 9: Continued.

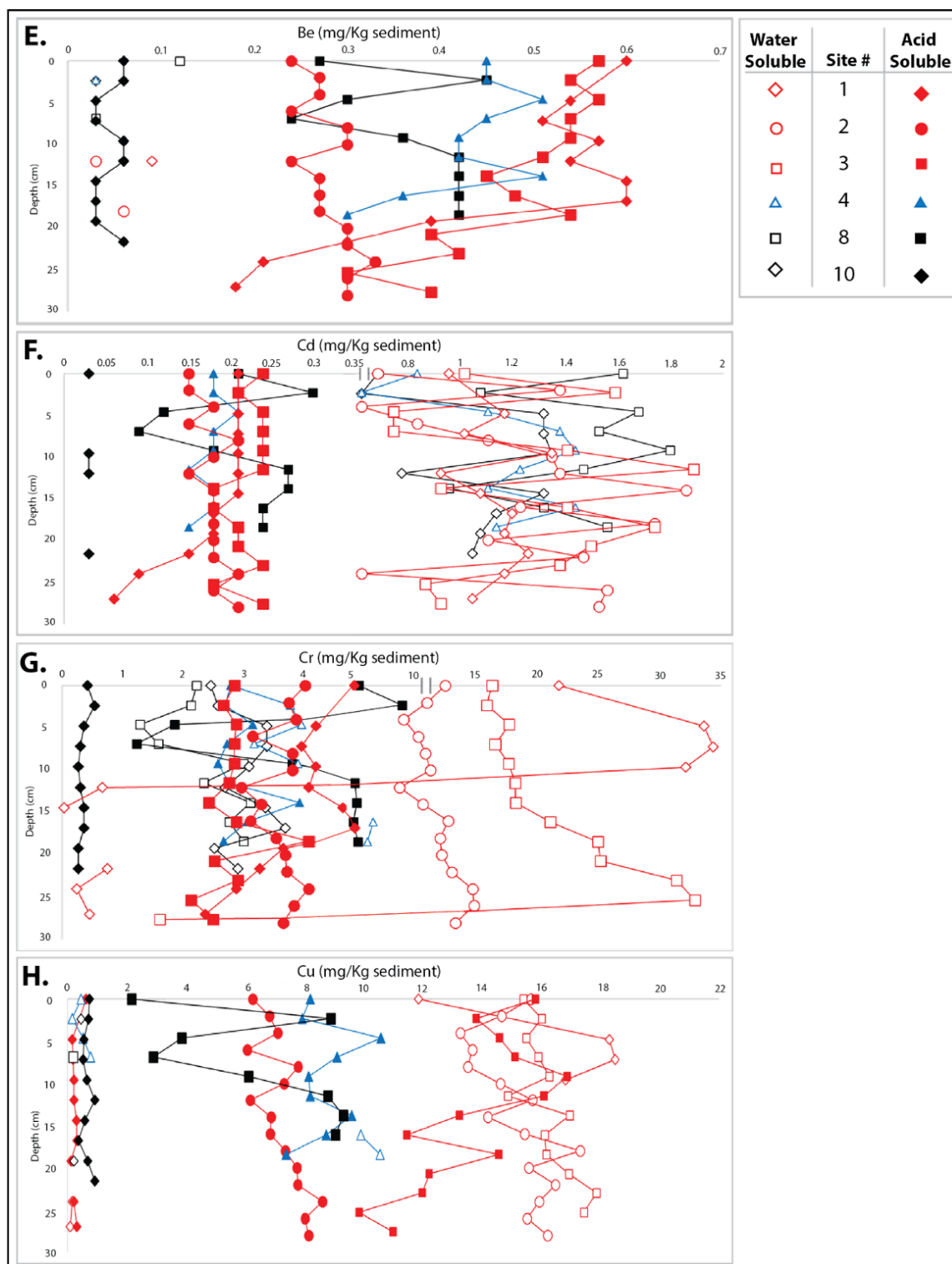


Figure 9: Continued.

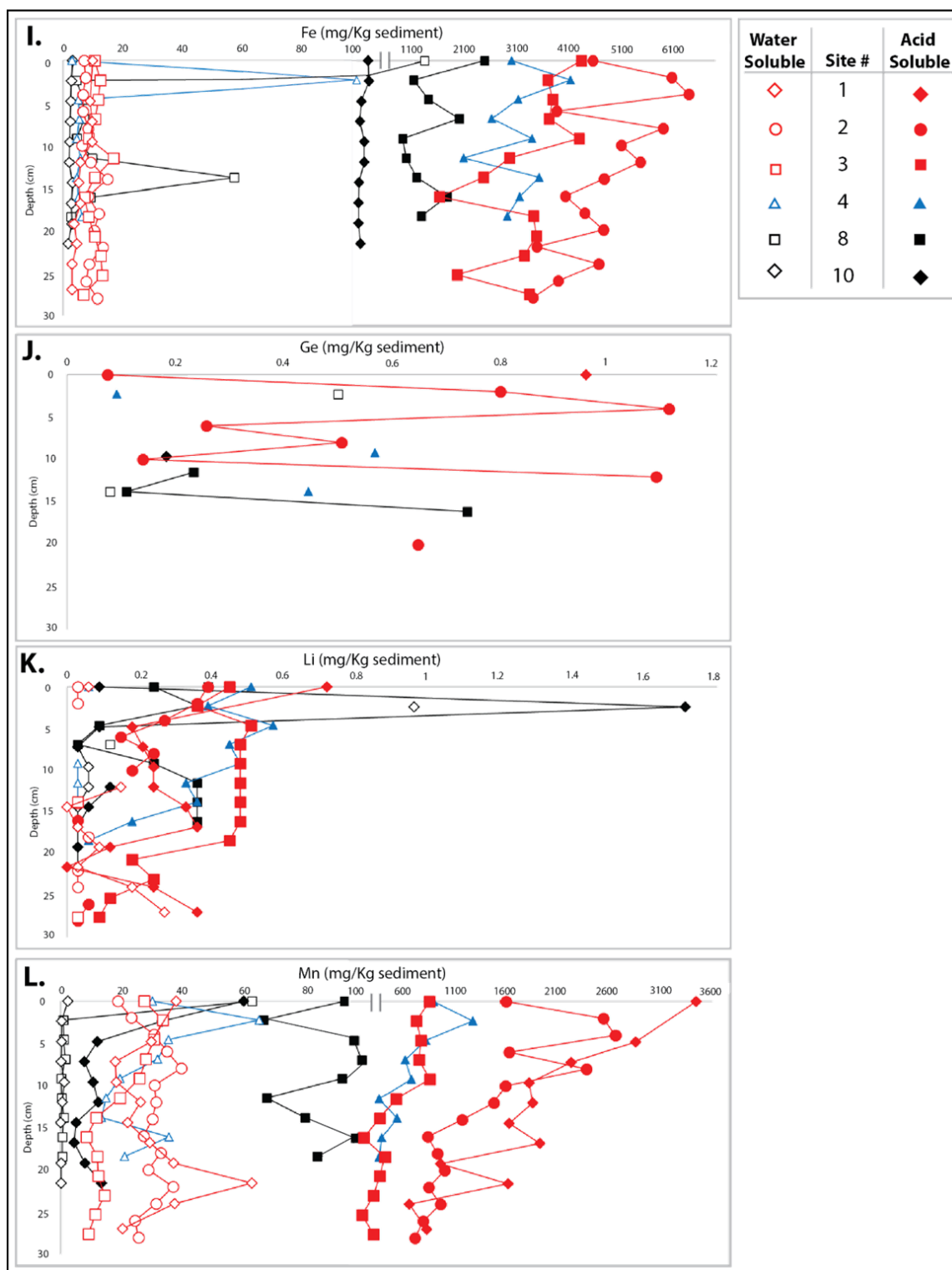


Figure 9: Continued.

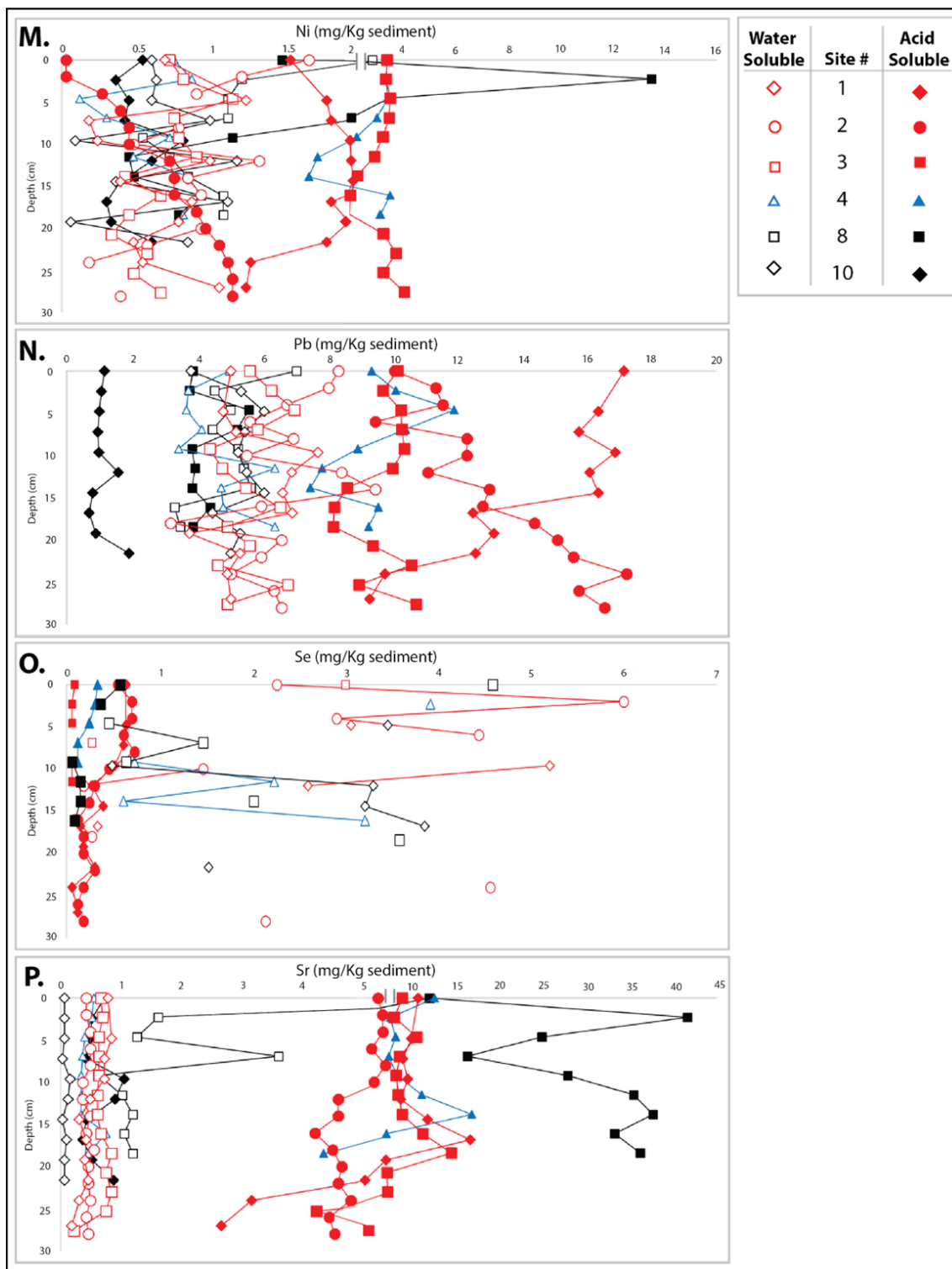


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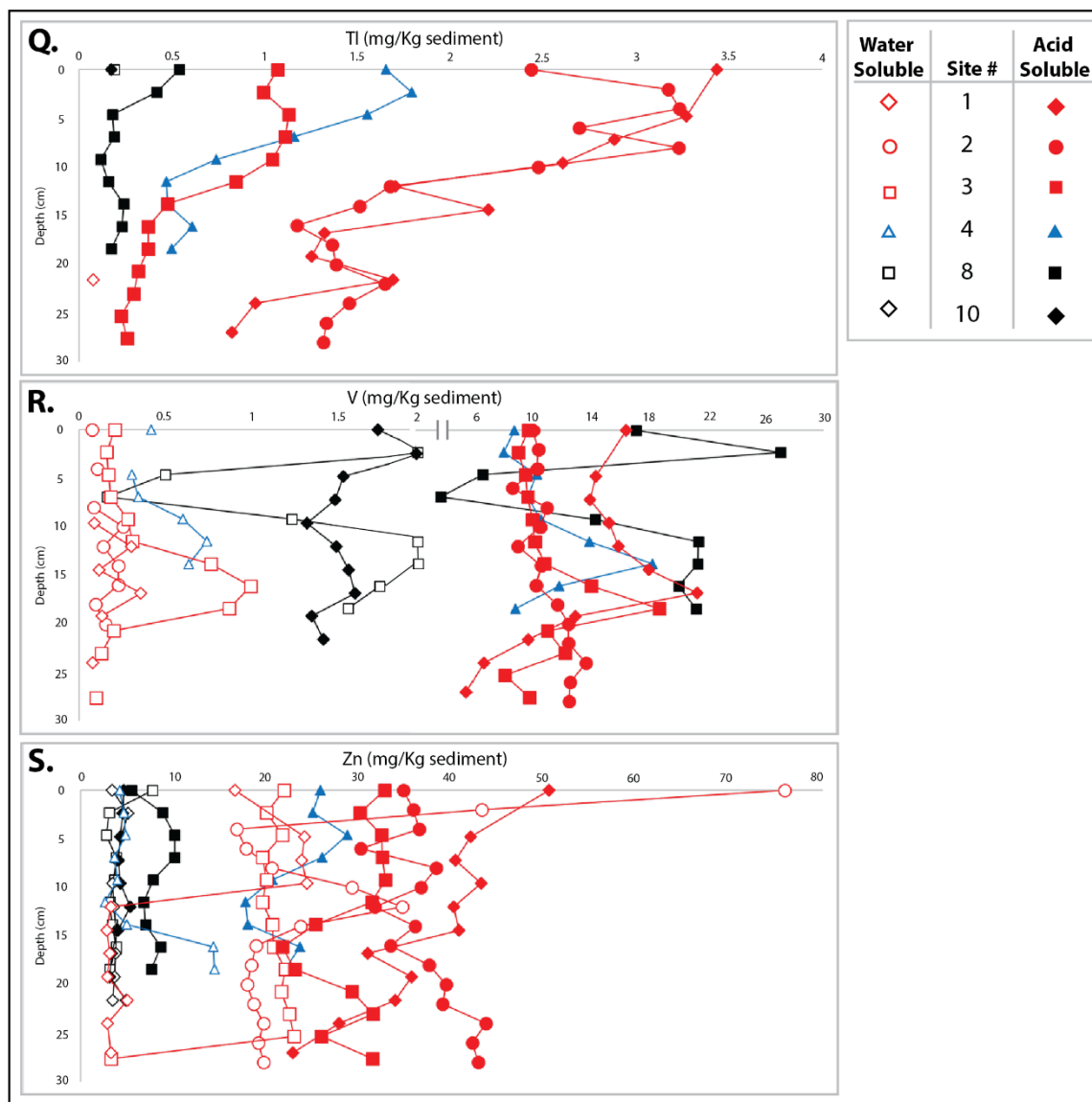


Figure 9: Continued.

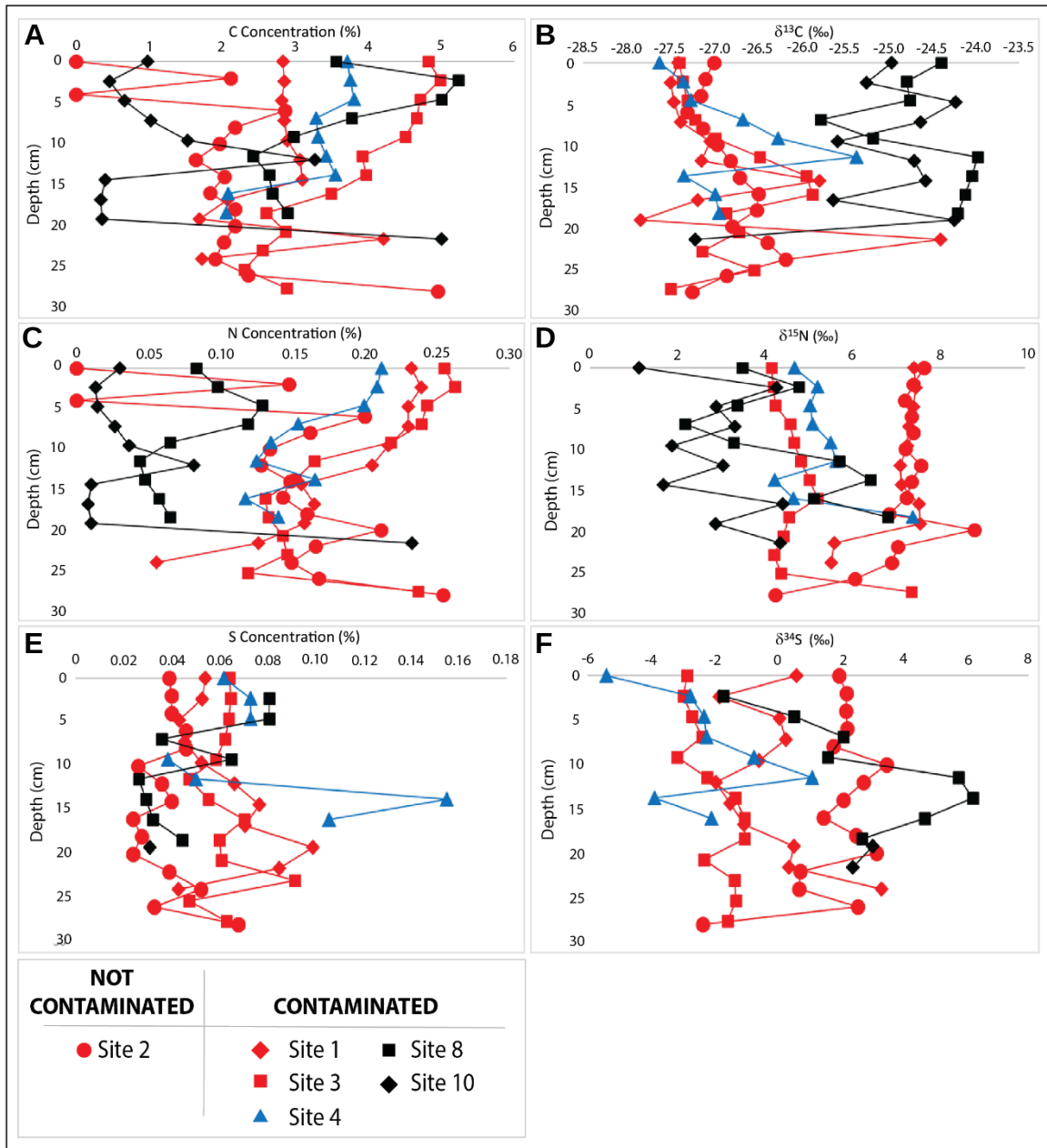


Figure 10: Variations of bulk C-N-S concentrations and isotope compositions with depth of the sediment cores.

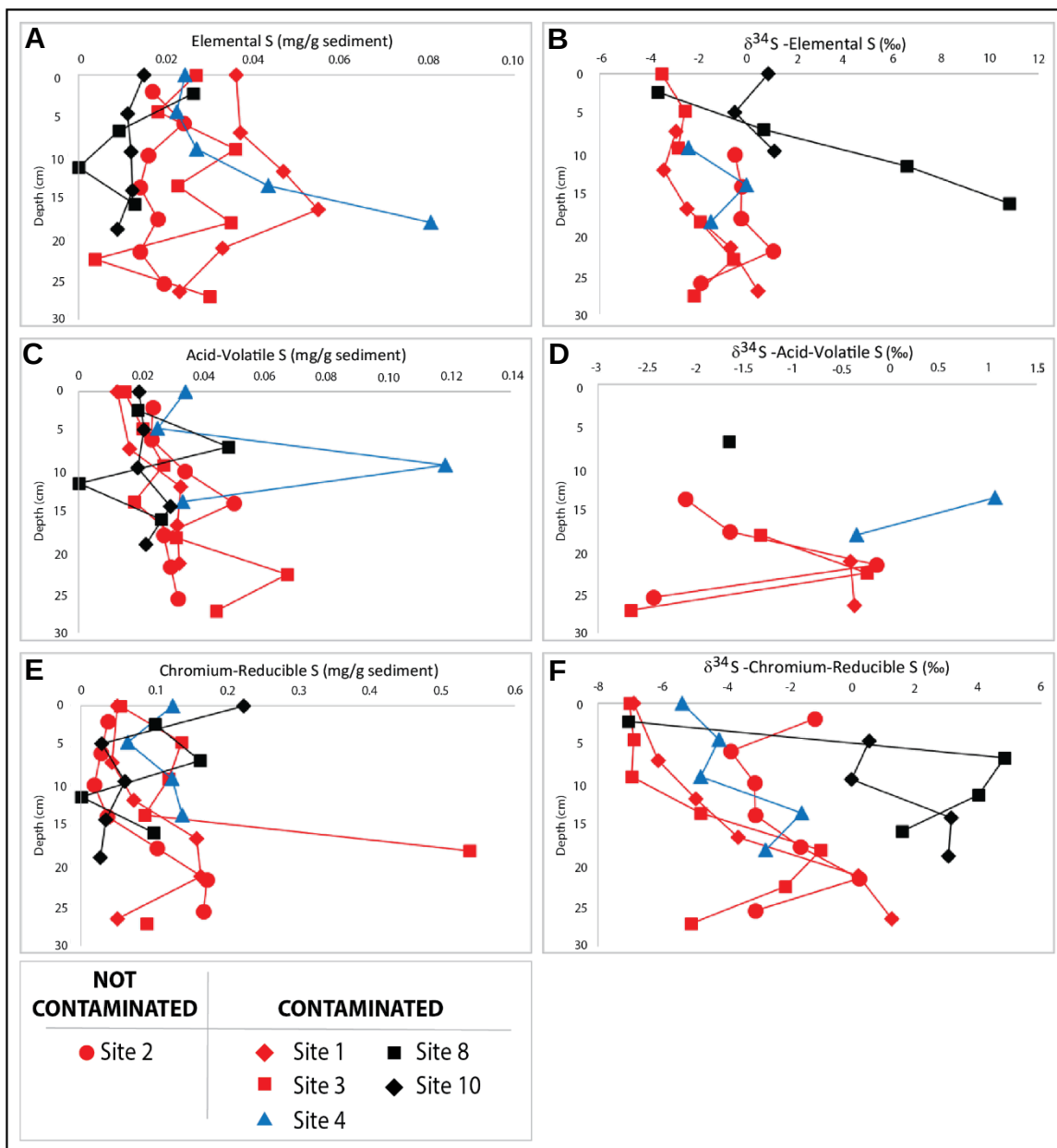


Figure 11: Variations of wt. S% and $\delta^{34}\text{S}$ of elemental S, acid-volatile sulfides, and chromium-reducible sulfides with depth of the sediment cores.

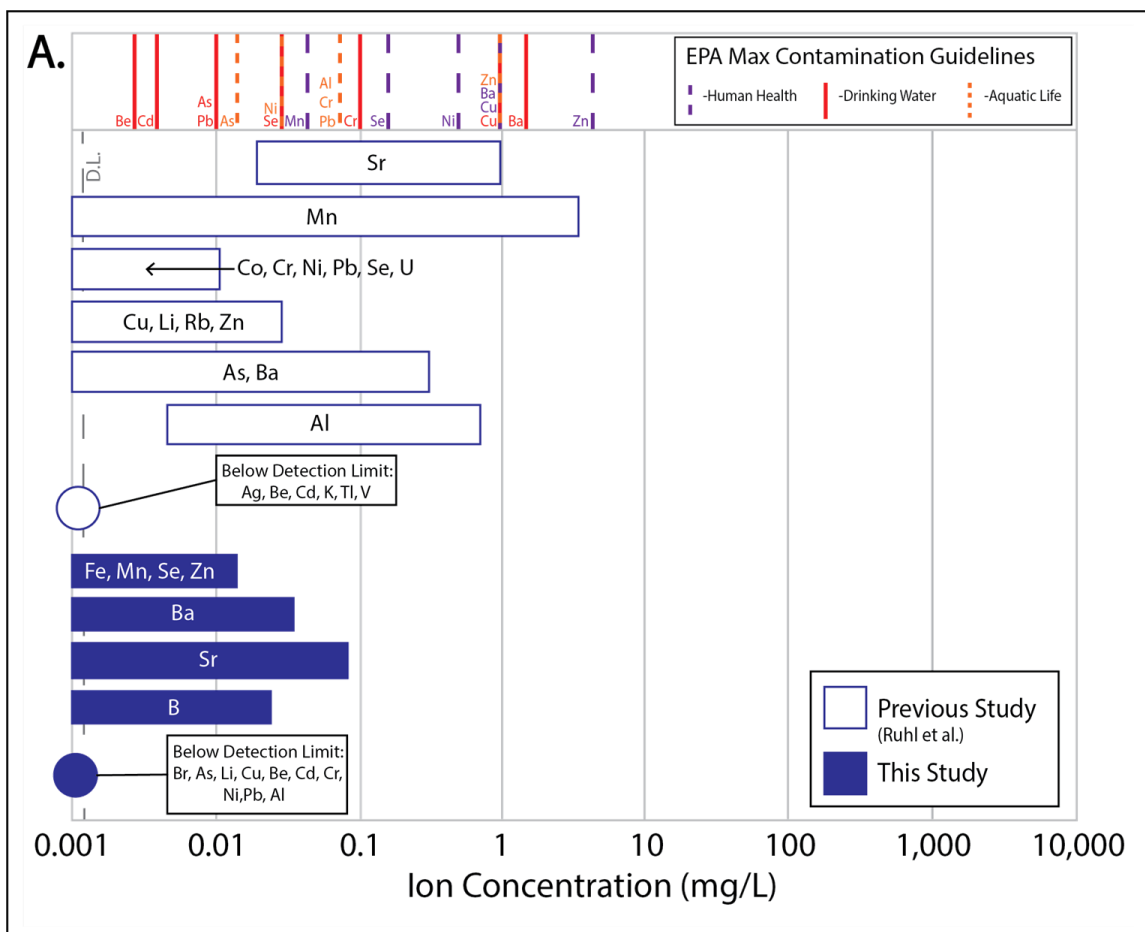


Figure 12: Comparison of dissolved trace metal concentrations (in white) determined by Ruhl et al. (2009) with concentrations determined by this study (in blue) in the water column. The EPA MCL guidelines are depicted in the top insert using purple and red lines.

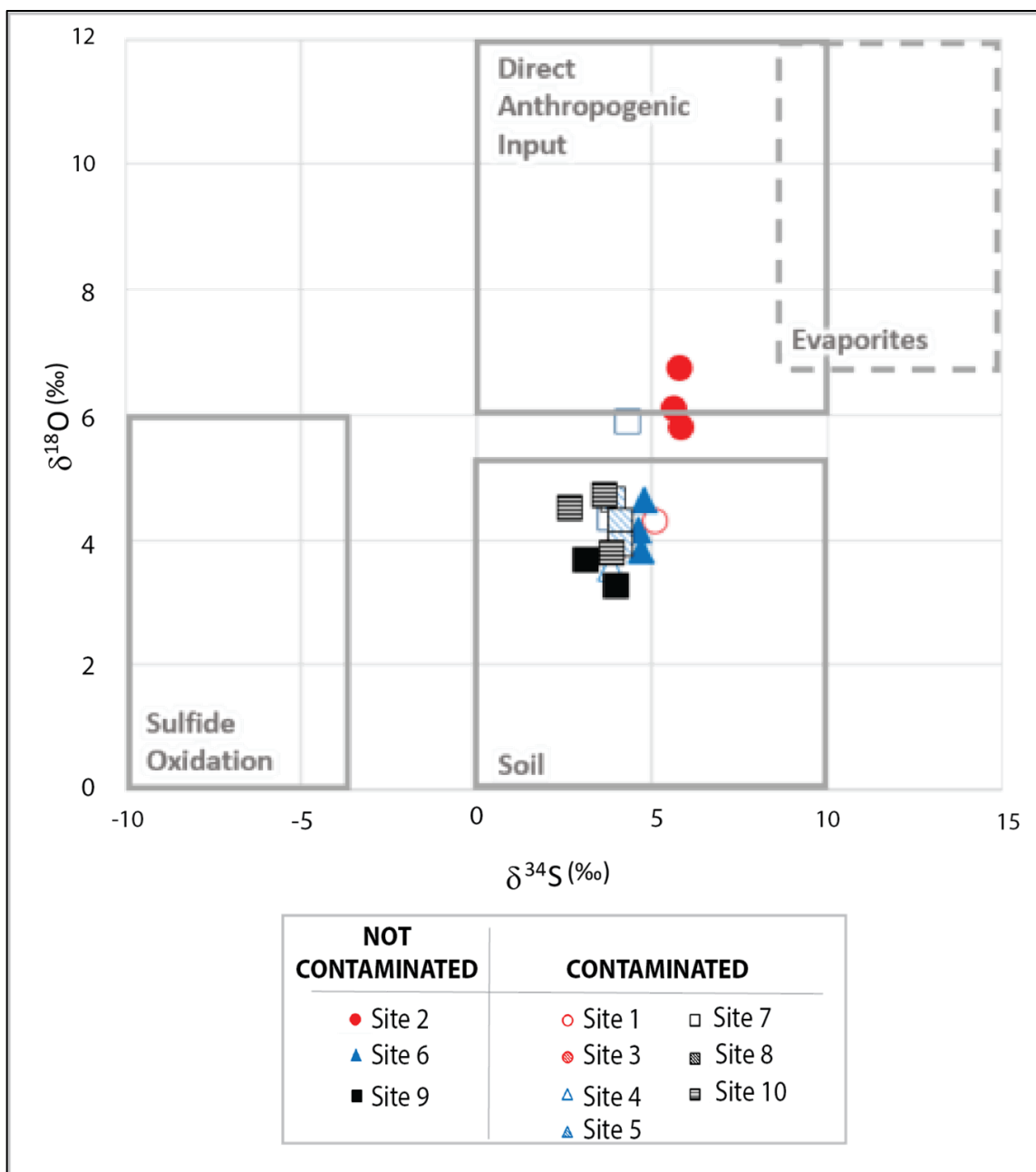


Figure 13: Variations of $\delta^{34}\text{S}$ vs. $\delta^{18}\text{O}$ of dissolved SO_4^{2-} in the water column. Boxes represent typical isotope compositions of SO_4^{2-} derived from different sources (after Knöller et al., 2005).

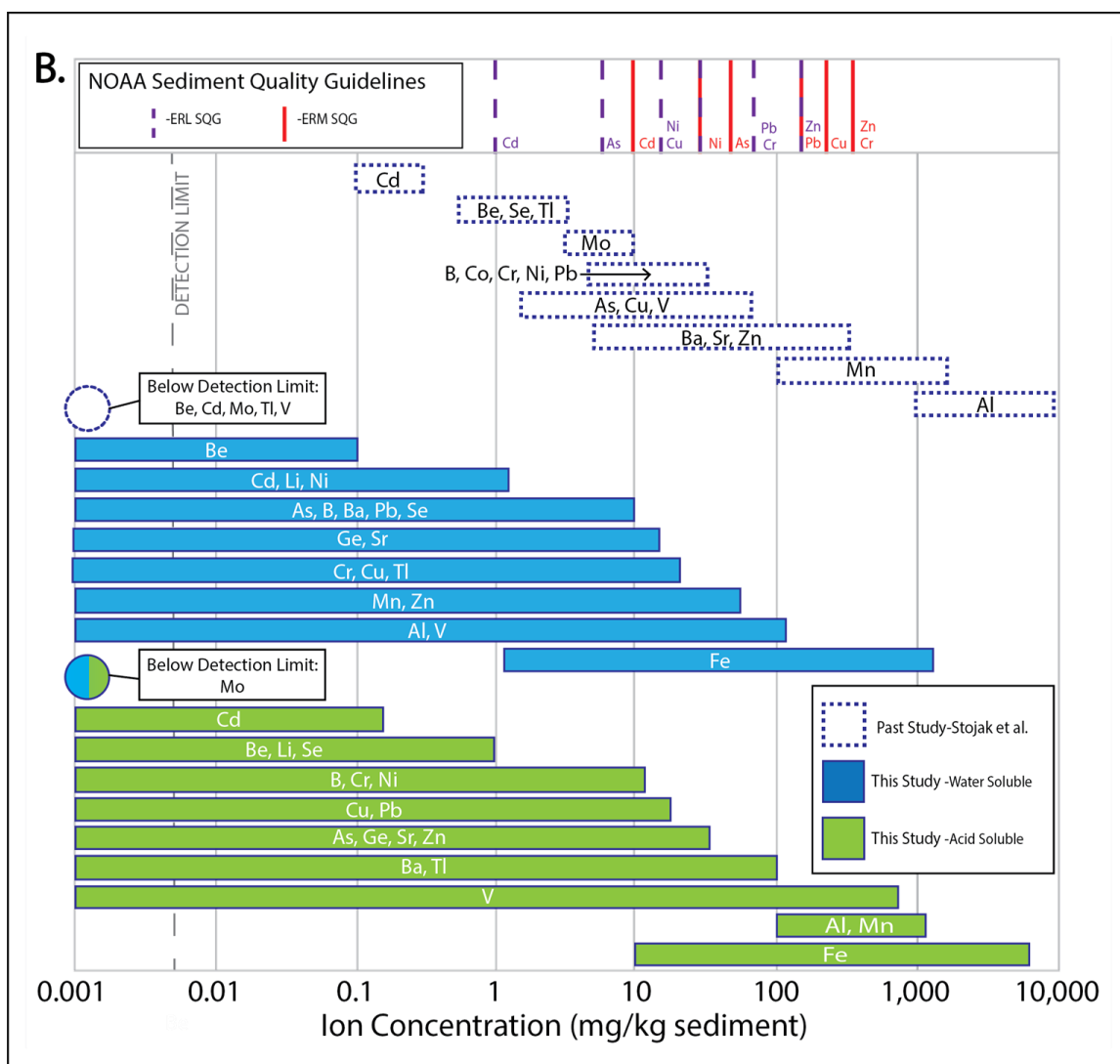


Figure 14: Comparison of trace metal concentrations determined by Stojak et al. (2014) in the sediments using HNO_3 digestion (in white) with those determined by this study through water- (in blue) and HCL- leaching (in green). The NOAA Sediment quality guidelines are presented in the top insert using purple and red lines.

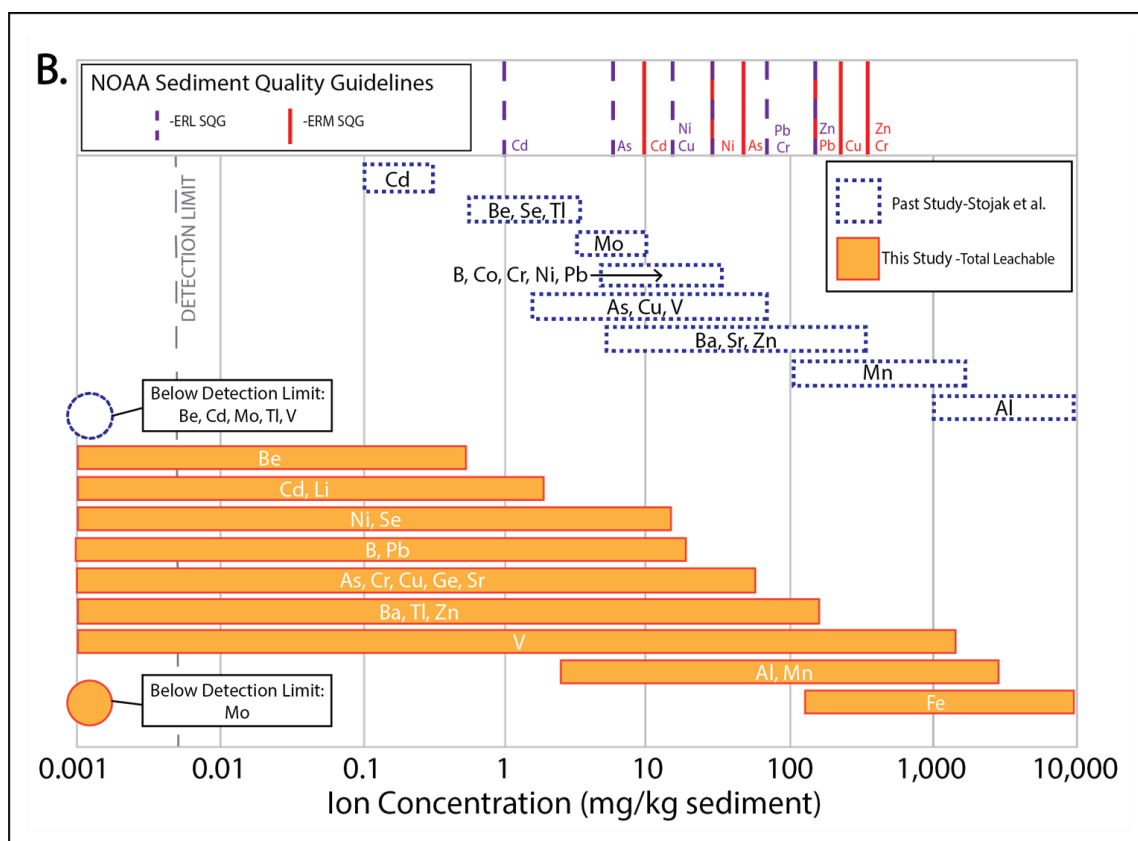


Figure 15: Comparison of trace metal concentrations determined by Stojak et al. (2014) in the sediments using HNO_3 digestion (in white) with the total concentrations (sum of water- and HCl-leaching) determined in this study (in orange). The NOAA Sediment quality guidelines are presented in the top insert using purple and red lines.

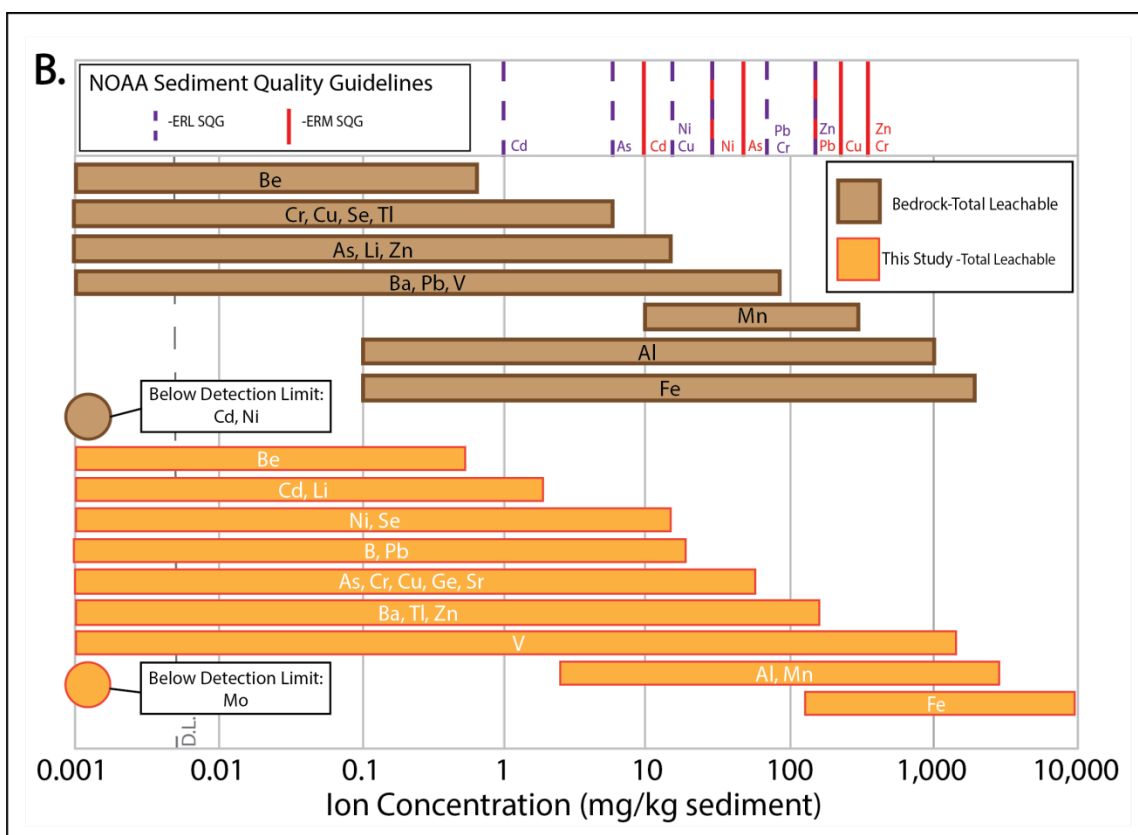


Figure 16: Comparison of total trace metal concentrations (sum of water- and HCl-leaching) determined in this study in the bedrock (in brown) and sediment (in orange). The NOAA Sediment quality guidelines are presented in the top insert using purple and red lines.



Figure 17: Photo of the Emory River sediment core sampled in Site 10 showing large visible non-combusted coal fragments in the upper half and smaller throughout. Top of the core (representing sediment-water interface) is on the left side.

Figure 18: Heat maps showing total trace metal concentrations (sum of water- and HCl-leaching) for each studied site along the Emory River, Clinch River, and Watts Bar Reservoir. Warmer colors represent higher concentrations. Black bars represent the approximate extent of coal ash flow after Ruhl et al. (2010). The spill location is denoted by black box.

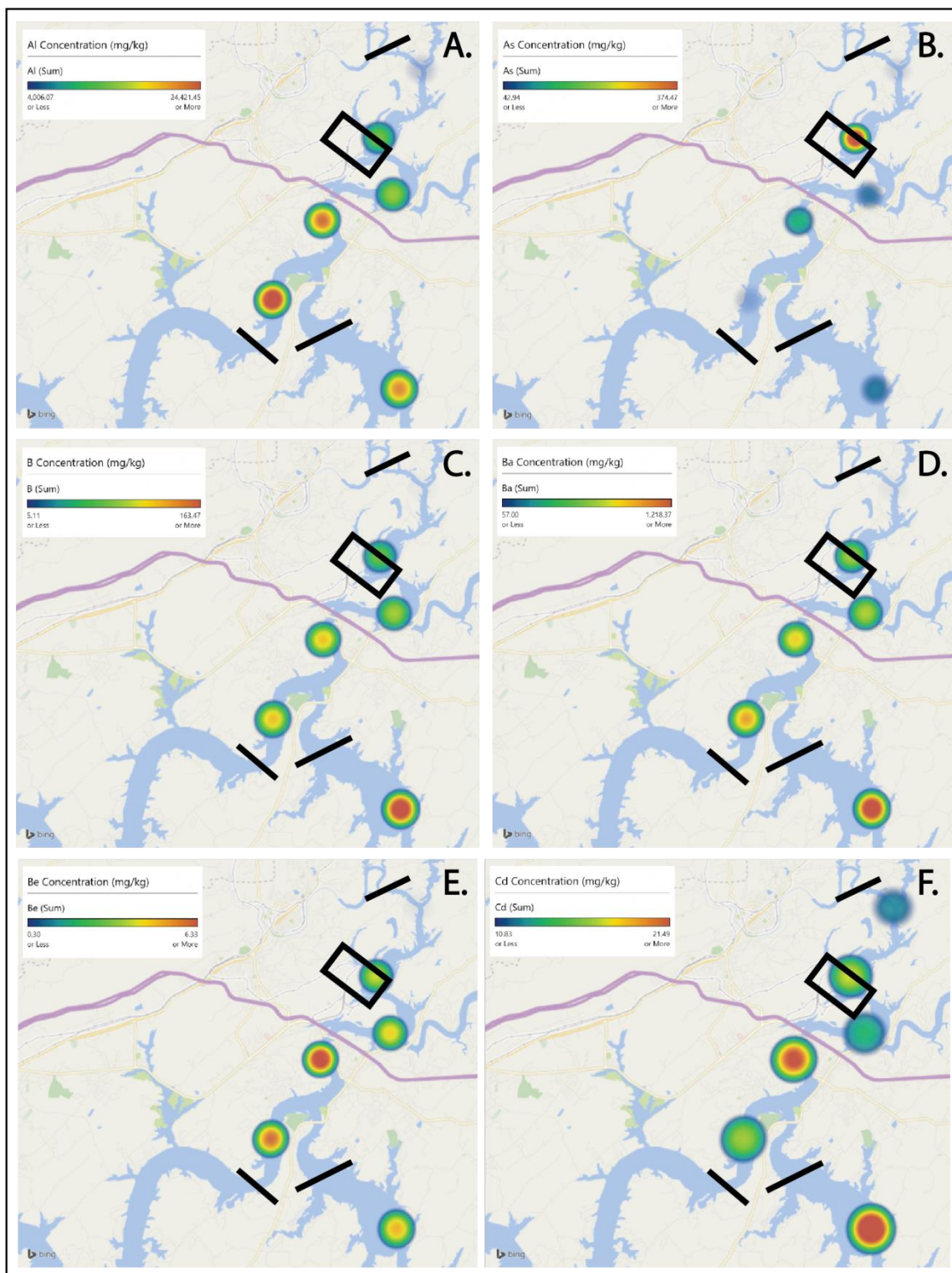


Figure 18: Continued.

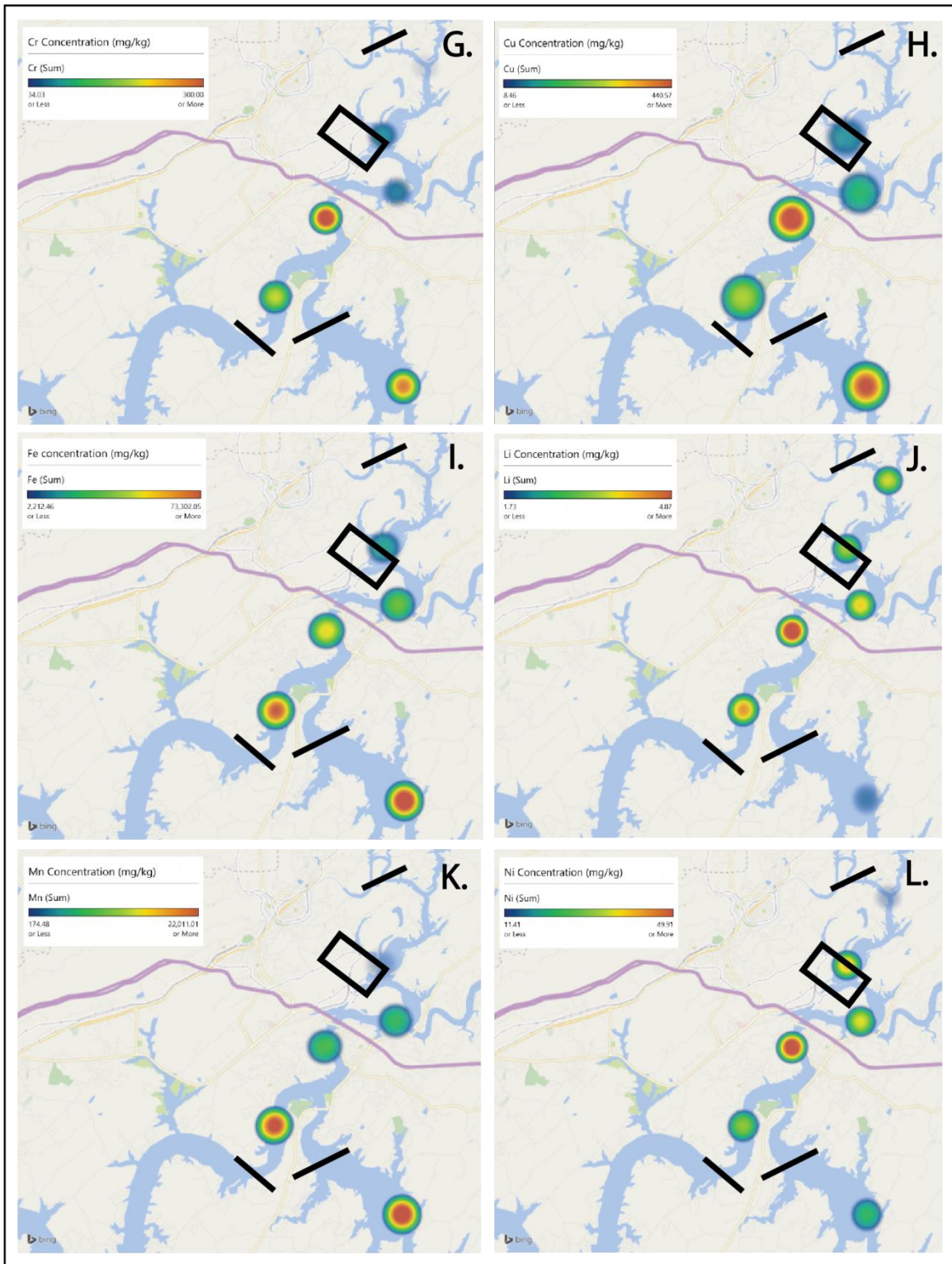


Figure 18: Continued.

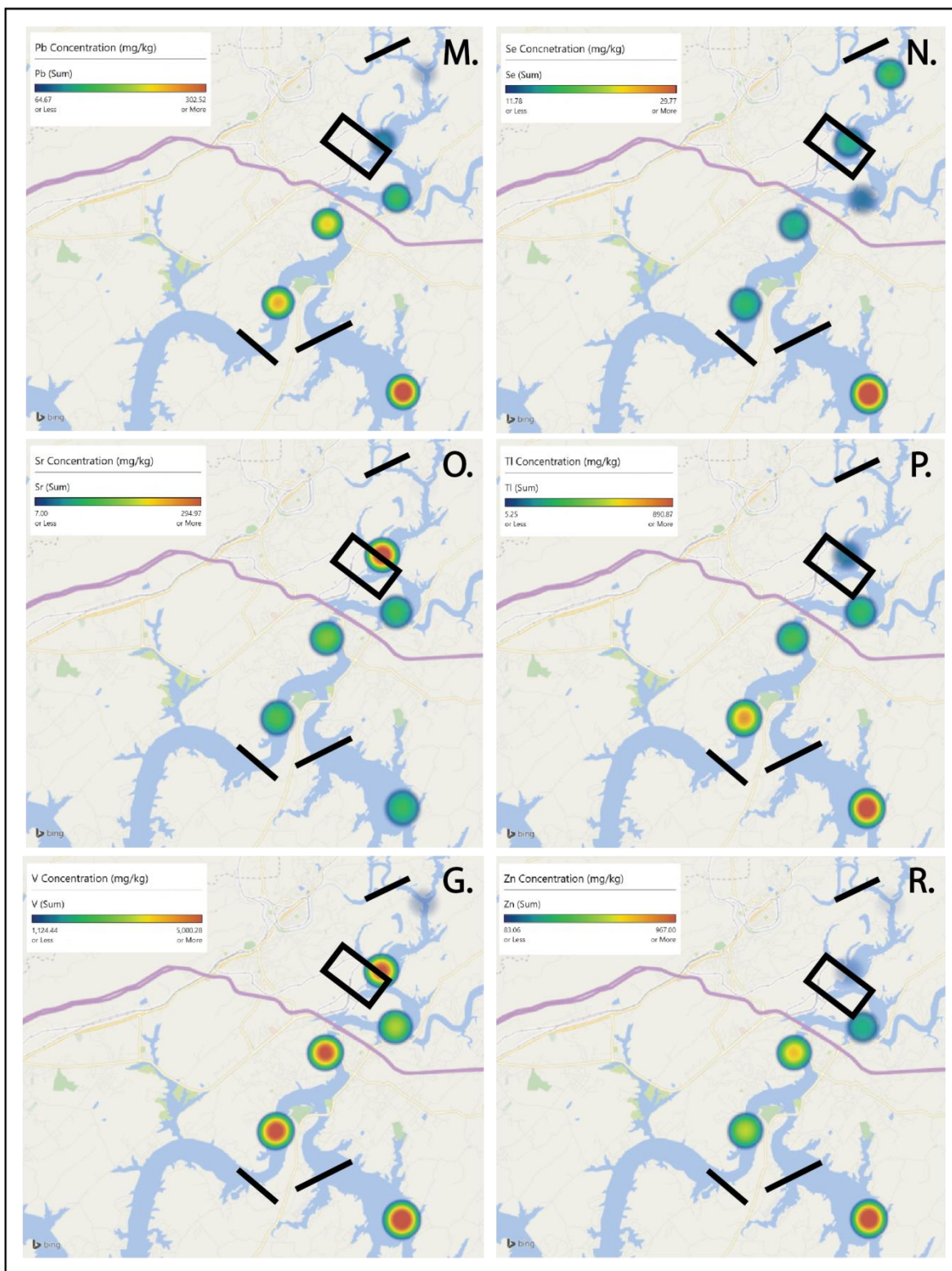


Figure 18: Continued.

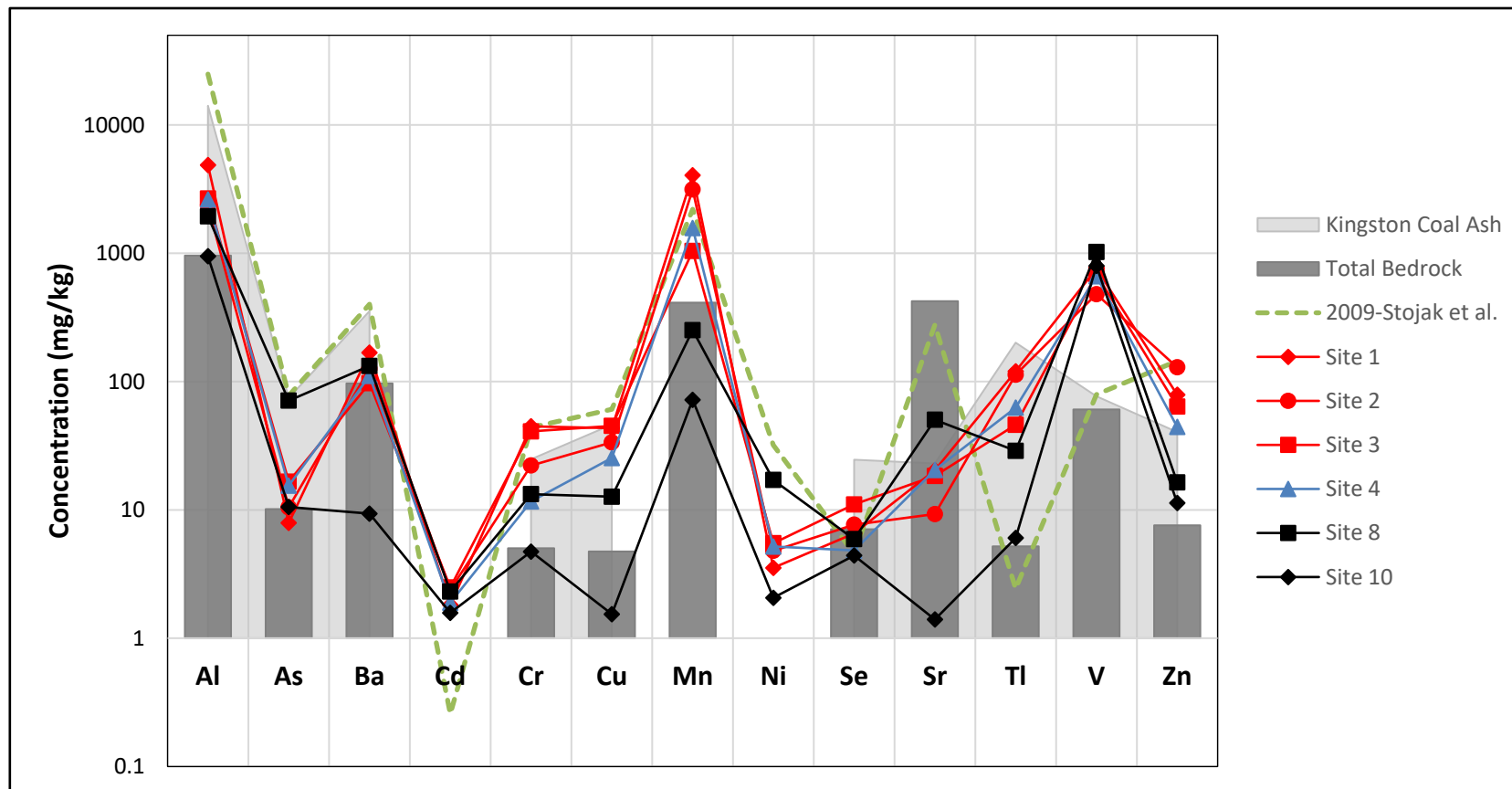


Figure 19: Comparison of maximum trace metal concentrations reported for the Kingston coal ash (light gray; Ruhl et al., 2009), the 2009 sediments analyzed using complete HNO₃ digestion (green; Stojak et al. 2015), the local bedrock samples analyzed in this study using water and HCl leaching (dark gray), and the 2016 sediments analyzed in this study using water and HCl leaching (red-Watts Bar Reservoir, blue-Clinch River, and black-Emory River).

Appendix B: Tables

Table 1: In situ measurements of temperature, pH, specific conductance, dissolved oxygen, and alkalinity in the water column (April 2016).

Site	Depth (m)	Temperature (°C)	pH	Specific Conductance (mEQ/L)	DO (mg/L)	Alkalinity (mg/L)
1	0	24	8.31	167	10.14	68
2	0	23	8.71	187	11.70	88
	2	22	8.65	194	11.71	N.A.
	4	21	8.37	208	10.80	84
	6	19	7.70	231	8.90	N.A.
	8	18	7.64	229	8.37	N.A.
	10	18	7.65	229	8.25	108
3	0	24	7.43	174	7.71	68
4	0	24	7.69	169	8.79	56
5	0	24	8.09	202	9.74	68
6	0	23	8.69	253	13.10	108
	2	23	8.49	263	12.01	N.A.
	4	20	7.73	275	8.75	116
	6	20	7.50	277	7.48	N.A.
	8	20	7.47	277	7.28	N.A.
	10	20	7.50	277	7.16	114
7	0	24	7.99	183	9.27	60
	2	24	7.98	182	9.35	N.A.
	4	23	7.54	197	8.04	N.A.
	6	22	7.45	220	7.25	92
8	0	24	7.64	146	8.41	56
	2	24	7.59	150	8.34	N.A.
	4	23	7.49	185	7.92	N.A.
	6	23	7.38	186	7.50	64
	8	21	7.48	240	7.53	N.A.
	10	21	7.47	254	7.38	80
9	0	24	7.97	78	9.46	20
	2	23	7.44	77	9.11	N.A.
	4	21	7.01	78	7.53	N.A.
	6	19	6.82	77	8.97	24
	8	14	6.57	76	5.79	N.A.
	10	14	6.55	80	4.98	N.A.
10	0	24	7.41	85	8.60	32
	2	24	7.17	90	7.81	N.A.
	4	21	6.96	77	7.77	28
	6	19	6.83	73	7.30	N.A.
	8	15	6.63	72	6.52	N.A.
	10	14	6.58	73	6.35	28
*N.A. represents samples that were not analyzed for a given parameter						

Table 2: Major ion concentrations measured in the water column (Apr 2016). Instrument detection limit was <0.001 mg/L.

WATER COLUMN MAJOR ION CONCENTRATIONS																
LOCATION #	SAMPLE NAME	DEPTH (m)	Na	K	Ca	Mg	NH ₄	Br	F	Cl	SO ₄	S ⁻	NO ₃	NO ₂	PO ₄	Si
1	TR1	0	4.207	1.114	19.233	5.312	B.D.	B.D.	0.047	4.825	10.527	4.065	0.077	0.008	B.D.	0.779
2	TR2-C	0	6.046	1.240	21.927	5.500	B.D.	B.D.	0.052	6.832	8.689	2.987	0.274	0.020	B.D.	0.572
	TR4-C	4	6.293	1.324	23.533	5.819	B.D.	B.D.	0.058	7.498	9.495	2.635	0.685	0.021	B.D.	0.314
	TR7-C	10	7.590	1.450	27.455	6.619	0.023	B.D.	0.022	2.304	2.668	4.005	0.770	0.007	B.D.	0.562
3	TR8	0	3.768	1.123	20.010	5.831	0.017	B.D.	0.064	4.371	14.001	4.707	0.542	0.014	B.D.	0.958
4	CR1	0	3.589	1.128	19.642	5.708	0.004	B.D.	0.056	4.169	13.693	4.689	0.384	0.009	B.D.	0.884
5	CR2	0	3.847	1.163	23.850	7.137	B.D.	B.D.	0.057	4.959	15.282	5.331	0.314	0.010	B.D.	0.963
6	CR3-C	0	4.683	1.428	31.442	9.735	B.D.	B.D.	0.060	4.896	16.697	5.959	0.256	0.015	0.006	0.752
	CR5-C	4	4.990	1.452	33.652	10.287	0.010	B.D.	0.064	4.943	17.530	6.000	0.931	0.019	B.D.	1.186
	CR8-C	10	5.349	1.395	33.799	10.072	B.D.	B.D.	0.069	5.048	17.665	6.098	1.251	0.020	0.014	0.832
7	ER1	0	3.803	1.069	21.345	6.271	B.D.	B.D.	0.073	4.840	14.908	4.999	0.258	0.013	B.D.	0.840
	ER4	6	4.451	1.220	26.791	7.924	0.046	B.D.	0.074	4.863	16.186	5.297	0.576	0.016	B.D.	0.928
8	ER5	0	3.381	0.996	17.088	4.878	B.D.	B.D.	0.046	2.807	8.555	4.151	0.408	0.009	B.D.	0.754
	ER8	6	3.711	1.059	20.858	6.134	B.D.	B.D.	0.059	4.628	14.713	4.822	0.427	0.012	B.D.	0.872
	ER10	10	3.821	1.201	23.029	6.823	0.019	B.D.	0.057	4.341	14.433	3.555	0.576	0.011	B.D.	0.591
9	ER11-C	0	2.346	0.773	8.556	1.921	B.D.	B.D.	0.040	2.802	10.621	3.043	0.034	0.003	0.029	0.595
	ER14-C	6	2.971	0.872	7.730	1.891	0.086	B.D.	0.040	3.349	9.573	3.188	0.399	0.009	B.D.	0.608
	ER16-C	10	2.152	0.699	8.976	1.976	0.072	B.D.	0.033	2.636	7.711	2.622	0.353	0.008	0.009	0.931
10	ER17	0	2.594	0.796	9.005	2.415	B.D.	B.D.	0.043	2.632	9.921	3.352	0.022	0.004	B.D.	0.814
	ER19	4	2.770	0.818	8.100	1.873	0.017	B.D.	0.042	3.100	9.408	3.121	0.210	0.009	B.D.	0.593
	ER22	10	2.038	0.740	8.152	1.860	0.085	B.D.	0.036	2.643	8.075	2.819	0.352	0.007	B.D.	0.821
*All ion concentrations are presented in mg/L; B.D. represents concentrations below the instrumental detection limit																

Table 3: Results of chemical and isotopic analyses of dissolved sulfate, nitrate, DIC and DOC in the water column.

WATER COLUMN ISOTOPE RESULTS												
LOCATION #	SAMPLE NAME	DEPTH (m)	$\delta^2\text{H}$	$\delta^{18}\text{O}$	BaSO_4		NO_3		DIC		DOC	
					$\delta^{34}\text{S}$	$\delta^{18}\text{O}$	$\delta^{15}\text{N}$	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	(mg/L)	$\delta^{13}\text{C}$	(mg/L)
1	TR1	0	-35.1	-6.0	+5.1	+4.3	N.D.	N.D.	-8.5	20.1	-29.9	7.1
2	TR2-C	0	-37.4	-6.2	+5.8	+6.7	N.D.	N.D.	-7.6	35.6	-29.6	8.0
	TR4-C	4	-37.3	-6.2	+5.6	+6.1	+10.8	+3.2	-8.7	37.9	-33.1	10.4
	TR7-C	10	-37.4	-6.4	+5.8	+5.8	+9.1	+0.5	-10.6	38.6	-30.9	8.4
3	TR8	0	-33.8	-5.7	+4.0	+3.9	+7.3	+0.6	-10.5	35.2	-31.8	9.0
4	CR1	0	-34.5	-5.9	+3.8	+3.6	+8.2	+1.1	-9.9	34.0	-29.8	10.2
5	CR2	0	-33.5	-5.7	+3.9	+4.4	+8.7	+3.9	-9.6	42.9	-31.5	9.0
6	CR3-C	0	N.D.	N.D.	+4.7	+3.8	N.D.	+3.9	-9.3	50.0	-31.2	11.7
	CR5-C	4	-33.9	-5.8	+4.6	+4.2	N.D.	N.D.	-10.5	54.9	-29.7	9.2
	CR8-C	10	-34.3	-5.8	+4.8	+4.6	N.D.	N.D.	-10.9	91.5	-31.5	10.8
7	ER1	0	-34.5	-6.0	+3.8	+4.3	+7.4	-0.5	-9.3	36.7	-29.6	8.3
	ER4	6	-34.1	-5.8	+4.3	+5.9	+10.2	+3.8	-10.6	54.9	-30.3	8.5
8	ER5	0	-33.0	-5.6	+3.9	+4.6	+7.7	+1.0			-32.1	11.2
	ER8	6	-34.1	-5.9	+4.1	+4.3	+6.8	+5.7	-10.1	42.4	-32.4	10.4
	ER10	10	-35.9	-6.0	+4.1	+3.9	+7.3	+1.3	-10.7	46.9	-29.0	10.7
9	ER11-C	0	-33.2	-5.9	+3.1	N.D.	+6.5	N.D.	-7.3	10.8	-29.3	9.7
	ER14-C	6	-34.9	-5.9	+4.0	N.D.	N.D.	N.D.	-11.7	7.7	-29.5	15.2
	ER16-C	10	-36.9	-6.4	+3.3	N.D.	+7.1	-2.7	-13.7	11.0	-29.2	7.5
10	ER17	0	-32.4	-5.6	+2.7	+4.5	+4.4	-1.7	-7.4	13.7	-30.3	13.9
	ER19	4	-34.7	-5.9	+3.7	+4.7	+8.4	+1.0	-8.8	15.0	N.D.	N.D.
	ER22	10	-35.2	-6.4	+3.9	N.D.	+5.1	-0.3	-13.1	14.3	-35.2	11.3
*All isotope results are presented in per mill (‰); N.D. represents values that were not detectable.												

Table 4: Concentrations of trace metals in the water column (Apr 2016). Instrument detection limit was <0.002 mg/L.

WATER COLUMN TRACE METAL ION CONCENTRATIONS																		
LOCATION #	SAMPLE NAME	DEPTH (m)	As	B	Se	Li	Cu	Ba	Be	Cd	Cr	Fe	Mn	Ni	Pb	Sr	Zn	Al
1	TR1	0	B.D.	0.040	B.D.	B.D.	B.D.	0.098	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.057	B.D.	B.D.
2	TR2-C	0	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.056	B.D.	B.D.
	TR4-C	4	B.D.	B.D.	B.D.	B.D.	B.D.	0.025	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.049	B.D.	B.D.
	TR7-C	10	B.D.	B.D.	B.D.	B.D.	B.D.	0.033	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.074	B.D.	B.D.
3	TR8	0	B.D.	B.D.	B.D.	B.D.	B.D.	0.048	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.061	B.D.	B.D.
4	CR1	0	B.D.	B.D.	B.D.	B.D.	B.D.	0.041	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.060	B.D.	B.D.
5	CR2	0	B.D.	B.D.	B.D.	B.D.	B.D.	0.040	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.071	B.D.	B.D.
6	CR3-C	0	B.D.	0.027	B.D.	B.D.	B.D.	0.066	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.083	B.D.	B.D.
	CR5-C	4	B.D.	B.D.	0.027	B.D.	B.D.	0.036	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.088	B.D.	B.D.
	CR8-C	10	B.D.	B.D.	B.D.	B.D.	B.D.	0.057	B.D.	B.D.	B.D.	B.D.	0.292	B.D.	B.D.	0.087	0.029	B.D.
7	ER1	0	B.D.	B.D.	B.D.	B.D.	B.D.	0.043	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.067	B.D.	B.D.
	ER4	6	B.D.	B.D.	B.D.	B.D.	B.D.	0.058	B.D.	B.D.	B.D.	B.D.	0.111	B.D.	B.D.	0.077	B.D.	B.D.
8	ER5	0	B.D.	B.D.	B.D.	B.D.	B.D.	0.049	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.055	B.D.	B.D.
	ER8	6	B.D.	B.D.	B.D.	B.D.	B.D.	0.042	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.065	B.D.	B.D.
	ER10	10	B.D.	B.D.	B.D.	B.D.	B.D.	0.030	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.049	B.D.	B.D.
9	ER11-C	0	B.D.	B.D.	0.025	B.D.	B.D.	0.032	B.D.	B.D.	B.D.	0.025	B.D.	B.D.	B.D.	0.031	B.D.	B.D.
	ER14-C	6	B.D.	B.D.	0.025	B.D.	B.D.	0.046	B.D.	B.D.	B.D.	0.025	B.D.	B.D.	B.D.	0.033	B.D.	B.D.
	ER16-C	10	B.D.	B.D.	B.D.	B.D.	B.D.	0.034	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.030	B.D.	B.D.
10	ER17	0	B.D.	B.D.	B.D.	B.D.	B.D.	0.033	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.031	B.D.	B.D.
	ER19	4	B.D.	B.D.	B.D.	B.D.	B.D.	0.036	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.032	B.D.	B.D.
	ER22	10	B.D.	B.D.	B.D.	B.D.	B.D.	0.035	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.029	B.D.	B.D.
*All ion concentrations are presented in mg/L; B.D. represents concentrations below the instrumental detection limit																		

Table 5: Concentrations of water-soluble trace metals in the sediment cores.

Site #	DEPTH (cm)	As	B	Se	Li	Cu	Ba	Be	Cd	Cr	Fe	Mn	Ni	Pb	Sr	Zn	Al	Ge	V	Tl
8	0-2.3	9.38	5.565	5.25	0.455	B.D.	12.5	0.14	1.89	2.59	1644	72.49	3.325	8.26	14.46	9.065	139.1	B.D.	192.1	28.85
	2.3-4.6	8.05	2.66	B.D.	B.D.	B.D.	1.645	B.D.	1.26	2.485	5.18	1.085	1.4	5.32	1.89	3.64	15.89	B.D.	B.D.	6.628
	4.6-6.9	5.845	8.54	0.525	B.D.	B.D.	1.05	B.D.	1.96	1.505	7.945	1.225	1.295	5.88	1.47	3.29	14.74	17.53	74.82	B.D.
	6.9-9.2	4.095	3.64	1.68	0.14	0.245	1.085	B.D.	1.785	1.855	8.155	1.785	1.295	5.25	4.235	4.48	18.76	B.D.	17.57	B.D.
	9.2-11.5	6.44	1.4	0.735	B.D.	B.D.	1.26	B.D.	2.1	3.5	5.215	0.28	0.63	6.16	0.735	4.305	27.23	B.D.	5.748	B.D.
	11.5-13.8	7.14	1.26	B.D.	B.D.	B.D.	1.26	B.D.	1.715	2.73	11.41	0.49	0.84	6.37	1.19	3.71	33.29	B.D.	43.27	B.D.
	13.8-16.1	6.965	1.225	2.31	B.D.	B.D.	1.47	B.D.	1.12	3.64	67.34	1.26	0.98	6.615	1.4	4.025	112.9	B.D.	74.52	B.D.
	16.1-18.4	2.835	1.645	B.D.	B.D.	B.D.	1.295	B.D.	1.54	3.22	10.68	0.77	1.26	3.885	1.225	4.55	32.62	2.778	75.3	B.D.
	18.4-20.7	4.025	1.75	4.095	B.D.	B.D.	1.33	B.D.	1.82	3.5	3.15	0.7	1.26	4.095	1.4	3.675	28.04	B.D.	61.19	B.D.
10	0-2.4	10.26	B.D.	B.D.	B.D.	B.D.	0.98	B.D.	0.805	2.87	3.605	2.765	0.7	4.48	0.07	3.99	23.52	B.D.	54.75	B.D.
	2.4-4.8	3.15	B.D.	B.D.	1.12	0.595	1.05	B.D.	0.735	3.01	3.29	0.56	0.735	6.265	0.07	5.985	26.99	B.D.	B.D.	B.D.
	4.8-7.2	9.52	B.D.	3.955	B.D.	B.D.	1.085	B.D.	1.54	3.955	3.08	0.455	0.7	7.105	0.07	5.18	23.77	B.D.	B.D.	B.D.
	7.2-9.6	6.335	0.105	B.D.	B.D.	B.D.	1.05	B.D.	1.54	3.955	2.87	0.385	1.155	6.405	B.D.	4.62	23.98	B.D.	B.D.	B.D.
	9.6-12	4.06	B.D.	0.56	0.07	B.D.	1.12	B.D.	1.575	3.605	2.695	1.4	0.105	6.16	0.175	4.06	23.66	B.D.	B.D.	B.D.
	12-14.4	0.735	B.D.	3.78	0.07	B.D.	1.05	B.D.	0.91	3.15	2.555	0.665	1.365	6.475	0.14	4.235	23.77	B.D.	B.D.	B.D.
	14.4-16.8	B.D.	B.D.	3.675	B.D.	B.D.	1.085	B.D.	1.54	3.92	3.675	0.07	0.42	7.105	B.D.	4.55	28.25	B.D.	B.D.	B.D.
	16.8-19.2	2.52	B.D.	4.41	B.D.	B.D.	1.12	B.D.	1.33	4.305	3.22	B.D.	1.295	5.25	0.105	4.445	24.78	B.D.	B.D.	B.D.
	19.2-21.6	4.025	B.D.	B.D.	B.D.	0.28	1.12	B.D.	1.26	2.94	3.465	0.35	0.07	6.23	0.07	4.305	24.29	B.D.	B.D.	B.D.
4	0-2.3	7	0.245	B.D.	0.07	0.595	1.645	B.D.	0.98	3.255	3.465	34.86	0.875	5.845	0.63	4.935	25.34	B.D.	B.D.	B.D.
	2.3-4.6	3.045	0.105	4.48	B.D.	0.21	3.29	B.D.	0.735	4.41	120.3	75.22	1.015	4.375	0.595	5.46	72.24	B.D.	14.71	B.D.
	4.6-6.9	2.45	0.35	B.D.	B.D.	0.7	1.54	B.D.	1.295	4.62	5.81	40.78	0.14	4.305	0.455	5.705	28.35	B.D.	B.D.	B.D.
	6.9-9.2	6.02	0.35	B.D.	B.D.	1.05	1.575	B.D.	1.61	3.71	6.195	36.75	0.35	4.865	0.42	4.27	25.83	B.D.	10.66	B.D.
	9.2-11.5	3.64	0.105	0.84	B.D.	B.D.	1.505	B.D.	1.68	4.55	5.355	22.47	0.84	4.025	0.385	4.69	26.46	B.D.	11.99	B.D.
	11.5-13.8	B.D.	0.175	2.555	B.D.	B.D.	1.26	B.D.	1.435	B.D.	6.615	17.29	0.56	7.49	0.385	3.15	2.835	B.D.	21.13	B.D.

Table 5: Continued.

Site #	DEPTH (cm)	As	B	Se	Li	Cu	Ba	Be	Cd	Cr	Fe	Mn	Ni	Pb	Sr	Zn	Al	Ge	V	Tl
4	13.8-16.1	7.595	0.105	0.7	B.D.	B.D.	3.325	B.D.	1.295	B.D.	5.355	15.44	0.98	5.565	0.385	5.81	B.D.	B.D.	26.01	B.D.
	16.1-18.4	5.985	0.455	3.675	B.D.	13.48	1.61	B.D.	1.68	8.085	5.845	40.99	1.085	5.635	0.875	16.73	13.76	B.D.	22.24	B.D.
	18.4-20.7	6.755	0.14	B.D.	B.D.	14.39	1.19	B.D.	1.33	7.56	7.315	24.19	0.945	7.49	0.525	16.84	17.54	B.D.	B.D.	B.D.
2	0-2	3.15	0.14	2.59	B.D.	21.32	2.345	B.D.	0.805	14.88	8.05	21.84	1.925	9.765	0.49	88.52	36.19	B.D.	B.D.	B.D.
	2-4	1.89	B.D.	6.86	B.D.	19.99	2.065	B.D.	1.61	13.13	8.75	26.81	1.4	9.415	0.49	50.44	38.29	B.D.	2.586	B.D.
	4-6	9.1	0.105	3.325	B.D.	18.06	1.89	B.D.	0.735	10.92	7.77	35.39	1.05	7.91	0.56	19.67	47.39	B.D.	B.D.	B.D.
	6-8	B.D.	B.D.	5.075	B.D.	18.62	2.1	B.D.	0.98	12.29	7.77	40.18	B.D.	6.58	0.56	20.86	44.94	B.D.	3.63	B.D.
	8-10	3.535	B.D.	B.D.	B.D.	18.41	2.065	B.D.	1.295	12.99	9.695	45.75	0.91	8.155	0.56	24.05	47.88	B.D.	B.D.	B.D.
	10-12	2.1	B.D.	1.68	B.D.	19.92	2.135	B.D.	1.575	13.44	7.21	35.63	0.56	6.475	0.42	34.13	39.87	B.D.	2.907	B.D.
	12-14	1.575	B.D.	0.21	B.D.	21.39	2.03	B.D.	1.61	10.54	10.82	36.16	1.54	9.87	0.42	40.43	35.67	B.D.	8.959	B.D.
	14-16	0.63	0.07	B.D.	B.D.	19.32	3.885	B.D.	2.17	12.74	17.29	34.86	0.98	11.1	0.56	27.69	63.74	B.D.	4.842	B.D.
	16-18	5.845	0.07	0.105	B.D.	21.04	2.275	B.D.	1.435	15.12	9.695	31.47	1.085	7	0.49	22.09	66.22	B.D.	7.989	B.D.
	18-20	4.2	0.07	0.315	0.07	23.59	2.555	0.07	2.03	14.39	13.86	37.98	B.D.	3.745	0.63	21.49	77.32	B.D.	7.988	B.D.
	20-22	4.97	0.175	B.D.	B.D.	21.21	2.415	B.D.	1.295	14.53	12.18	33.22	1.085	7.735	0.525	20.97	68.67	B.D.	3.316	B.D.
	22-24	8.155	B.D.	B.D.	B.D.	22.44	2.66	B.D.	1.715	15.47	15.51	42.56	0.665	7	0.525	21.77	73.82	B.D.	5.405	B.D.
	24-26	7.7	0.175	5.215	B.D.	21.7	2.625	B.D.	0.735	17.43	10.08	36.26	0.21	5.915	0.56	23.03	77.21	B.D.	B.D.	B.D.
	26-28	7.42	0.105	B.D.	B.D.	21.14	2.485	B.D.	1.82	17.61	8.89	28.21	B.D.	7.455	0.49	22.4	76.83	B.D.	B.D.	B.D.
	28-30	1.085	0.07	2.45	B.D.	22.09	2.695	B.D.	1.785	15.82	13.3	29.58	0.455	7.735	0.525	23.03	77.56	B.D.	B.D.	B.D.
3	0-2.3	3.255	0.245	3.43	B.D.	20.97	2.835	B.D.	1.19	19.25	12.36	31.64	0.84	6.58	0.77	25.62	95.94	B.D.	B.D.	B.D.
	2.3-4.6	4.13	0.28	B.D.	B.D.	21.81	2.905	B.D.	1.855	18.8	14.49	38.68	0.945	7.35	0.805	23.38	88.87	B.D.	7.2	B.D.
	4.6-6.9	1.995	0.245	B.D.	B.D.	21.11	2.87	B.D.	0.875	20.86	13.69	35.49	1.33	8.19	0.735	25.38	85.75	B.D.	5.577	B.D.
	6.9-9.2	8.54	0.28	0.315	B.D.	21.67	2.835	B.D.	0.875	19.57	12.5	32.2	0.875	6.86	0.735	22.93	88.55	B.D.	5.962	B.D.
	9.2-11.5	3.605	0.245	B.D.	B.D.	22.16	2.87	B.D.	1.645	20.83	9.87	29.86	0.91	5.145	0.735	23.42	87.12	B.D.	6.376	B.D.
	11.5-13.8	1.47	0.35	B.D.	B.D.	20.27	2.975	B.D.	2.205	21.42	19.78	22.58	1.05	5.6	0.7	22.86	93.42	B.D.	9.908	B.D.
	13.8-16.1	8.47	0.175	B.D.	B.D.	23.1	3.115	B.D.	1.085	21.49	12.29	13.65	0.49	6.44	0.7	24.12	90.23	B.D.	10.87	B.D.
	16.1-18.4	6.475	0.105	B.D.	B.D.	21.95	4.235	B.D.	1.645	24.75	8.295	9.8	0.77	7.665	0.77	24.26	105.3	B.D.	26.87	B.D.

Table 5: Continued.

Site #	DEPTH (cm)	As	B	Se	Li	Cu	Ba	Be	Cd	Cr	Fe	Mn	Ni	Pb	Sr	Zn	Al	Ge	V	Tl
3	18.4-20.7	5.81	0.175	B.D.	B.D.	22.02	3.605	B.D.	2.03	29.26	9.905	14.04	0.525	5.775	0.98	25.73	123.3	B.D.	34.97	B.D.
	20.7-23	12.74	0.42	B.D.	B.D.	23.07	3.535	B.D.	1.75	29.51	12.32	14.28	0.385	6.58	0.875	25.27	122.8	B.D.	30.52	B.D.
	23-25.3	8.47	0.315	B.D.	B.D.	24.33	4.2	B.D.	1.61	36.65	14.74	16.63	0.665	5.425	0.98	26.25	167.6	B.D.	6.979	B.D.
	25.3-27.6	6.65	0.28	11.03	B.D.	23.77	4.235	B.D.	1.015	38.4	15.3	13.2	0.56	7.945	0.875	26.88	174.7	B.D.	4.522	B.D.
	27.6-29.9	6.335	0.105	1.33	B.D.	B.D.	1.015	B.D.	1.085	1.89	7.805	10.54	0.77	5.775	0.245	3.885	20.16	B.D.	B.D.	B.D.
1	0-4.8	B.D.	0.105	B.D.	0.07	16.14	3.395	B.D.	1.12	25.55	11.59	43.79	0.805	5.915	0.91	19.46	140.6	B.D.	3.405	B.D.
	4.8-7.2	3.325	0.21	3.5	B.D.	24.92	4.445	B.D.	1.365	39.27	10.54	34.51	1.435	5.635	0.98	28.18	197.8	B.D.	B.D.	B.D.
	7.2-9.6	4.13	B.D.	B.D.	B.D.	25.2	4.305	B.D.	1.19	40.15	11.41	20.86	0.21	6.09	0.84	27.83	190.1	B.D.	B.D.	B.D.
	9.6-12	0.455	0.105	5.95	B.D.	22.93	4.06	B.D.	1.575	37.52	11.41	21.18	0.28	9.03	0.84	28.49	179.6	B.D.	B.D.	B.D.
	12-14.4	0.525	0.21	2.975	0.175	B.D.	1.295	0.105	1.085	0.77	6.755	30.28	1.155	8.085	0.56	3.885	14.11	B.D.	3.046	B.D.
	14.4-16.8	B.D.	12.99	B.D.	B.D.	B.D.	0.91	B.D.	1.26	B.D.	6.055	25.38	0.455	7.77	0.35	3.36	15.3	B.D.	10.63	B.D.
	16.8-19.2	1.365	13.27	0.385	B.D.	B.D.	1.085	B.D.	1.4	B.D.	6.65	33.92	1.015	8.12	0.49	3.71	14.98	B.D.	3.986	B.D.
	19.2-21.6	3.395	9.695	B.D.	0.105	0.245	1.155	B.D.	1.365	B.D.	4.235	42.74	0.91	4.41	0.455	3.43	14.95	B.D.	12.57	B.D.
	21.6-24	1.26	9.485	B.D.	B.D.	B.D.	1.855	B.D.	1.47	0.875	5.215	72.42	0.56	6.23	0.525	5.915	19.74	B.D.	4.604	B.D.
	24-27	2.065	7	B.D.	0.21	0.21	0.945	B.D.	1.365	0.28	3.43	43.12	0.63	5.775	0.35	3.395	12.22	B.D.	B.D.	2.674
	27-30	4.97	5.285	B.D.	0.315	0.105	0.805	B.D.	1.225	0.525	3.395	23.56	1.225	5.915	0.21	3.885	12.88	B.D.	2.727	B.D.
Blanks	2% HCL	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.009	0.002	N.D.	N.D.	N.D.	N.D.	0.014	N.D.	N.D.	N.D.
	Graduated Cylinder	N.D.	N.D.	N.D.	N.D.	N.D.	0.001	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
		N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Ultra Pure DI	N.D.	N.D.	N.D.	N.D.	0.001	0.001	N.D.	N.D.	0.001	N.D.	N.D.	0.001	N.D.	N.D.	0.001	N.D.	N.D.	0.001	N.D.
*All ion concentrations are presented in mg/L; B.D. represents concentrations below the instrumental detection limit; N.A. represents samples not analyzed for a given parameter																				

Table 6: Concentrations of acid-soluble trace metals in the sediment cores.

Site #	DEPTH (cm)	As	B	Se	Li	Cu	Ba	Be	Cd	Cr	Fe	Mn	Ni	Pb	Sr	Zn	Al	Ge	V	Tl
8	0-2.3	61.5	B.D.	0.665	0.28	2.94	54.5	0.315	0.245	6.755	2996	107.6	1.715	4.55	14.53	6.405	1489	B.D.	B.D.	B.D.
	2.3-4.6	62.97	B.D.	0.42	0.42	12.11	130.8	0.525	0.35	10.78	1393	76.83	15.72	4.41	48.51	10.33	1791	B.D.	599.2	18.82
	4.6-6.9	17.4	B.D.	B.D.	0.105	5.25	31.33	0.35	0.14	2.17	1726	158.3	4.06	6.545	29.33	11.9	741	B.D.	947.4	14.54
	6.9-9.2	10.68	B.D.	B.D.	B.D.	3.92	18.97	0.28	0.105	1.435	2427	249.9	2.38	6.125	19.53	11.9	708.4	B.D.	230.5	6.318
	9.2-11.5	30.91	B.D.	0.07	0.28	8.33	59.36	0.42	0.21	4.445	1148	106.6	1.33	4.515	32.73	9.135	1006	B.D.	130.9	6.574
	11.5-13.8	49.63	11.24	0.175	0.42	11.97	92.33	0.49	0.315	6.37	1227	78.16	0.525	4.62	41.41	7.98	1528	B.D.	501.8	4.07
	13.8-16.1	51.35	11.48	0.175	0.42	12.67	99.51	0.49	0.315	6.545	1460	92.58	0.56	4.515	44	8.155	1824	8.194	748.7	5.524
	16.1-18.4	44.52	11.87	0.105	0.42	12.32	89.01	0.49	0.28	6.195	2147	175.7	1.085	5.18	38.92	10.12	1813	3.848	748.6	8.399
	18.4-20.7	46.94	11.87	B.D.	0.49	11.9	98.88	0.49	0.28	6.615	1566	97.23	0.91	4.55	42.28	8.925	1876	25.86	701.7	8.052
10	0-2.4	0.28	0.945	B.D.	0.105	0.98	8.365	0.07	B.D.	0.49	382.6	69.3	0.63	1.365	0.84	5.495	548.8	B.D.	743.4	6.041
	2.4-4.8	0.175	0.63	B.D.	1.995	0.945	7.14	0.07	B.D.	0.63	404.6	38.47	0.42	1.26	0.595	5.32	919.8	B.D.	60.84	B.D.
	4.8-7.2	0.14	0.525	B.D.	0.105	0.735	4.97	B.D.	B.D.	0.42	231.7	13.97	0.525	1.19	0.56	5.04	448.7	B.D.	70.99	B.D.
	7.2-9.6	0.07	0.595	B.D.	B.D.	0.7	4.62	B.D.	B.D.	0.35	193.9	9.1	0.49	1.12	0.49	4.795	363	B.D.	53.8	B.D.
	9.6-12	0.175	0.63	B.D.	B.D.	0.875	5.075	0.07	B.D.	0.315	295.2	12.39	0.945	1.155	1.225	5.04	274.8	B.D.	52.11	B.D.
	12-14.4	0.14	0.665	B.D.	0.14	1.225	6.335	0.07	B.D.	0.35	288.4	14.39	0.7	1.855	1.05	6.265	367.5	6.413	46.37	B.D.
	14.4-16.8	0.07	0.42	B.D.	0.07	0.77	4.235	B.D.	B.D.	0.42	174.2	6.02	0.455	0.945	0.49	4.725	415.1	B.D.	52.38	B.D.
	16.8-19.2	0.105	0.525	B.D.	B.D.	0.49	3.92	B.D.	B.D.	0.42	169.8	5.25	0.35	0.805	0.42	3.92	449.8	B.D.	54.89	B.D.
	19.2-21.6	0.105	0.315	B.D.	B.D.	0.91	3.99	B.D.	B.D.	0.315	169.6	9.345	0.385	1.05	0.595	3.71	330	B.D.	56.18	B.D.
4	21.6-24	0.21	0.525	B.D.	B.D.	1.225	6.23	0.07	B.D.	0.315	203.8	15.44	0.7	2.24	1.015	5.74	241.9	B.D.	47.35	B.D.
	0-2.3	3.045	11.69	0.385	0.595	11.17	85.93	0.525	0.21	3.255	3591	1053	3.955	10.96	15.16	30.14	1364	B.D.	49.73	B.D.
	2.3-4.6	2.625	10.85	0.35	0.455	10.78	86.52	0.525	0.21	3.15	4925	1497	3.92	11.83	9.345	29.23	1857	B.D.	307	57.8
	4.6-6.9	2.45	12.15	0.28	0.665	14.42	95.69	0.595	0.245	3.675	3738	966	3.99	13.93	10.05	33.57	1558	3.206	281.2	62.64
	6.9-9.2	2.485	10.15	0.14	0.525	12.39	79.17	0.525	0.21	3.185	3150	733.3	3.535	12.18	9.17	30.42	1402	B.D.	360.5	54.25
	9.2-11.5	2.73	8.26	0.14	0.56	11.1	72.66	0.49	0.21	3.01	4050	802.6	2.625	10.47	10.22	24.15	2188	B.D.	339.4	40.48
	11.5-13.8	4.165	7.63	B.D.	0.385	11.17	80.71	0.49	0.175	3.22	2521	446.3	1.995	9.17	13.44	20.76	1581	19.88	370.8	25.78
	13.8-16.1	7.875	10.61	B.D.	0.42	13.06	107.3	0.595	0.21	4.585	4211	643.7	1.925	8.75	20.09	21.04	2620	B.D.	487.6	16.4

Table 6: Continued.

Site #	DEPTH (cm)	As	B	Se	Li	Cu	Ba	Be	Cd	Cr	Fe	Mn	Ni	Pb	Sr	Zn	Al	Ge	V	Tl
4	16.1-18.4	4.095	11.55	B.D.	0.21	11.9	61.88	0.42	0.21	3.57	3773	471.5	4.095	11.2	8.82	27.58	1131	15.6	639.8	16.66
	18.4-20.7	2.24	8.715	B.D.	0.07	10.05	42.7	0.35	0.175	3.115	3492	442.4	3.675	10.85	5.11	25.76	1021	B.D.	414.6	21.26
2	0-2	1.19	12.67	0.63	0.455	8.505	104.6	0.28	0.175	4.69	5429	1870	B.D.	11.8	7.735	40.6	2008	B.D.	309.6	17.39
	2-4	1.225	13.23	0.805	0.42	9.275	118.4	0.315	0.175	4.375	7186	2973	B.D.	13.27	8.33	41.86	2310	2.603	352.4	85.24
	4-6	1.365	13.37	0.805	0.315	9.66	117.5	0.315	0.21	4.515	7574	3106	0.315	13.51	8.365	42.6	2138	28.01	365.4	111.05
	6-8	1.19	11.24	0.7	0.175	8.26	88.1	0.28	0.175	3.675	4610	1902	0.455	11.1	6.86	35.21	1277	38.91	361.8	113.09
	8-10	1.47	14.11	0.84	0.28	10.61	123.8	0.35	0.245	4.445	6993	2778	0.525	14.39	8.715	44.73	1899	9.013	303.2	94.25
	10-12	1.505	13.76	0.525	0.21	9.94	110.5	0.35	0.21	4.445	6059	1867	0.525	14.39	7.21	42.84	1570	17.74	385	113.03
	12-14	1.155	10.89	0.35	B.D.	8.4	72.8	0.28	0.175	3.465	6486	1737	0.84	12.99	5.39	37	1330	4.917	369.9	86.56
	14-16	1.225	11.38	0.28	B.D.	9.345	76.5	0.315	0.21	3.85	5670	1379	0.875	15.19	5.39	42.07	1219	38.05	316.4	58.61
	16-18	1.19	10.85	0.14	B.D.	9.31	68.7	0.315	0.21	3.64	4802	987.7	0.875	14.95	4.935	38.99	1014	B.D.	371.8	52.9
	18-20	1.4	11.94	0.21	B.D.	10.01	74.6	0.315	0.21	4.13	5247	1101	1.05	16.8	5.285	43.82	1101	B.D.	360.3	41.08
	20-22	1.435	12.71	0.21	B.D.	10.54	79.2	0.35	0.21	4.305	5660	1183	1.12	17.64	5.46	45.99	1179	B.D.	410.5	47.65
	22-24	1.435	12.5	0.35	B.D.	10.57	81.9	0.35	0.21	4.34	4165	1001	1.225	18.2	5.39	45.54	878.5	22.66	437.8	48.48
	24-26	1.645	13.62	0.21	B.D.	11.73	90.6	0.385	0.245	4.76	5548	1134	1.295	20.13	5.635	51	1160	B.D.	437.2	57.66
	26-28	1.575	12.6	0.14	0.07	10.92	78.6	0.35	0.21	4.48	4638	935.2	1.33	18.41	5.215	49.28	946.4	B.D.	479.7	50.88
	28-30	1.575	12.18	0.21	B.D.	11.1	79.2	0.35	0.245	4.27	4074	844.6	1.33	19.32	5.32	50.02	881	B.D.	441.7	46.61
3	0-2.3	4.55	10.78	0.105	0.525	21.53	70.4	0.665	0.28	3.325	5170	1009	3.955	11.9	10.85	38.26	2151	B.D.	439.1	46.01
	2.3-4.6	4.025	10.19	0.07	0.42	18.8	66.6	0.63	0.245	3.115	4410	860.3	3.92	11.38	9.835	35.18	1863	B.D.	340.7	37.47
	4.6-6.9	4.515	11.17	0.07	0.595	19.88	74.3	0.665	0.28	3.36	4522	914.2	4.095	12.01	12.78	37.87	1884	B.D.	317.5	34.76
	6.9-9.2	4.34	10.71	B.D.	0.56	20.58	72.2	0.63	0.28	3.325	4435	887.6	4.06	12.04	10.57	37.94	1863	B.D.	333.7	39.46
	9.2-11.5	3.815	10.43	0.07	0.56	23	70.7	0.63	0.28	3.325	5110	1011	3.78	12.15	10.08	38.29	2142	B.D.	339.5	38.86
	11.5-13.8	4.025	9.87	0.07	0.56	21.91	66	0.595	0.28	3.22	3549	631.1	3.43	11.73	10.36	36.65	1555	B.D.	351.1	36.38
	13.8-16.1	3.325	7.245	B.D.	0.56	18.03	61.5	0.525	0.21	2.835	2970	451.2	2.66	10.08	10.89	29.58	1787	B.D.	357.2	29.59
	16.1-18.4	4.795	7.28	B.D.	0.56	15.61	74.7	0.56	0.21	3.36	1977	272.3	2.345	9.625	13.55	25.41	1370	B.D.	379.7	16.69
	18.4-20.7	7.63	9.59	B.D.	0.525	19.85	93.5	0.63	0.245	4.76	4081	506.1	2.31	9.59	17.4	26.95	2549	B.D.	492.1	12.99

Table 6: Continued.

Site #	DEPTH (cm)	As	B	Se	Li	Cu	Ba	Be	Cd	Cr	Fe	Mn	Ni	Pb	Sr	Zn	Al	Ge	V	Tl
3	20.7-23	3.85	7.98	B.D.	0.21	16.63	54.5	0.455	0.245	2.94	4148	447.7	3.815	10.99	8.89	34.16	1469	B.D.	656.7	13.01
	23-25.3	3.955	8.54	B.D.	0.28	16.31	53.9	0.49	0.28	3.395	3882	379.4	4.375	12.39	8.995	36.79	1352	B.D.	386.7	11.12
	25.3-27.6	2.31	6.545	B.D.	0.14	13.41	33.3	0.35	0.21	2.485	2370	250.7	3.815	10.5	4.97	30.35	720.7	B.D.	428.5	10.25
	27.6-29.9	3.08	8.155	B.D.	0.105	14.98	41.93	0.455	0.28	2.905	3990	379.4	4.725	12.57	6.475	36.72	1166	B.D.	284.5	7.996
1	0-4.8	2.905	17.19	0.735	0.84	19.22	B.D.	0.7	0.245	6.3	B.D.	4011	1.785	20.02	12.99	58.94	4725	B.D.	343.9	9.087
	4.8-7.2	3.01	14.35	0.735	0.21	18.48	B.D.	0.63	0.245	4.9	8540	3330	2.065	19.11	12.04	49.07	2668	33.54	576.4	120.2
	7.2-9.6	2.975	13.2	0.7	0.245	17.82	148.8	0.595	0.245	4.62	6769	2604	2.1	18.41	10.92	47.15	2221	B.D.	503.2	114.5
	9.6-12	2.905	13.23	0.595	0.28	19.39	163.9	0.665	0.245	4.9	6111	2129	2.345	19.71	11.62	50.37	2149	B.D.	489.9	100.9
	12-14.4	2.625	B.D.	0.315	0.28	18.2	129.9	0.63	0.245	4.76	8148	2169	2.38	18.8	10.71	46.94	3338	B.D.	534.5	91.17
	14.4-16.8	4.025	B.D.	0.455	0.385	19.08	164.6	0.7	0.245	5.425	6143	1906	2.485	19.11	14.25	47.6	2574	B.D.	557.1	59.56
	16.8-19.2	6.545	0.595	0.175	0.42	17.01	153.3	0.7	0.21	6.37	8022	2250	2.1	14.6	19.88	36.09	3749	B.D.	631.2	77.1
	19.2-21.6	2.905	5.67	0.21	0.14	14.42	84.42	0.455	0.21	4.27	4337	1132	2.24	15.37	8.75	41.65	1590	B.D.	746.4	46.23
	21.6-24	1.995	B.D.	0.35	B.D.	13.02	64.79	0.35	0.175	3.815	6108	1890	2.065	14.7	5.985	39.55	1588	B.D.	453.9	43.78
	24-27	1.4	B.D.	0.07	0.28	7.14	43.33	0.245	0.105	3.36	3223	781.6	1.47	11.45	3.71	32.55	1212	B.D.	340.7	59.17
	27-30	1.26	B.D.	0.14	0.42	4.445	25.97	0.21	0.07	2.765	3343	977.2	1.435	10.89	3.115	26.74	1458	B.D.	234.5	33.22
Blanks	2% HCL	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.009	0.002	N.D.	N.D.	N.D.	N.D.	0.014	N.D.	N.D.	N.D.
	Graduated Cylinder	N.D.	N.D.	N.D.	N.D.	N.D.	0.001	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
		N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Ultra Pure DI	N.D.	N.D.	N.D.	N.D.	0.001	0.001	N.D.	N.D.	0.001	N.D.	N.D.	0.001	N.D.	N.D.	0.001	N.D.	N.D.	0.001	N.D.
*All ion concentrations are presented in mg/L; B.D. represents concentrations below the instrumental detection limit; N.A. represents samples not analyzed for a given parameter																				

Table 7: Significant probability values determined through multiple linear regression of leachable trace metal concentrations with depth and distance from the coal ash spill

		Distance From Spill (mi)	Depth (cm)			Distance From Spill (mi)	Depth (cm)
Water Soluble	As	0.16	0.58	Acid Soluble	As	1.00	0.90
	B	0.19	0.36		B	0.13	0.21
	Se	0.29	0.93		Se	0.31	0.20
	Li	0.13	0.55		Li	0.78	0.60
	Cu	0.27	0.69		Cu	0.01	0.42
	Ba	0.97	0.37		Ba	0.36	0.66
	Be	0.88	0.45		Be	0.27	0.52
	Cd	0.06	0.15		Cd	0.18	0.12
	Cr	0.18	0.86		Cr	0.13	0.66
	Fe	0.79	0.41		Fe	0.36	0.22
	Mn	0.15	0.97		Mn	0.89	0.44
	Ni	0.32	0.53		Ni	0.91	0.99
	Pb	0.90	0.07		Pb	0.32	0.75
	Sr	0.39	0.18		Sr	0.31	0.47
	Zn	0.64	0.78		Zn	0.32	0.82
	Al	0.10	0.94		Al	0.30	0.23
	Ge	0.32	0.59		Ge	0.13	0.77
	V	0.20	0.75		V	0.65	0.61
	Tl	0.02	0.72		Tl	0.63	0.46
*Significance values ≤0.05 are considered significant							

Table 8: Results of bulk chemical and C-N-S isotope analyses in the sediment cores.

SEDIMENT BULK ISOTOPE RESULTS								
LOCATION #	SAMPLE NAME	DEPTH (cm)	CARBON		NITROGEN		SULFUR	
			$\delta^{13}\text{C}$	(%)	$\delta^{15}\text{N}$	(%)	$\delta^{34}\text{S}$	(%)
8	1-1	0.0	-24.4	3.56	+3.5	0.08	N.D.	N.D.
	1-2	2.3	-24.8	5.24	+4.8	0.10	-1.7	0.08
	1-3	4.6	-24.8	5.00	+3.4	0.13	+0.6	0.08
	1-4	6.9	-25.8	3.77	+2.2	0.12	+2.1	0.04
	1-5	9.2	-25.2	2.98	+3.3	0.07	+1.6	0.07
	1-6	11.5	-24.0	2.42	+5.7	0.04	+5.8	0.03
	1-7	13.8	-24.0	2.64	+6.4	0.05	+6.2	0.03
	1-8	16.1	-24.1	2.69	+5.2	0.06	+4.7	0.03
	1-9	18.4	-24.2	2.89	+6.9	0.07	+2.7	0.04
10	3-1	0.0	-25.0	0.98	+1.1	0.03	N.D.	N.D.
	3-2	2.4	-25.2	0.46	+4.3	0.01	N.D.	N.D.
	3-3	4.8	-24.2	0.66	+2.9	0.01	N.D.	N.D.
	3-4	7.2	-24.6	1.02	+3.3	0.03	N.D.	N.D.
	3-5	9.6	-25.6	1.53	+1.9	0.04	N.D.	N.D.
	3-6	12.0	-24.7	3.27	+3.1	0.08	N.D.	N.D.
	3-7	14.4	-24.6	0.40	+1.7	0.01	N.D.	N.D.
	3-8	16.8	-25.6	0.34	+4.4	0.01	N.D.	N.D.
	3-9	19.2	-24.2	0.36	+2.9	0.01	+3.1	0.03
4	5-1	0.0	-27.6	3.72	+4.7	0.21	+2.4	0.05
	5-2	2.3	-27.4	3.76	+5.2	0.21	-5.4	0.06
	5-3	4.6	-27.3	3.81	+5.1	0.20	-2.8	0.07
	5-4	6.9	-26.7	3.29	+5.1	0.15	-2.3	0.07
	5-5	9.2	-26.3	3.32	+5.5	0.14	-2.2	N.D.
	5-6	11.5	-25.4	3.42	+5.7	0.13	-0.7	0.04
	5-7	13.8	-27.3	3.55	+4.2	0.17	+1.1	0.05
	5-8	16.1	-27.0	2.08	+4.7	0.12	-3.9	0.16
	5-9	18.4	-26.9	2.06	+7.4	0.14	-2.1	0.11
2	7-1	0.0	-27.0	N.D.	+7.7	N.D.	N.D.	N.D.
	7-2	2.0	-27.1	2.11	+7.4	0.15	+2.0	0.04
	7-3	4.0	-27.2	N.D.	+7.2	N.D.	+2.2	0.04
	7-4	6.0	-27.3	2.86	+7.4	0.20	+2.2	0.04
	7-5	8.0	-27.1	2.18	+7.4	0.16	+2.2	0.05
	7-6	10.0	-27.0	1.96	+7.2	0.13	+1.8	0.05
	7-7	12.0	-26.8	1.64	+7.6	0.13	+3.5	0.03
	7-8	14.0	-26.7	2.03	+7.4	0.15	+2.8	0.04
	7-9	16.0	-26.5	1.83	+7.3	0.14	+2.1	0.04
	7-10	18.0	-26.5	2.18	+6.9	0.16	+1.5	0.02
	7-11	20.0	-26.8	2.17	+8.8	0.21	+2.5	0.03
	7-12	22.0	-26.4	2.02	+7.1	0.17	+3.2	0.02
	7-13	24.0	-26.2	1.90	+6.9	0.15	+0.8	0.04
	7-14	26.0	-26.9	2.36	+6.1	0.17	+0.7	0.05
	7-15	28.0	-27.3	4.95	+4.3	0.25	+2.6	0.03
3	9-1	0.0	-27.4	4.83	+4.2	0.26	-2.3	0.07
	9-2	2.3	-27.4	4.99	+4.2	0.26	-2.8	0.06
	9-3	4.6	-27.3	4.71	+4.3	0.24	-3.0	0.06
	9-4	6.9	-27.2	4.66	+4.6	0.24	-2.7	0.06
	9-5	9.2	-27.0	4.51	+4.7	0.22	-2.4	0.06
	9-6	11.5	-26.5	3.92	+4.8	0.17	-3.2	0.06
	9-7	13.8	-25.9	3.97	+5.1	0.15	-2.2	0.05
	9-8	16.1	-25.9	3.49	+5.2	0.13	-1.3	0.06
	9-9	18.4	-26.9	2.61	+4.6	0.13	-1.0	0.07
	9-10	20.7	-26.7	2.87	+4.4	0.14	-1.0	0.06
	9-11	23.0	-27.1	2.55	+4.2	0.15	-2.3	0.06
	9-12	25.3	-26.5	2.30	+4.4	0.12	-1.3	0.09
	9-13	27.6	-27.5	2.89	+7.4	0.24	-1.3	0.05
1	11-1	0.0	-27.4	2.83	+7.4	0.23	-1.5	0.06
	11-2	2.4	-27.5	2.85	+7.5	0.24	+0.6	0.05
	11-3	4.8	-27.5	2.81	+7.4	0.23	-1.8	0.05
	11-4	7.2	-27.4	2.85	+7.3	0.23	+0.1	0.04
	11-5	9.6	-27.0	2.89	+7.3	0.22	+0.3	0.05
	11-6	12.0	-27.1	3.06	+7.1	0.20	-0.6	0.05
	11-7	14.4	-25.8	3.10	+7.2	0.16	-1.9	0.07
	11-8	16.8	-27.2	2.07	+7.6	0.17	-1.5	0.08
	11-9	19.2	-27.8	1.68	+7.6	0.16	-1.0	0.07
	11-10	21.6	-24.4	4.21	+5.6	0.13	+0.6	0.10
	11-11	24.0	-26.2	1.72	+5.6	0.06	+0.4	0.09
	11-12	27.0	-24.4	3.56	+3.5	0.08	+3.3	0.04
*All isotope results are presented in per mill (‰); N.D. represents values that were not detectable.								

Table 9: Results of wt. S% and $\delta^{34}\text{S}$ of elemental S, acid-volatile S, and chromium-reducible S analyses in the sediment cores using S sequential extraction method.

Site	Depth (cm)	Elemental S		Acid-Volatile S		Chromium-Reducible S	
		$\delta^{34}\text{S}$ (‰)	(%)	$\delta^{34}\text{S}$ (‰)	(%)	$\delta^{34}\text{S}$ (‰)	(%)
8	2.3-4.6	-3.6	B.D.	B.D.	B.D.	-7.1	0.01
	6.9-9.2	0.7	B.D.	-1.7	B.D.	4.8	0.02
	11.5-13.8	6.6	B.D.	B.D.	B.D.	4.0	0.01
	16.1-18.4	10.8	B.D.	B.D.	B.D.	0.6	0.01
10	0-2.4	0.9	B.D.	B.D.	B.D.	B.D.	0.02
	4.8-7.2	-0.5	B.D.	B.D.	B.D.	0.6	B.D.
	9.6-12.0	1.2	B.D.	B.D.	B.D.	0.0	0.01
	14.4-16.8	B.D.	B.D.	B.D.	B.D.	3.2	B.D.
	19.2-21.6	B.D.	B.D.	B.D.	B.D.	3.1	B.D.
4	0-2.3	B.D.	B.D.	B.D.	B.D.	-5.3	0.01
	4.6-6.9	B.D.	B.D.	B.D.	B.D.	-4.2	0.01
	9.2-11.5	-2.4	B.D.	B.D.	0.01	-4.8	0.01
	13.8-16.1	0.0	B.D.	1.1	B.D.	-1.6	0.01
	18.4-20.7	-1.5	0.01	-0.3	B.D.	-2.7	0.01
2	2-4	B.D.	B.D.	B.D.	B.D.	-1.2	B.D.
	6-8	B.D.	B.D.	B.D.	B.D.	-3.8	B.D.
	10-12	-0.5	B.D.	B.D.	B.D.	-3.1	B.D.
	14-16	-0.2	B.D.	-2.1	0.01	-3.0	B.D.
	18-20	-0.2	B.D.	-1.6	B.D.	-1.6	0.01
	22-24	1.1	B.D.	-0.1	B.D.	0.2	0.02
	26-28	-1.9	B.D.	-2.4	B.D.	-3.0	0.02
3	0-2.3	-3.5	B.D.	B.D.	B.D.	-7.0	0.01
	4.6-6.9	-2.5	B.D.	B.D.	B.D.	-6.9	0.01
	9.2-11.5	-2.8	B.D.	B.D.	B.D.	-6.9	0.01
	13.8-16.1	B.D.	B.D.	B.D.	B.D.	-4.8	0.01
	18.4-20.7	-1.9	B.D.	-1.3	B.D.	-1.0	0.06
	23-25.3	-0.5	B.D.	-0.2	0.01	-2.1	B.D.
	27.6-29.9	-2.2	B.D.	-2.7	B.D.	-5.1	0.01
1	0-4.8	B.D.	B.D.	B.D.	B.D.	-6.9	0.01
	7.2-9.6	-2.9	B.D.	B.D.	B.D.	-6.1	B.D.
	12-14.4	-3.4	B.D.	B.D.	B.D.	-4.9	0.01
	16.8-19.2	-2.4	B.D.	B.D.	B.D.	-3.6	0.02
	21.6-24	-0.6	B.D.	-0.4	B.D.	0.2	0.02
	27-30	0.5	B.D.	-0.4	B.D.	1.3	0.01
*All isotope results are presented in per mill (‰); B.D. indicates samples whose concentrations of Ag ₂ S were too low to be analyzed by the mass spectrometer							

Table 10: EPA MCL water quality guidelines (after REFERENCE) used for comparison with trace metal concentrations measured in the water column in Apr 2016.

	Al	As	Ba	Be	Cd	Cr	Cu	Mn	Ni	Pb	Se	Tl	Zn
Aquatic Life	0.750	0.340	-	-	0.002	0.016	-	-	0.470	0.650	-	-	0.120
Human Health	-	1.80E-05	1.000	-	-	Any	1.300	0.050	0.610	-	0.170	2.40E-04	7.400
Drinking Water	0.010	-	2.000	0.004	0.005	0.100	1.300	-	-	0.015	0.050	0.002	-
*All guidelines are presented in mg/L													

Table 11: Sediment Quality Guidelines (SQGs) used in this study for comparisons with trace metal concentrations in the sediment cores.

	As	Cd	Cr	Cu	Ni	Pb	Zn
Effects Range Low (ERL)	8.2	1.2	81.0	34.0	20.9	46.7	150.0
Effects Range Medium (ERM)	70.0	9.6	370.0	270.0	51.6	218.0	410.0
*All guidelines are presented in mg/Kg							

Table 12: Concentrations of water- and acid-soluble trace metals in local bedrock.

	Bedrock Type	As	Se	Li	Cu	Ba	Be	Cd	Cr	Fe	Mn	Ni	Pb	Sr	Zn	Al	V	Tl
DI-Soluble	Knox Gp. Dolomite	B.D.	1.939	B.D.	B.D.	0.281	B.D.	B.D.	B.D.	0.102	2.451	B.D.	B.D.	0.135	0.092	0.128	B.D.	B.D.
	U. Chickamauga Gp. Limestone	0.122	3.317	0.084	B.D.	0.084	B.D.	B.D.	B.D.	0.104	B.D.	B.D.	0.258	1.400	0.132	16.717	B.D.	0.364
	U. Chickamauga Gp. Limestone	B.D.	2.147	B.D.	0.118	1.144	B.D.	B.D.	B.D.	0.139	B.D.	B.D.	34.734	2.314	0.170	20.096	B.D.	B.D.
	Rome Fm. Limestone	1.049	3.487	B.D.	B.D.	0.263	B.D.	B.D.	0.170	3.379	B.D.	B.D.	0.152	0.179	0.122	12.286	B.D.	1.339
	L. Chickamauga Gp. Limestone	B.D.	B.D.	B.D.	B.D.	0.054	B.D.	B.D.	B.D.	1.234	B.D.	B.D.	0.074	1.619	0.070	13.102	B.D.	4.077
	Rome Fm. Sandstone	1.203	1.213	0.061	0.066	0.058	B.D.	B.D.	0.077	1.173	0.110	B.D.	0.108	B.D.	0.174	2.210	B.D.	0.656
	U. Chickamauga Gp. Shale	1.995	0.734	B.D.	0.053	0.103	B.D.	B.D.	B.D.	2.115	B.D.	B.D.	0.089	0.441	B.D.	12.390	B.D.	0.406
	Rome Fm. Shale	0.248	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.557	B.D.	B.D.	0.123	B.D.	B.D.	1.130	B.D.	B.D.
Acid-Soluble	L. Chickamauga Gp. Shale	3.178	1.371	0.088	B.D.	0.095	B.D.	B.D.	B.D.	1.262	B.D.	B.D.	0.120	0.159	0.136	5.395	B.D.	B.D.
	Knox Gp. Dolomite	0.218	2.156	B.D.	0.268	6.740	B.D.	B.D.	0.153	15.242	10.345	B.D.	0.255	0.461	0.956	85.671	B.D.	B.D.
	U. Chickamauga Gp. Limestone	6.977	B.D.	9.310	0.858	15.297	0.128	B.D.	1.658	1839.7	144.64	B.D.	5.158	400.11	2.687	279.06	B.D.	B.D.
	U. Chickamauga Gp. Limestone	2.920	2.445	10.886	1.472	95.552	0.148	B.D.	2.487	B.D.	258.89	B.D.	7.833	421.23	4.139	296.63	7.626	0.743
	Rome Fm. Limestone	4.464	B.D.	2.672	4.627	34.137	0.376	B.D.	4.852	B.D.	409.98	B.D.	1.406	33.171	4.140	738.95 ₂	48.380	B.D.
	L. Chickamauga Gp. Limestone	B.D.	2.198	9.193	0.337	3.096	B.D.	B.D.	0.997	423.66 ₇	58.402	B.D.	0.830	257.40	7.418	25.635	60.598	B.D.
	Rome Fm. Sandstone	0.053	0.926	0.239	0.459	15.477	0.084	B.D.	0.531	259.07	30.081	B.D.	0.554	1.709	1.716	938.68	B.D.	1.117
	U. Chickamauga Gp. Shale	B.D.	3.583	7.010	2.785	29.895	0.222	B.D.	2.012	1851.8	217.80	B.D.	7.960	305.84	4.848	395.90	3.113	B.D.
	Rome Fm. Shale	0.778	1.066	0.829	0.842	80.427	0.743	B.D.	1.142	532.87	68.095	B.D.	0.751	3.876	3.657	B.D.	B.D.	0.329
	L. Chickamauga Gp. Shale	B.D.	B.D.	2.501	1.251	78.130	0.216	B.D.	3.282	1606.1	163.92	B.D.	0.877	4.442	4.681	B.D.	B.D.	0.066
	DI Blank	B.D.	1.371	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.058	B.D.	0.158	B.D.	B.D.	0.121
	HCl Blank	B.D.	1.050	B.D.	0.105	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	0.070	B.D.	B.D.	0.108	B.D.	0.945
*All ion concentrations are presented in mg/Kg; B.D. represents concentrations below the instrumental detection limit																		

VITA

Ashley Brooke Ramsey was born in Grapevine, Texas in 1994. She moved with her family when she was 4 months old to West Des Moines, Iowa. Here, Ashley made many lifelong friends and thrived in sports. At the age of 10, her family moved to Johnson City, Tennessee. In Tennessee, Ashley played tennis and swam competitively. She also excelled in academics, served on her student council board, and competed in public speaking and job interview with the Future Business Leaders of America. Before her junior year of high school, Ashley and her family moved one last time, to Katy, Texas. Ashley continued competing in public speaking and job interview and served as the president of her Future Business Leaders of America chapter. It was also during these last two high school years that Ashley discovered her love for math, chemistry, and theater tech. These hobbies followed her to college at Baylor University where she obtained her Bachelor of Science degree in Geology in 3.5 years.

At Baylor, Ashley was very active in her sorority, and worked as a theater tech and lab assistant in the Geoluminescence Dating Research Laboratory. Additionally, she completed an undergraduate thesis project with Dr. Steve Forman. This project studied the age anomaly associated with the radiocarbon dating of terrestrial gastropods. Ashley presented this work as a poster at GSA 2015 before graduating that December.

After graduation, Ashley quickly packed her bags and moved back to Tennessee to obtain her Master of Science degree in Geology at the University of Tennessee at Knoxville under the auspice of Dr. Anna Szyrkiewicz. During her two years at UT, Ashley successfully conducted a thesis studying the current state of the Emory River, Clinch River, and Watts Bar Reservoir in respect to the Kingston Fossil Plant coal ash spill of 2008, served as Vice President of GeoClub, helped start an AAPG chapter, participated on UT's IBA team, interned at Hess Corporation in the summer of 2017, gave an oral presentation at GSA 2017 with plans to graduate in December.