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Geochemical Fractionation, Speciation, and Bioavailability of Heavy Metals in Stream Sediments in Aurora, MO

Miles Pearson

Missouri State University, Miles27@live.missouristate.edu

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**GEOCHEMICAL FRACTIONATION, SPECIATION, AND BIOAVAILABILITY
OF HEAVY METALS IN STREAM SEDIMENTS IN AURORA, MO**

A Masters Thesis

Presented to

The Graduate College of
Missouri State University

In Partial Fulfillment

Of the Requirements for the Degree
Master of Science, Chemistry

By

Miles A. Avery Pearson

August 2017

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**GEOCHEMICAL FRACTIONATION, SPECIATION, AND BIOAVAILABILITY
OF HEAVY METALS IN STREAM SEDIMENTS IN AURORA, MO**

Chemistry

Missouri State University, August 2017

Master of Science

Miles A. Avery Pearson

ABSTRACT

Stream sediments from Chat Creek in Aurora, MO, part of the former Tristate Mining District, were digested via a sequential extraction procedure modeled after the Tessier method. Prior sampling had shown elevated levels of zinc, lead, and cadmium in sediments located near former chat piles. Metals in sediments were divided into four geochemical fractions: 1) easily exchangeable, 2) carbonate-bound, 3) iron-manganese oxides-bound, and 4) organic matter-bound. The distribution of the metals within these fractions can help predict the bioavailability and speciation of said metals. The majority of metals were contained in the third and to a lesser extent the fourth fraction. In these four fractions, 73.5 percent of zinc, 54.0 percent of lead, and 73.4 percent of cadmium was recovered from total metals present in sediment samples relative to preliminary total metal analysis. Metals in plant samples also showed significant contamination and suggested bioavailability of metals. Water samples were also analyzed, but showed no significant metal contamination.

KEYWORDS: bioavailability, speciation, fractionation, Tri-State Mining District, TSMD, zinc, lead, cadmium, contamination, heavy metals, Aurora, chat, sediment

This abstract is approved as to form and content

Richard N. Biagioni, Ph.D.
Chairperson, Advisory Committee
Missouri State University

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August 2017

Approved:

Richard N. Biagioni, PhD

Mélida Gutiérrez, PhD

Adam Wanekaya, PhD

Nikolay Gerasimchuk, PhD

Julie Masterson, PhD: Dean, Graduate College

In the interest of academic freedom and the principle of free speech, approval of this thesis indicates the format is acceptable and meets the academic criteria for the discipline as determined by the faculty that constitute the thesis committee. The content and views expressed in this thesis are those of the student-scholar and are not endorsed by Missouri State University, its Graduate College, or its employees.

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INTRODUCTION

Aurora, MO is a small city situated on the edge of what is known as the Tristate Mining District, which was home to a plethora of zinc and lead mines during the last two centuries. Remediation actions have been undertaken by the EPA, but residual contamination still exists. Previous research in Aurora has found elevated levels of zinc, lead, and cadmium in stream sediments along Chat Creek. Abandoned zinc and lead mines and chat piles had left behind residual contamination. This research examines the state of metal contamination in stream sediments in Aurora, MO. Here, sediments are analyzed in four different fractions to provide an assessment of the state of contamination of the area. The bioavailability of these metals is also assessed.

Tri-State Mining District and Aurora, Missouri

In the late 1800s and early 1900s, the Tri-State Mining District (TSMD) was known as one the most abundant sources of zinc and lead ores. For years, the TSMD was the largest producer of zinc in the world (1). The geographical boundary of the TSMD spans the southwest part of Missouri, northeastern Oklahoma, and eastern Kansas. Mining activities flourished during this time resulting in great production. However, this also left behind over 100 million tons of mining waste that contained zinc, lead, and cadmium (2). The common practice was to dispose of mine tailings in large piles, known as “chat” piles. “Chat” was a common term for mining and milling wastes. These chat piles contained zinc in the highest concentration and to a smaller extent lead and cadmium, but lead and (especially) cadmium are much more potently toxic.

In 1990, the Environmental Protection Agency (EPA) designated parts of the TSMD as superfund sites. Assessment of the sites were completed in 1995, and by 2012 1,500 acres of contaminated soil had been remediated. However, chat piles were widely dispersed throughout the area and large amounts of contaminated soil still exist throughout the area (2). Since lead was a major contaminant, and the negative health effects of lead were widely known, the EPA's approach to remediation gave high health hazard areas priority. Soil was given priority over stream sediments as humans encounter soil more frequently than sediments. The first objective was to remediate daycares and playgrounds with levels of >500 ppm lead and residences of >2,500 ppm in soils, then to remediate residences with lead levels of >800 ppm (3).

Aurora is a city within the TSMD with a population of 7,450 (2014). Aurora is the site of one of the isolated zinc/lead deposits of the TSMD. Previous research has found highest levels of zinc, lead, and cadmium contamination in north/northeastern Aurora where there used to be abundant chat piles and mining operations (Figure 1). Chat Creek runs through Aurora, MO from southeast to northwest and drains the area of former chat piles. (4). Contamination of sediments within the creek is the major focus of this study.

Heavy Metals

The term "heavy metal" is a relative term. There are several different definitions given by different sources. The minimalist definition usually describes heavy metals as elements on the periodic table which are considered to be metals with relatively high atomic masses or densities. Some sources may place further limitations on what classifies as a heavy metal. The EPA alone has several different definitions; a more exhaustive one

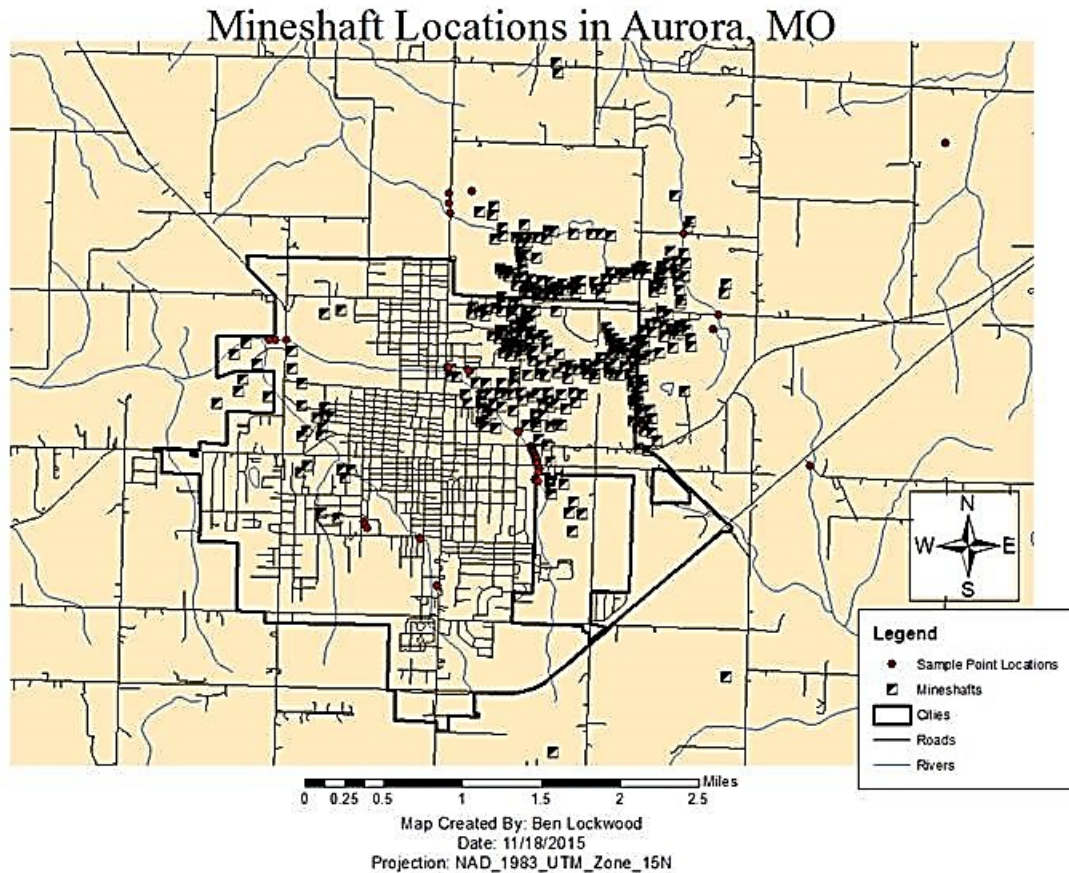


Figure 1. Former mineshaft locations located around Aurora, MO.

under the Resource Conservation and Recovery Act (RCRA) says heavy metals are, “Metallic elements with high atomic weights; (e.g., mercury, chromium, cadmium, arsenic, and lead); can damage living things at low concentrations and tend to accumulate in the food chain.” (5). Other definitions state that they must have negative health effects on plants, animals, or people; or that heavy metals have an atomic weight and density that is at least five times that of water (6). Some elements such as zinc, copper, or selenium are considered to be heavy metals. These are essential nutrients for humans in small quantities, but are also toxic at elevated levels. Heavy metals occur naturally in the Earth’s crust in various mixtures. Metals are neither created nor destroyed by normal

chemical or biological processes, but can transfer between different valence states that influence toxicity (7). Many native forms are frequently innocuous, but some anthropogenic activities such as mining can concentrate metals into atypically high amounts that can be problematic for both humans and the environment. Elevated heavy metal levels can be dangerous. There are a variety of mechanisms by which a metal can be toxic to an organism: they could displace another metal or element by binding to the site to which it should bind, they could block the receptors or disrupt enzyme activity. These are a few reasons why it is important to be able to recognize areas that contain high levels of heavy metal contamination.

The EPA has provided primary and secondary regulations concerning many heavy metals in a variety of media. Regulatory levels vary based on the medium of the metal. Regulations may exist for the maximum allowable amount of a metal that can be in drinking water, effluent water, soil, food, etc. (8). Primary regulations represent legally enforceable standards. Secondary standards are not enforced by the EPA, but act as a guideline for aesthetic reasons such as taste, smell, and color in drinking water (9).

Clear guidelines for allowable amounts of heavy metals in stream sediments are not as clearly defined as they are for other media, such as drinking water. Limits on the amount of lead in soils differ in regards to the type of area. Different allowable levels exist for child-occupied facilities, public use areas, leased properties, etc. For the Oronogo-Duenweg mining belt site in Jasper County, Missouri, the EPA established action levels for the remediation of mine tailings and soils at 6,400 ppm zinc, 400 ppm lead, and 40 ppm cadmium. The action levels for tributary sediments and delta were 250 ppm zinc, 70 ppm lead, and 2 ppm cadmium (10).

Zinc. Zinc (Zn) is an essential nutrient for humans and many other animals. Zn is atomic number 30 on the periodic table (Figure 2). It is a group twelve element and a d-block transition metal. Its electron configuration is $[Ar]3d^{10}4s^2$. It is the 24th most abundant element in the Earth's crust (76 ppm). It is most commonly found as sphalerite (ZnS) or zinc blende, a zinc sulfide compound that also contains iron. It is usually found with galena (PbS), pyrite (FeS₂), calcite (CaCO₃), dolomite (CaMg(CO₃)₂), and fluorite (CaF₂) (11). Zinc is an important industrial metal and is used in galvanized steel, alloys (e.g. brass), paints, soaps, textiles, pharmaceuticals, and many other products. Within the human body, zinc is present in the active sites of many enzymes, such as alcohol dehydrogenase. It is frequently bound via sulfur linkages. Since it is an essential human nutrient, it has a relatively low toxicity and is not of primary concern in regards to human health. The EPA has established a National Secondary Drinking Water Regulation (NSDWR) of 5 ppm for zinc in drinking water. It is not considered a health hazard at this level, it merely gives a metallic taste which may be unpleasant to the drinker.

| | | | | | | | | | | | | | | | | | | | | | | | |
|--------------------------------|---------------------------------|----------------------------------|---------------------------------|--------------------------------|---------------------------------|---------------------------------|---------------------------------|-------------------------------|---------------------------------|-------------------------------|-------------------------------|--------------------------------|--------------------------------|--------------------------------|---------------------------------|-------------------------------|-------------------------------|--------------------------------|-------------------------------|---------------------------------|-----------------------------|--------------------------------|-----------------------------|
| hydrogen 1 H 1.00794 | | | | | | | | | | | | | | | | | helium 2 He 4.002602 | | | | | | |
| lithium 3 Li 6.941 | beryllium 4 Be 9.0122 | | | | | | | | | | | | | | | | | boron 5 B 10.811 | carbon 6 C 12.011 | nitrogen 7 N 14.007 | oxygen 8 O 15.999 | fluorine 9 F 18.998 | neon 10 Ne 20.180 |
| sodium 11 Na 22.990 | magnesium 12 Mg 24.305 | | | | | | | | | | | | | | | | | aluminum 13 Al 26.982 | silicon 14 Si 28.086 | phosphorus 15 P 30.974 | sulfur 16 S 32.065 | chlorine 17 Cl 35.453 | argon 18 Ar 39.948 |
| potassium 19 K 39.098 | calcium 20 Ca 40.078 | scandium 21 Sc 44.956 | titanium 22 Ti 47.867 | vanadium 23 V 50.942 | chromium 24 Cr 51.996 | manganese 25 Mn 54.938 | iron 26 Fe 55.845 | cobalt 27 Co 58.933 | nickel 28 Ni 58.693 | copper 29 Cu 63.546 | zinc 30 Zn 65.39 | gallium 31 Ga 69.723 | germanium 32 Ge 72.61 | arsenic 33 As 74.922 | selecnium 34 Se 78.96 | bromine 35 Br 79.904 | krypton 36 Kr 83.80 | | | | | | |
| rubidium 37 Rb 85.468 | strontium 38 Sr 87.62 | yttrium 39 Y 88.906 | zirconium 40 Zr 91.224 | niobium 41 Nb 92.906 | molybdenum 42 Mo 95.94 | technetium 43 Tc [98] | ruthenium 44 Ru 101.07 | rhodium 45 Rh 101.07 | palladium 46 Pd 106.42 | silver 47 Ag 107.868 | cadmium 48 Cd 112.41 | indium 49 In 114.82 | tin 50 Sn 118.71 | antimony 51 Sb 121.76 | tellurium 52 Te 127.60 | iodine 53 I 126.90 | xenon 54 Xe 131.29 | | | | | | |
| cesium 55 Cs 132.91 | barium 56 Ba 137.33 | lanthanum 57 La 138.905 | hafnium 71 Hf 178.49 | tantalum 72 Ta 180.95 | tungsten 73 W 183.84 | rhenium 74 Re 186.21 | osmium 75 Os 190.23 | iridium 76 Ir 192.22 | platinum 77 Pt 195.08 | gold 78 Au 196.967 | mercury 79 Hg 200.59 | thallium 80 Tl 204.38 | lead 81 Pb 207.2 | bismuth 82 Bi 208.98 | polonium 83 Po [209] | astatine 84 At [210] | radon 85 Rn [222] | | | | | | |
| francium 87 Fr [223] | radium 88 Ra [226] | actinium 89 Ac [227] | actinide series | actinide series | actinide series | actinide series | actinide series | actinide series | actinide series | actinide series | actinide series | actinide series | actinide series | actinide series | actinide series | actinide series | actinide series | | | | | | |
| | | * Lanthanide series | | | | | | | | | | | | | | | | | | | | | |
| | | ** Actinide series | | | | | | | | | | | | | | | | | | | | | |

Figure 2. Periodic table of elements with zinc, lead, and cadmium highlighted. Adapted from Google image (31).

In sediments, zinc is most mobile in oxidizing and acidic environments. Greater mobility equals greater bioavailability. Zinc is least mobile and therefore least bioavailable in slightly basic and anoxic conditions, such as a marsh environment (12).

Elements such as lead and cadmium, discussed next, are of much greater concern and have enforceable primary regulations. Both lead and cadmium share some chemical properties with zinc, such as the formation of 2+ cations and the propensity to form strong bonds with sulfur (11). These metals are usually found together in ores with zinc.

Lead. Lead is one of the oldest metals known to be used by mankind. It was used as a pottery glaze in ancient Egypt around 7,000-5,000 B.C. It was also used by Romans for plumbing and water pipes and mentioned in the Old Testament (11). Lead still has numerous applications today. Several current and previous uses include car batteries, paints, ammunition alloys, solder, and anti-knocking agents in gasoline.

Lead has an atomic number of 82 and an average atomic mass of 207.12 amu. It is in group 14 (carbon group) in the p-block and period 6 on the periodic table. It is classified as a post-transition metal and has an electron configuration of [Xe] $4f^{14}5d^{10}6s^26p^2$. As a metal, lead has a bluish-white, silvery, grey color (14). It is soft, malleable, and ductile. Lead's oxidation states include 4, 3, 2, 1, -1, -2, and -4. Lead is usually found in the +2 form and to a lesser extent +4. Lead (II) compounds are the dominant inorganic form of lead. Though lead is in the same group as carbon, which has a tendency to form four bonds to make +4 or -4 ions, lead's inert pair affects its tendency to form +2 ions. An inert pair occurs in some heavier elements in groups 13 through 16 that have stable oxidation states that are two less than the group's typical valency. This happens when the electrons from the d- and f-blocks do not sufficiently shield the

s-electrons resulting in them being more tightly held by the nucleus. Lead is amphoteric and can react with either acids or bases. Lead tends to form covalent bonds and can bond with itself to form chains, rings, or polyhedral structures (11).

Lead is rather abundant when compared to the other relatively heavy members of its group, with an abundance of 13 ppm in Earth's crust, versus germanium and tin which have abundances of 2.1 and 1.5 respectively. Lead owes its prevalence to the fact that three of its isotopes; 208 (52.4%), 206 (24.1%), and 207 (22.1%), are end products of three naturally occurring radioactive decay series (11).

The most abundant lead ore is galena, PbS (lead sulfide). Other ores include anglesite (PbSO₄), cerussite (PbCO₃), pyromorphite [Pb₅(PO₄)₃Cl], and mimetesite [Pb₅(AsO₄)₃Cl]. Other naturally occurring species also include lead chloride, lead bicarbonate, lead (II) hydroxide, lead (II) nitrate, lead acetate, lead (II) fluoride, and lead (II) chalcogenides (11).

While lead has a wide array of applications in industry, it has no necessary biological function in humans nor any known beneficial effects on the body. Moreover, when lead enters the human body, it has the potential to become very problematic. Lead will complex with oxo-groups in enzymes and disrupt heme synthesis and porphyrin metabolism. It inhibits a number of enzymes including acetylcholinesterase, acid phosphatase, ATPase, carbonic anhydrase, and thiol-enzymes. Lead alters cell connectivity in the brain and can replace calcium and zinc in transmitters or bind directly to receptors. This can be especially dangerous in infants and small children. Lead can also cause high blood pressure and nephropathy (kidney problems) (11).

Lead has entered the aquatic environment primarily as a gasoline additive and through mining operations (14). Inorganic forms of lead are largely sulfides, sulfates, and carbonates. Natural forms of lead have low mobility. However, that mobility is increased in acidic environments. The EPA regulates the amount of lead that can be present in drinking water, air, paint, dust, and soil; as well as lead's proper waste disposal (15).

Cadmium. Cadmium is a d-block transition metal in group 12 on the periodic table. It composes 0.16 ppm of Earth's crust. It is one row directly below zinc, and like zinc, it forms sulfide minerals such as Greenockite (CdS). The mobility of cadmium is highly subject to the redox potential of its environment. In anoxic conditions, it nears complete unavailability. River sediments that are exposed to oxidation and acidification produce more soluble forms of cadmium: carbonates, hydroxides, and other exchangeable forms. Studies of lake sediments have shown that the majority of cadmium is bound to exchangeable sites, iron or manganese oxides, or carbonates (11).

Cadmium is similar to zinc in its tendency to form $2+$ cations. This leads to some of the biological problems that cadmium can cause. Cadmium may displace zinc in enzymes, which can disrupt enzyme function and lead to kidney damage. Cadmium also displaces calcium and magnesium ($2+$) ions in bones, which can lead to joint and skeletal problems. Over long periods, this can result in the demineralization of bones, and devastating diseases like Itai-Itai disease. There is some transport of cadmium across the blood brain barrier, which can result in central nervous system damage. Acute toxicity for cadmium is relatively low, but uncommon; chronic low-level exposure is of higher concern. Short term low level exposure can cause nausea, diarrhea, muscle cramps, and liver and kidney damage. In cases of long term exposure, kidney damage may become

irreversible and the likelihood of bone demineralization increases. It may also negatively affect enzymes and regulatory systems and is a suspected carcinogen (12).

Cadmium has been shown to be toxic to small sediment dwelling organisms even at small concentrations (3). The study examined the effects on organisms such as the mayfly (*Hexagenia limbata*), amphipod (*Hyalella azteca*), midge (*Chironomus tentans*), oligochaete (*Lumbriculus variegatus*), daphnid (*Ceriodaphnia dubia*), and bacterial luminescence (*Photobacterium phosphoreum*). An equation was developed based on the sediment-toxicity thresholds of amphipod survival: zinc (2083 mg/kg), lead (150 mg/kg), and cadmium (11.1 mg/kg). Sediments posed a low health risk if the combined metal concentrations (mg/kg) were less than 7.92 via the following equation:

$$\frac{[\text{Cd}]}{4.98} + \frac{[\text{Pb}]}{128} + \frac{[\text{Zn}]}{459} < 7.92$$

The denominators in the equation are the probable effect concentrations (PECs) in mg/kg above which harmful effects are likely to occur. Most significant here is the smaller PEC for cadmium, reflecting the higher toxicity of that element compared to lead and zinc (3).

Chemistry of zinc, lead, and cadmium in water and sediments. Figures 3, 4, and 5 show the Pourbaix (Eh-pH) diagrams for zinc, lead, and cadmium in the presence of inorganic carbon (carbonate/bicarbonate) and sulfur (sulfide, sulfate). For each of these, reducing conditions lead to the formation of the metal sulfides throughout the pH range of interest. Under less reducing conditions, zinc tends to be soluble as $\text{Zn}^{2+}(\text{aq})$ below pH 7.5. Above that pH, precipitation of $\text{ZnCO}_3(\text{s})$ occurs, with $\text{ZnO}(\text{s})$ forming at higher pH. $(\text{Zn}(\text{OH})_2(\text{s}))$ is metastable with respect to $\text{ZnO}(\text{s})$, but is likely the species first

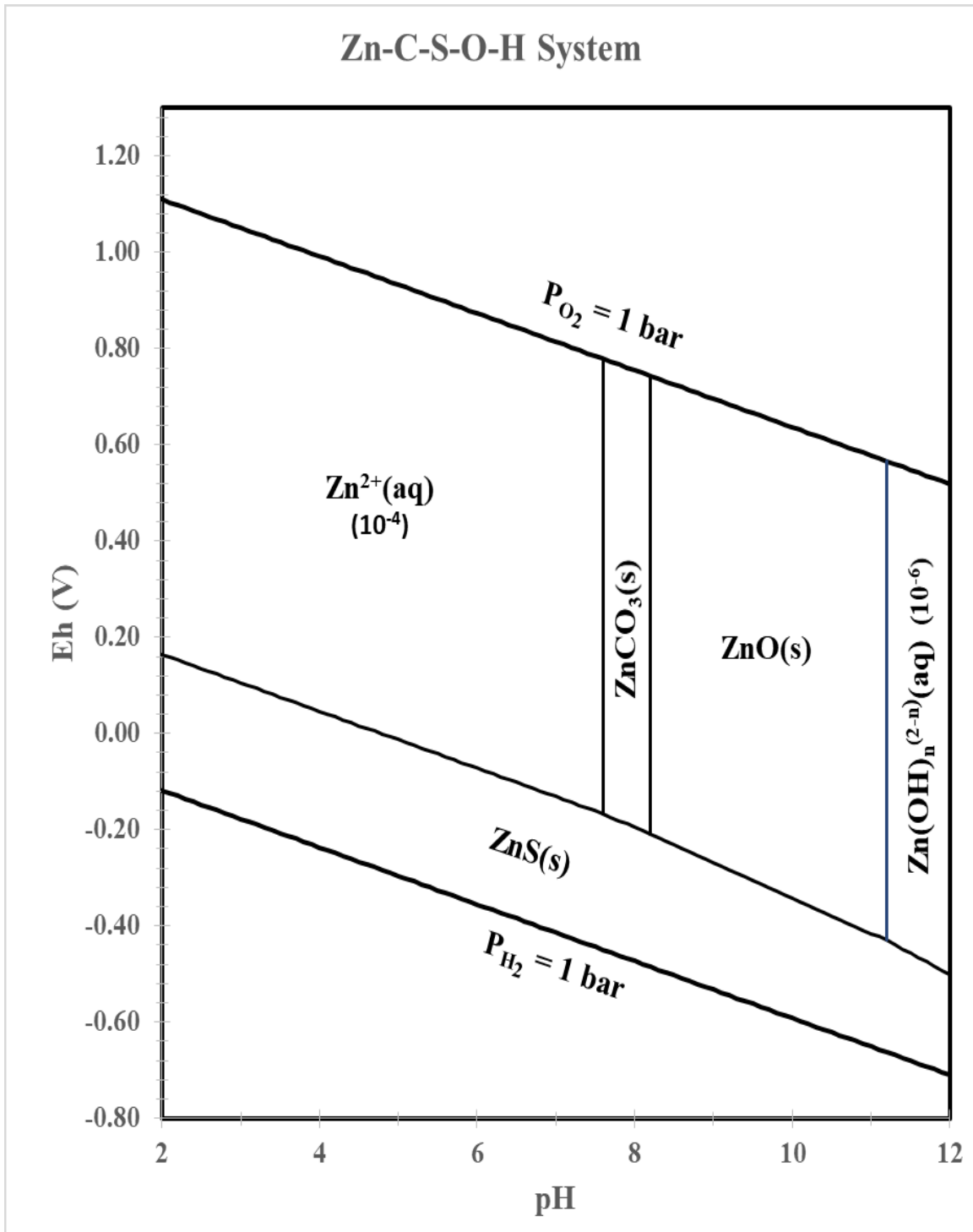


Figure 3. Eh-pH Pourbaix diagram for zinc calculated from free energy of formation values. Total soluble inorganic sulfur and carbon (bicarbonate and carbonate) = 10^{-3} M; soluble cadmium = 10^{-6} M for zinc hydroxo complexes, and 10^{-4} M for $Zn^{2+}(aq)$ ($ZnCO_3$ does not form at 10^{-6} M Zn^{2+}). ΔG°_f for $ZnS(s)$ from Eh-pH Diagrams for Geochemistry, Douglas Brookins. Springer-Verlag, 1988; All other free energies of formation from Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters, 3rd ed, Werner Stumm and James J. Morgan, Wiley, 1996.

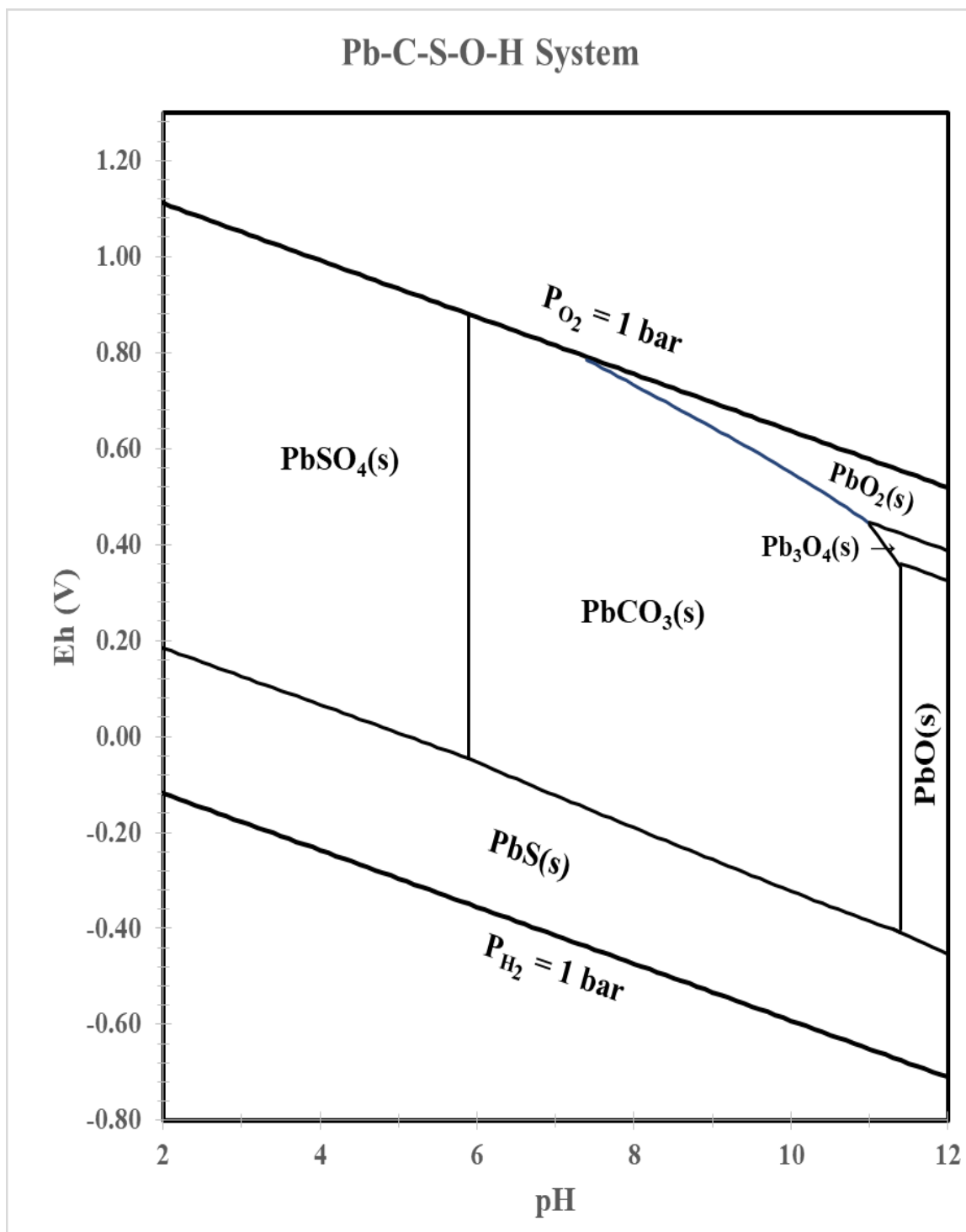


Figure 4. Eh-pH Pourbaix diagram for lead calculated from free energy of formation values. Total soluble inorganic sulfur and carbon (bicarbonate and carbonate) = 10^{-3} M. All ΔG°_f values from Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters, 3rd ed, Werner Stumm and James J. Morgan, Wiley, 1996.

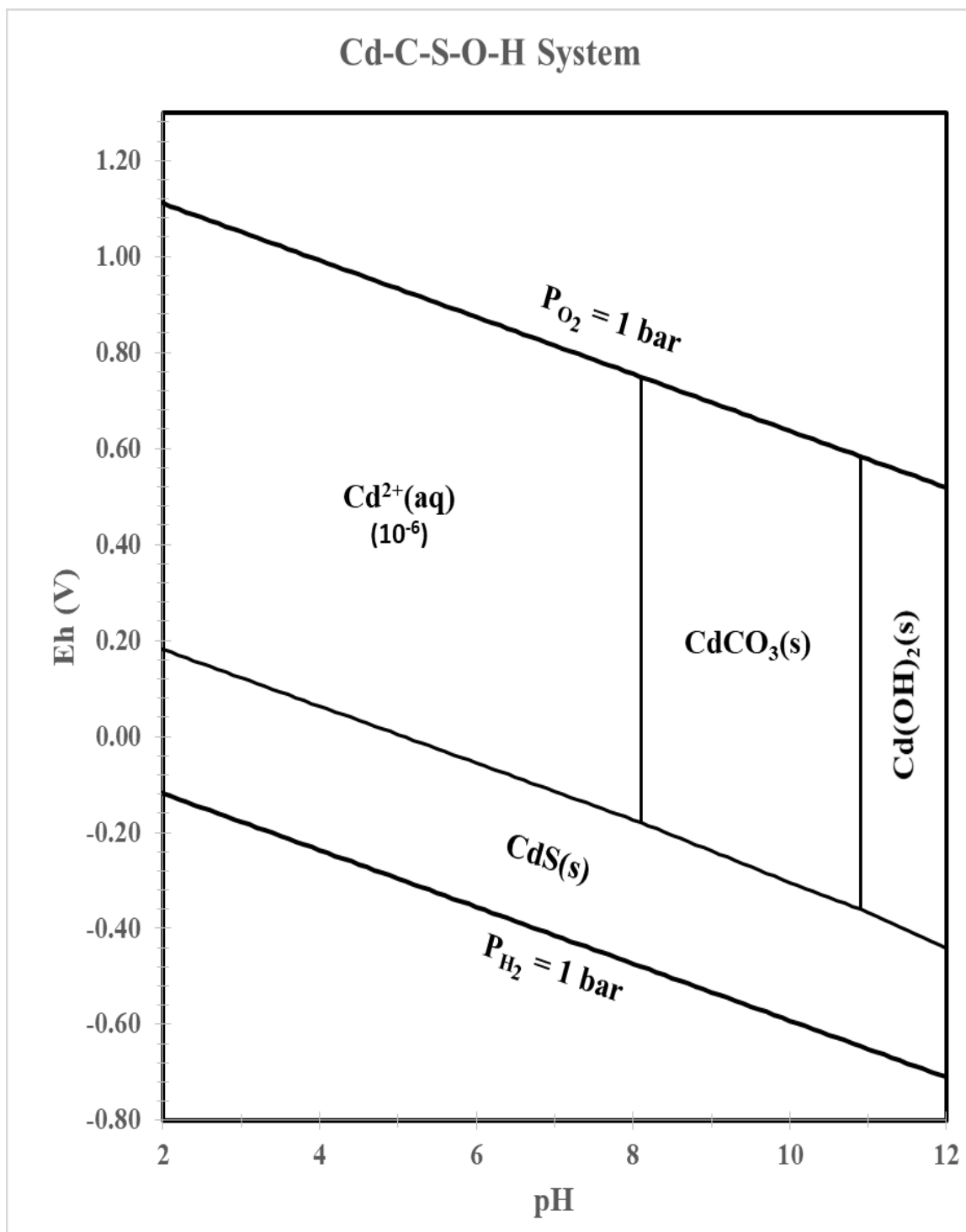


Figure 5. Eh-pH Pourbaix diagram for cadmium calculated from free energy of formation values. Total soluble inorganic sulfur and carbon (bicarbonate and carbonate) = 10^{-3} M; soluble cadmium = 10^{-6} M. ΔG°_f for $CdS(s)$ from Eh-pH Diagrams for Geochemistry, Douglas Brookins. Springer-Verlag, 1988; All other free energies of formation from Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters, 3rd ed, Werner Stumm and James J. Morgan, Wiley, 1996.

formed from the reaction of Zn^{2+} with base) (16). Lead's behavior is somewhat different throughout the pH range relevant to this study. Throughout the near-neutral to moderately basic pH range, $PbCO_3(s)$ is the preferred species. In the more acidic pH range, formation of $PbSO_4(s)$ predominates. Cadmium forms $CdCO_3(s)$ when $pH \geq 8$, but is soluble as $Cd^{2+}(aq)$ at lower pHs. A limitation to Pourbaix diagrams is that they do not incorporate interactions (especially sorption) of the species of interest with other components of complex environmental systems.

According to Carroll et al. (17) the fate of zinc, lead, and cadmium in TSMD waters is most heavily determined by the degassing of CO_2 (carbon dioxide) rich waters, their uptake/release kinetics, iron oxyhydroxide and carbonate competition, and iron catalyzed sulfide dissolution. CO_2 is deterministic in the pH of water, and pH changes control the release and uptake of metals by iron oxyhydroxides and carbonates.

Sediments such as sphalerite, pyrite, and galena are dissolved more quickly in waters with high iron (III) concentration via oxidation reduction reaction. Zinc is preferentially divided into zinc hydroxide or iron oxyhydroxide in sediments. In neutral waters, lead is taken up by carbonates and iron oxyhydroxides and is mostly insoluble. Cadmium has the greatest mobility of the three metals because its sulfide form will more readily dissolve. It is also not taken up by calcite in waters with $pH < 7$. Thermodynamic data is provided in Table 1.

Speciation, Geochemical Fractionation, and Bioavailability

Speciation. The total concentration of metals does not accurately reflect a sediment's toxicity profile. Rather, the forms or species the metals take more accurately

Table 1. Thermodynamic Data for Zinc, Lead, and Cadmium Compounds (17).

| Chemical Equation | log K (25°C) |
|----------------------------------------------------------------------------------------------------------------------------------------|--------------|
| CaCO_3 (calcite) = $\text{Ca}^{2+} + \text{CO}_3^{2-}$ | -8.48 |
| $\text{CaMg}(\text{CO}_3)_2$ (dolomite) = $\text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$ | -18.14 |
| $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) = $\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$ | -4.48 |
| $\text{Cd}^{2+} + \text{H}_2\text{O} = \text{CdOH}^+ + \text{H}^+$ | -10.08 |
| $\text{Cd}^{2+} + 2\text{H}_2\text{O} = \text{Cd}(\text{OH})_2 + 2\text{H}^+$ | -20.34 |
| $\text{Cd}^{2+} + 3\text{H}_2\text{O} = \text{Cd}(\text{OH})_3^- + 3\text{H}^+$ | -33.29 |
| $\text{Cd}^{2+} + 4\text{H}_2\text{O} = \text{Cd}(\text{OH})_4^{2-} + 4\text{H}^+$ | -47.33 |
| $\text{Cd}^{2+} + \text{CO}_3^{2-} = \text{CdCO}_3$ | 3 |
| $\text{Cd}^{2+} + 2\text{CO}_3^{2-} = \text{Cd}(\text{CO}_3)_2^{2-}$ | 6.4 |
| $\text{Cd}^{2+} + \text{CO}_3^{2-} + \text{H}^+ = \text{CdHCO}_3^+$ | 11.83 |
| $\text{Cd}^{2+} + \text{SO}_4^{2-} = \text{CdSO}_4$ | -0.003 |
| $\text{Cd}(\text{OH})_2$ (β) + $2\text{H}^+ = \text{Cd}^{2+} + 2\text{H}_2\text{O}$ | 13.74 |
| CdSO_4 (solid) = $\text{Cd}^{2+} + \text{SO}_4^{2-}$ | -0.11 |
| CdCO_3 (otavite) = $\text{Cd}^{2+} + \text{CO}_3^{2-}$ | -12.1 |
| CdO (monteponite) + $2\text{H}^+ = \text{Cd}^{2+} + \text{H}_2\text{O}$ | 15.1 |
| Fe_2O_3 (hematite) + $6\text{H}^+ = 2\text{Fe}^{3+} + 3\text{H}_2\text{O}$ | 0.11 |
| FeOOH (goethite) + $3\text{H}^+ = \text{Fe}^{3+} + 2\text{H}_2\text{O}$ | 0.53 |
| $\text{Fe}(\text{OH})_3$ (am) + $3\text{H}^+ = \text{Fe}^{3+} + 3\text{H}_2\text{O}$ | 5.66 |
| $\text{Pb}^{2+} + \text{H}_2\text{O} = \text{PbOH}^+ + \text{H}^+$ | -7.7 |
| $\text{Pb}^{2+} + 2\text{H}_2\text{O} = \text{Pb}(\text{OH})_2 + 2\text{H}^+$ | 17.09 |
| $\text{Pb}^{2+} + 3\text{H}_2\text{O} = \text{Pb}(\text{OH})_3^- + 3\text{H}^+$ | -28.09 |
| $\text{Pb}^{2+} + \text{CO}_3^{2-} = \text{PbCO}_3$ | 6.58 |
| $\text{Pb}^{2+} + 2\text{CO}_3^{2-} = \text{Pb}(\text{CO}_3)_2^{2-}$ | 9.4 |
| PbCO_3 (cerussite) = $\text{Pb}^{2+} + \text{CO}_3^{2-}$ | -13.54 |
| $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (hydrocerussite) + $2\text{H}^+ = 2\text{CO}_3^{2-} + 3\text{Pb}^{2+} + 2\text{H}_2\text{O}$ | -18.81 |
| PbSO_4 (anglesite) = $\text{Pb}^{2+} + \text{SO}_4^{2-}$ | -7.85 |
| SiO_2 (quartz) = SiO_2 (aq) | -4 |
| SiO_2 (am) = SiO_2 (aq) | -2.71 |
| $\text{Zn}^{2+} + \text{H}_2\text{O} = \text{ZnOH}^+ + \text{H}^+$ | -8.96 |
| $\text{Zn}^{2+} + 2\text{H}_2\text{O} = \text{Zn}(\text{OH})_2 + 2\text{H}^+$ | -17.33 |
| $\text{Zn}^{2+} + 3\text{H}_2\text{O} = \text{Zn}(\text{OH})_3^- + 3\text{H}^+$ | -28.83 |
| $\text{Zn}^{2+} + 4\text{H}_2\text{O} = \text{Zn}(\text{OH})_4^{2-} + 4\text{H}^+$ | -41.61 |
| $\text{Zn}^{2+} + \text{CO}_3^{2-} + \text{H}^+ = \text{ZnHCO}_3^+$ | 11.75 |
| $\text{Zn}^{2+} + \text{CO}_3^{2-} = \text{ZnCO}_3$ | 3.9 |
| $\text{Zn}^{2+} + \text{SO}_4^{2-} = \text{ZnSO}_4$ | -2.31 |
| $\text{Zn}(\text{OH})_2$ (β) + $2\text{H}^+ = \text{Zn}^{2+} + 2\text{H}_2\text{O}$ | 11.93 |
| $\text{Zn}(\text{OH})_2$ (ϵ) + $2\text{H}^+ = \text{Zn}^{2+} + 2\text{H}_2\text{O}$ | 11.66 |

Table 1 continued on next page.

Table 1 continued.

| | |
|---------------------------------------------------------------------------------------------------------------------------------------------|-------|
| $\text{Zn(OH)}_2 (\gamma) + 2\text{H}^+ = \text{Zn}^{2+} + 2\text{H}_2\text{O}$ | 11.88 |
| $\text{ZnSO}_4 (\text{solid}) = \text{Zn}^{2+} + \text{SO}_4^{2-}$ | 3.55 |
| $\text{ZnCO}_3 (\text{smithsonite}) = \text{Zn}^{2+} + \text{CO}_3^{2-}$ | -9.87 |
| $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2 (\text{hydrozincite}) + 6\text{H}^+ = 5 \text{Zn}^{2+} + 2 \text{CO}_3^{2-} + 6\text{H}_2\text{O}$ | 9.65 |

characterizes the toxic potential. “Speciation” is a relatively vague term in chemistry without a single set definition. Instead, it has a variety of definitions, which often leads to its misunderstanding. The same can be said for two other terms: bioavailability and geochemical fractionation. For purposes here, the definition used by the EPA in their Framework for Metal Risk Assessment should suffice, “The distribution of a given constituent among its possible chemical forms, including metal complexes, which have differing tendencies to be adsorbed or desorbed” (7). While all three terms differ from one another, they are closely related and the boundaries between them are not always clear.

The primary source of metal introduction is an important consideration in speciation. Was the metal deposited by natural processes, industrial activities, aerially, leaching from wastes, etc.? Without anthropogenic contamination, metal species are determined by elemental composition of rocks. The toxicity profile of a metal is directly linked to its environmental parameters. Frequently, contamination with heavy metals comes with co-contamination of other metals or chemicals that may alter the sediment environment and contribute to the toxicity profile. With acid mine drainage, pH of the environment is lower which increases the mobility of many heavy metals that might otherwise be locked up in solid phases. (18).

When metals enter sediments, there are a variety of dynamic pathways on which they can proceed. Pathways are not necessarily exclusive; they can overlap. There are three main categories of metals that can be found in soils: “in soil solutions, sorbed onto solid phases, (or) as part of the structure of solid phases” (18). With a soil solution, metals may be present as free ions or complexed ligands, which can be either organic or inorganic. These mobile metals forms could be uptaken by plants or organic matter or adsorbed onto mineral surfaces. Or, they may transport through the vadose zone, diffuse into porous material, or precipitate (18). These phases are also variable and in dynamic equilibrium with one another. A detailed description of a species should include the contaminant’s identity, its oxidation state, associations and complexes with solids, and its molecular geometry and coordination environment (18).

Regulations that are imposed on heavy metals by organizations such as the EPA, the Occupational Safety and Health Administration (OSHA), the Center for Disease Control and Prevention (CDC), etc. are based on the total concentration of a metal in the environment. The EPA provides official methods for determining metal species. Method 1632 provides a procedure to determine dissolved inorganic arsenic, total dissolved arsenic, and total arsenic (19). However, the only official regulations for arsenic are for total arsenic concentration. Beyond total concentration, speciation is a vital factor in accessing a substances toxicity and effects in general. Different forms (or species) of metals have highly different toxicity profiles. For instance, lead sulfide (PbS), or galena, is virtually innocuous, but tetraethyl lead, the once popular anti-knocking agent in gasoline, is a central nervous system toxin that can produce acute toxic psychosis (20).

Bioavailability. The species or form of a metal is directly correlated with its bioavailability. While there are also various definitions of bioavailability, here it may be considered the ability of a metal (or elemental species) to be taken in by an organism and affect its life cycle. Bioavailability is a term that can be used to describe both toxins and essential nutrients, both harmful and beneficial/necessary substances. It is important to note that the ability of a substance to affect an organism's life cycle is an important requirement for bioavailability. A metal that gets taken into an organism and passes through without affecting it in any significant way is not considered to be bioavailable. There are fungi and bacteria that have mechanisms to tolerate high metal concentrations by binding metals with proteins to form insoluble metal sulfides thereby decreasing metal uptake (18).

Measuring metal speciation directly/in situ is a complicated process. Often, natural environments are mimicked in a laboratory in order to attempt to create a simulation of the environment. As metal species are in constant flux, measuring environmental metal concentrations will only give a snapshot of metal species at a specific time. Environments are dynamic and species are continuously changing with environmental influences (18).

Sorption processes are one of the biggest players in determining a metal's bioavailability. Sorption can be broadly thought of as any process that removes a metal (ion) from solution. Such processes include absorption, adsorption, diffusion into a solid, and precipitation. The reverse process is called desorption, when metals are dissolved into solution (18).

Geochemical fractionation. This term represents any of numerous operationally defined methodologies intended to determine the chemical state of elements of interest within a sample. Methods process samples using various extractants that are intended to selectively dissolve a particular mineral component or phase, thereby solubilizing any contaminants associated with the phase. The Tessier method, described in the following section, is one of the more common fractionation methods.

Previous Aurora Research

There has been extensive research on the TSMD and the after effects of mining. This research is part of a larger collaborative project to characterize the contaminant profile of Aurora, MO. Dylan Jones, a chemistry undergraduate student, and Misty Strickland, a Geology, Geography, and Planning undergraduate, had begun the project of examining fractional exchangeability of metals in mine tailings of Aurora waterways. This was done under the direction of Dr. Gutiérrez, a geology professor at Missouri State University. The research group analyzed stream sediments (previously collected by Dr. Gutierrez) along Chat Creek, as well as other creeks and streams upstream and downstream of Chat Creek. Streams all around the town were sampled to develop a good characterization of the area. Samples were collected from a total of 74 areas. Samples were processed in a similar manner to this current research as described in the “sample preparation” section; sediments were dried and sifted through a 1 mm sieve. Sediments were digested in two different geochemical fractions, which simulated an acidic environment and a reducing environment (21).

This thesis developed out of this aforementioned research. The intention was to better characterize the sediments which showed high metal content. This thesis analyzes four fractions of metals in sediments and looks for evidence of contamination in plant and water samples as well. The geochemical fractionation and bioavailability of metals is analyzed and provides a way to assess the current contamination level of several creeks in Aurora, MO. The previous research had accounted for only ~48 percent of the total metals in sediments (21). There were also issues measuring cadmium, which is found in much lower quantities than zinc or lead. Detection limits on instruments used were not sufficient to account for cadmium.

METHODS

Chemicals

Metals standards: Separate Ricca stock standards of 10,000 ppm in 5% nitric acid were used for each zinc, lead, and cadmium. Sigma-Aldrich standard 1,000 ppm scandium in 5% nitric acid was used.

Other chemicals: The following chemicals were from Fisher Chemical: concentrated nitric acid; glacial acetic acid (HPLC grade); ammonium acetate (HPLC grade); washed sand. The following were Sigma-Aldrich brand: hydrogen peroxide solution (35% by weight in water); anhydrous sodium acetate ($\geq 99.0\%$ purity); hydroxyl amine hydrochloride ($\geq 96.0\%$ purity).

Water: Water from a Thermo Scientific Barnstead E-Pure water purification system (18 M Ω -cm) was used for all dilutions and solution preparations.

Instrumentation

ICP-AES. The basis of inductively coupled plasma-atomic emission spectrometry (ICP-AES) involves the nebulization of a sample which is then transported to a plasma torch that causes atomization and excitation of the sample. When relaxation occurs, an intensity of light is emitted and is measured optically at wavelengths that are specific to the element of interest. This measurement is compared to a standard which enables the determination of amount of analyte present in the sample (22). ICP-AES has detection limits ranging between 100 to 0.1 ppb depending on the element (23). Specific to the

elements of interest, ICP-AES ideally has a detection limit around 0.1 ppb for cadmium, 1 ppb for lead, and 0.2 ppb zinc (23), though actual detection limits are often higher.

The primary instrument used for this work was a Varian Liberty 150 AX Turbo ICP-AES at Missouri State University (MSU). This instrument was ~20 years old and was run with a DOS software program. The program was initially set up to analyze zinc, lead, and cadmium relative to an internal standard, scandium. The greatest intensity wavelengths were chosen for lead (220.353 nm), cadmium (228.802 nm), and scandium (361.384). The second most sensitive wavelength was chosen for zinc, 334.502 nm, since it had much higher concentrations in the samples. The instrument ran three sequential scans and reported an average concentration, which was used as the sample measurement.

ICP-MS. Inductively coupled plasma – mass spectrometry is an instrumental method related to ICP-AES. Like ICP-AES, ICP-MS (in the format employed here) uses a plasma torch to atomize a nebulized sample. At the high temperatures of the plasma, a significant amount of sample atoms are ionized, and these ions are directed through an interface into a mass spectrometer. Elements are identified and quantified by the mass to charge ratios of the ions and their abundances relative to standards. ICP-MS generally has significantly lower detection limits than ICP-AES.

Due to the low cadmium content, it was necessary to use an instrument with lower detection limits than MSU's ICP-AES. Missouri State had recently acquired a graphite furnace atomic absorption spectrophotometer (GFAA). GFAA's have detection limits for cadmium down to 2 ppt, or 50 times lower than ICP-AES's (23). However, the GFAA never became operational during the course of this research. So, arrangements were made with connections at the local Blackman Water Treatment facility (operated by City

Utilities of Springfield, MO) to use their ICP-MS. The instrument was a Thermo Scientific iCAP-Q. The staff at Blackman helped to set up a method to run samples for zinc, lead, and cadmium. Samples and standards were prepared at MSU and brought to Blackman, where they were put in autosampler tubes. The method was able to run on its own after initial setup.

AAS. Atomic absorption spectrophotometry (AAS) is a commonly-used method for measuring element (mainly metal) concentrations. In its most commonly used form, the sample solution is aspirated and nebulized, where the sample is mixed with a fuel-oxidant combination (most commonly acetylene-air) and burned in a “slot burner” where samples are atomized. Measurements are based on the absorbance of light at a specific wavelength characteristic of the element of interest. Light sources are normally hollow cathode lamps, which are designed to produce atomic emission from a target composed on the specified element. AAS measurements are generally somewhat less sensitive than ICP-AES or ICP-MS methods.

Extract 4, the organic matter-bound fraction, was largely composed of hydrogen peroxide and nitric acid. The ICP-AES repeatedly gave inconsistent readings. It was believed that the issue related to nebulization of the solution, but the exact cause of this issue was never fully isolated. Since the metal concentrations in this fraction were rather high, they were able to be run on the AAS. The AAS used was a Varian SpectrAA 220FS. The wavelengths used on this instrument were 213.9 for zinc, 217.0 for lead, and 228.8 for cadmium.

Field Sampling and Sample Preparation

The sampling sites from which sediment samples were taken were located throughout Aurora, MO. Many samples were taken along Chat Creek which runs directly through the town. Samples were taken close to known chat piles and both upstream and downstream in attempt to examine mobility of the metals. Samples were also taken from smaller side streams in and around Aurora. Much of the sampling was performed by previous researchers who had performed preliminary analysis on sediment samples. Sediment samples were collected from 74 different locations in this previous of the research. Samples were sifted through 1 mm mesh, and a portion of each sample was sent to an outside laboratory, ALS Minerals, for 35 metal analysis by aqua regia digestion.

This researcher sampled the area again to gain additional sediment samples, but mainly to focus on the collection of plant samples in order to create a better picture of metal bioavailability. Several water samples were also collected at this time. A total of 15 plant samples, 8 water samples, and 3 sediment samples were collected from areas along Chat Creek and side streams. Sites were marked with GPS coordinates which were added to the previously constructed map of sampling sites (Figure 6). Sediment samples were dug shallowly from areas along creek beds with a stainless-steel trowel to avoid metal contamination. Both aquatic (fully underwater) and terrestrial (along the creek sides) were collected. Plants were either pulled or snipped with garden snips. Water samples were collected by submerging 500 mL sample bottles into the surface of the water. Sediment and plant samples were added to quart-sized Ziploc bags. After collection was complete samples were transported back to the lab. Each site appeared to have somewhat

distinct vegetation (and some sites had no visible aquatic plants that were readily accessible), so it was not possible to collect the same types of plants at each site.

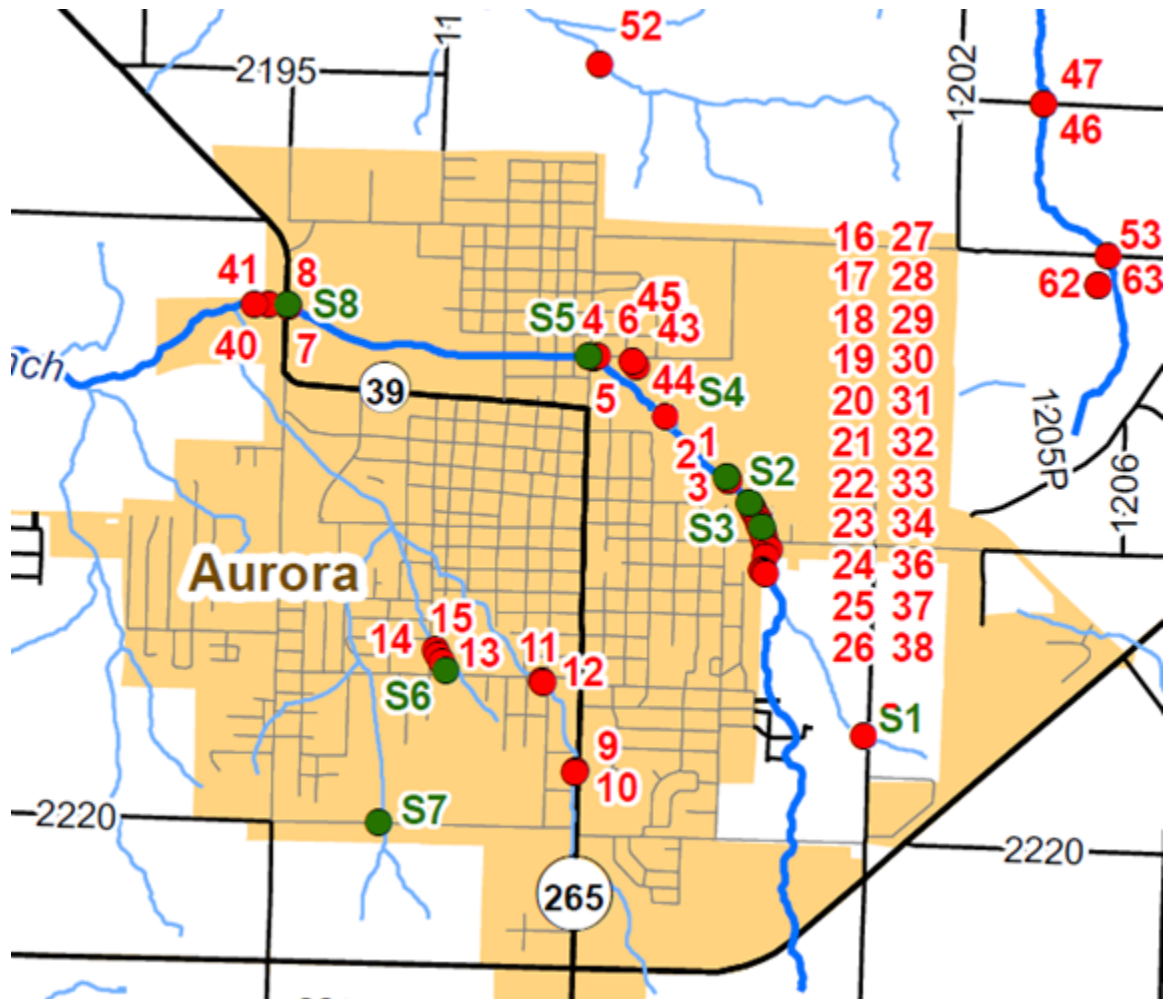


Figure 6. Map of Aurora, MO and surrounding area with sampling sites denoted by dots.

Upon return to the laboratory, water samples were acidified with 2 mL of concentrated nitric acid (per ~500 mL sample) and placed in the refrigerator to await analysis. Samples were analyzed by ICP-AES.

Plant samples were washed thoroughly with tap water until water was no longer brown. The point was to remove as much sediment from the plant samples as possible.

This was followed by several rinses with deionized water. Aquatic plant samples required much more rinsing to remove sediments than other types. It was difficult to remove sediment from the roots of plants. Samples were then transferred to evaporating dishes or beakers and dried in an oven at $\sim 75^{\circ}\text{C}$ for ~ 3 days. Slight charring was observed on some of the samples upon removal from the oven. Dried plant samples were ground in a coffee grinder until a fine material was achieved. Samples were stored in plastic sandwich bags to await ashing via muffle furnace.

One-gram dried ground plant samples were weighed into 15 mL nickel crucibles and 2 mL 50% (w/v) magnesium nitrate solution was added to each sample. Samples were placed in an oven at 120°C for 1 hour to evaporate off water. Samples were then placed into a programmable muffle furnace. Samples were brought to 200°C and held there for 3 hours. The furnace temp then increased to 400°C and held for an additional 3 hours. Finally, the oven temperature was increased to 550°C where it was held for 18 hours, after which the furnace decreased to room temperature and samples were allowed to cool before they were removed. Upon cooling to room temperature, samples were transferred to Falcon centrifuge tubes (15 mL) and filled to the 10 mL mark with 50% (v/v) nitric acid. Samples were sonicated until dissolution of dry ash residue was achieved. Samples were then centrifuged to compact any undissolved ash components, then analyzed by ICP-AES.

Sediment samples were frozen upon return to the lab until they could be dried. Three days after freezing sediment samples were transferred into beakers and placed in an oven at 60°C for about 2 days. After cooling, sediments were passed through a 1 mm

sieve to achieve appropriate size and placed in plastic bags until they could be digested via sequential extraction procedure with the other previously collected sediments.

Total metal analysis was performed by ALS Minerals, an outside commercial laboratory. ALS Minerals determined total metal content in the sediment for 35 metals by aqua regia digestion and ICP-AES analysis.

Standards

Standards were made in order to calibrate the instrument. Standards were made in the same matrix as the samples, however they were not digested under identical conditions. A set of standards was prepared for each individual extract with matrix matching. Four standards and a blank were prepared for each extract. Standard A contained 200 ppm of zinc and lead and 10 ppm cadmium. Standard B contained 20 ppm of zinc and lead and 1 ppm cadmium. Standard C contained 2 ppm of zinc and lead and 0.1 ppm cadmium. Standard D contained 0.2 ppm zinc and lead and 0.01 ppm cadmium. Each standard was spiked with scandium to give a concentration of 5 ppm scandium. Only standards A and B were used in the calibration of zinc because the lower standards were throwing off the calibration curve. For the same reasons, only standards B and C were used in the calibration of lead, and only B, C, and D were used for cadmium.

Quality Control

To assure quality control, several measures were taken throughout this research: blank checks, laboratory control checks (LCC), laboratory duplicates (LD), field duplicates (FD), matrix spikes (MS), and method blank (sand) checks.

Blanks checks were prepared by in the same matrix as each of the extracts. Blanks were not added to any sediments, nor were they exposed to any metals. Therefore, they should ideally show concentrations of zero for zinc, lead, and cadmium and serve as a background reference to samples

Laboratory control checks were prepared for each extraction step using the same matrix as samples. The LCCs were prepared to be equivalent to 20 ppm zinc, 20 ppm lead, and 1 ppm cadmium. The purpose of the LCC was to have a known concentration in a sample to measure in order to confirm the accuracy and precision of the analysis.

Laboratory duplicates were made by taking two samples from the same sediment sample. These two samples are then digested separately and treated as independent samples. The agreeability of these can help to measure precision of the digestion process and analysis.

Field duplicates were made by taking two separate samples from the same field site. This also provided a degree of measuring precision, but due to the heterogeneity of sediments it was expected that field duplicates would have much less agreement than lab duplicates.

To prepare matrix spikes, laboratory duplicates were made from select samples, and the duplicates were spiked with a known concentration of metals (50 ppm zinc, 50 ppm lead, and 10 ppm cadmium). These samples were subjected to the same digestion procedures and analysis. Upon analysis, the MS should ideally show a higher metal concentration than its counterpart by the amount of the spike.

Method blanks prepared from sand served a purpose similar to that of the blank checks. Laboratory grade sand should contain no zinc, lead, or cadmium. Three sand

samples were prepared and treated in the same manner as the sediment samples. It was expected that these sand samples should show no metal content upon analysis. This can help serve as a background sample and aid in the identification of any contamination that may occur during digestion.

EPA Methods

There are a variety of methods that are used to analyze metal content in a sample. Methods can be qualitative to test for any presence of a metal, quantitative to test for specific concentration of a metal, or semi-quantitative methods that give an estimate of metal concentration. With the passage of the Clean Water Act in (CWA) 1972 the EPA approved specific test methods that can be used for metal analysis (24). The CWA was an amendment to the Federal Water Pollution Control Act of 1948, the first major United States law that addressed water pollution. EPA approved chemical test methods are subdivided into categories for determination of inorganic nonmetals, organics, and metals. Determination of metals in environmental samples can be found in the 200 series methods (24). In 1992, the EPA published 13 different analytical laboratory methods for metals in *Methods for the Determination of Metals in Environmental Samples* (25). These analyses use different instruments including inductively coupled plasma atomic emission spectroscopy (ICP-AES), ICP-mass spectrometry (MS), atomic absorption spectroscopy (AAS), graphite furnace AAS, ion chromatography (IC), and high performance liquid chromatography (HPLC).

Sequential Extraction Procedure

The Tessier method was selected as a model for this extraction procedure. The Tessier method is a sequential extraction procedure designed to characterize the metal concentration in different geochemical fractions. Tessier separates five different geochemical fractions:

- 1) easily exchangeable, extracted with 1 M $\text{NaC}_2\text{H}_3\text{O}_2$ or 1 M MgCl_2
- 2) bound to carbonates, extracted with 1 M $\text{NaC}_2\text{H}_3\text{O}_2/\text{HC}_2\text{H}_3\text{O}_2$ pH = 5
- 3) bound to Fe-Mn Oxide, extracted with 0.3 M $\text{Na}_2\text{S}_2\text{O}_4$ + 0.175 M Na-citrate + 0.025 M H-citrate + heat (96°C) or 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) $\text{HC}_2\text{H}_3\text{O}_2$ + heat (96°C)
- 4) bound to organic matter, extracted with 0.02 M HNO_3 + 30% H_2O_2 pH = 2 with HNO_3 + heat (85°C) + 3.2 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ in 20% (v/v) HNO_3
- 5) residual, extracted with HF- HClO_4 mixture (26)

Several other sequential extraction procedures were examined that closely resembled Tessier. A method by Favas et al. (27) describes six different fractions, which are only slightly modified from the Tessier method. For the exchangeable fraction, Favas uses ammonium acetate instead of sodium acetate. The bound to Fe-Mn oxides fraction is divided into two: easily reducible and moderately reducible; the latter uses 0.1 M ammonium oxalate at pH=3. The other fractions are essentially the same, using hydrogen peroxide, nitric acid, and ammonium acetate for what Favas calls the “sulfidic/organic” fraction and a mixture of hydrofluoric, perchloric, and nitric acids for the residual (27). Several other authors, including Krupadam et al. (28), Cappuyns et al. (29), and Rodrigues et al. (30) detail methods that are similar/slightly altered forms of the Tessier method.

In this research the residual fraction was not extracted. Instead, it was approximated by finding the difference between the total metal aqua regia digestion performed by ALS Minerals and the four other fractions.

Samples were digested in Fisherbrand sterile, disposable, 50 mL, polypropylene centrifuge tubes. Approximately 2 g of each sediment was weighed out (actual mass recorded) and placed in appropriately labeled centrifuged tubes. Samples were then digested sequentially in the aforementioned media (details provided below). After the extraction of each of these fractions, samples were centrifuged for 30 minutes, decanted, and filtered through Fisherbrand G4 glass fiber filters. Samples were then analyzed by ICP-AES, AAS, or ICP-MS.

Internal Standard. Originally, it was thought best to measure metal concentrations against an internal standard. To select an appropriate metal to use as an internal standard, the results from previous total metal analysis were examined. It was found that scandium was in very low concentrations in every sample. The average concentration of scandium in dried sediments was 1.77 ppm. Since there would be no significant interference from metal concentrations this low in sediments, scandium was selected as the internal standard. Extract one was made in accordance to the aforementioned procedure. Twenty-mL of 1000 ppm scandium standard was added to 1 L of extract one solution, giving the solution a concentration of 20 ppm scandium. Since the first extract was 1M sodium acetate it was known from previous tests that it would have to be diluted fourfold in order for it to give an accurate and precise reading on ICP-AES. The amount added would result in a desired concentration of 5 ppm scandium in each of the samples. The ICP-AES was set up with an internal standard program with scandium

as the selected element for the metals concentration to be measured against. After completion of the first extraction, samples were measured on ICP-AES. Metal concentration readings for zinc, lead, and cadmium were unexpectedly high by orders of magnitude. Intensity of the peaks for scandium were significantly lower than they had been in initial testing. In order to determine the root of this cause, a series of sediment samples was prepared. The amount of time the sediment samples spent in the extractant was varied and scandium concentrations were then measured. Results showed that as the amount of time that sediments spent in the extract with the internal standard increased, the intensity of the scandium peak decreased on ICP-AES. This showed that scandium was likely binding to the sediments in the sample or precipitating out of solution. Therefore, accurate and precise concentrations of internal standards could not be recovered. This gave inaccurately high readings of the other metals: zinc, lead, and cadmium. At this point, it was decided that the internal standard method should be discarded and metal concentrations would be measured directly. While this was not ideal, accurate measures of metal concentrations could still be determined by a direct measurement method.

Extractable Fractions. Four fractions of metals (described earlier) were extracted from the sediments. These fractions may also be referred to as extracts in this thesis. The first fraction was digested by adding 16 mL of 1 M sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$) to each sample. Samples were vortexed then continuously agitated for 1 hour at room temperature. After decanting, each sample was preserved with 2 mL of concentrated nitric acid and stored in the refrigerator before analysis. Because of the high salt (sodium acetate) content, initial sample readings on the ICP-AES were unstable.

Samples were diluted 4-fold with deionized water (10 mL sample and 30 mL of water), which solved this issue. The high sodium acetate also made the torch dirty very quickly. The torch had to be disassembled and cleaned by soaking in aqua regia several times. Without cleaning, concentrations were much more erratic, and the torch would frequently go out. The high salt content may have also been interfering with effective nebulization.

Upon optimization of the measurement of extract 1, it was discovered that it had rather low concentrations of lead and especially cadmium and could not be confidently measured on AES. These, and a few samples from extract 2 and 3 with low metal concentrations, were run on ICP-MS. The ICP-MS that was used was located at Blackman Water Treatment Plant (City Utilities of Springfield) that is responsible for providing clean drinking water to a large portion of the population of Springfield, MO. These low concentration samples were further diluted to 10:1 from the original volume of the extracts to get within range of the ICP-MS and to minimize interference from high salt content. Since both samples and standards were diluted by the same factor, the concentrations measured by the instrument were still actual concentration and not diluted ones. This exempted the need for an extra dilution calculation. The staff at Blackman aided in setting up the instrument method. An autosampler was used, so after the method was set up and samples were poured into autosampler tubes, the program ran itself. Results were automatically compiled into an excel file, which were email to this researcher.

The second fraction obtained metals that were bound to carbonates, using an extractant consisting of 1 M acetic acid/sodium acetate adjusted to pH 5 with glacial acetic acid. To the sediment residues of the first extraction step, 16 mL of extractant was

added. Samples were vortexed and agitated continuously for 2 hours at room temperature. Samples were diluted 2-fold before metal concentrations were measured on ICP-AES.

The third fraction, bound to Fe-Mn oxides, was extracted with a reducing agent solution that was 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ (hydroxylamine hydrochloride) in 25% (v/v) $\text{HC}_2\text{H}_3\text{O}_2$. Forty milliliters of this extractant was added to the residues from the second fraction. Samples were shaken and vortexed then added to hot water bath ($\sim 96^\circ\text{C}$). Samples were kept in the bath for 6 hours with occasional agitation via vortexing. Samples were then centrifuged then decanted. Decantation of each sample yielded about 40 mL solution, to which 1 mL of nitric acid was added to deter precipitation or molding. Samples were filtered through Fisherbrand G4 glass fiber filters after digestion and decantation to avoid clogging of the ICP-AES nebulizer. All standards and samples in extract 3 were diluted 2-fold with deionized water. Since standards were diluted as well, concentration readings were autocorrected on the instrument and did not require dilution calculations.

The fourth fraction was digested in an oxidizing agent. To the residues of the third fraction were added 6 mL of 0.02 M nitric acid and 10 mL of 30% H_2O_2 (hydrogen peroxide) adjusted to $\text{pH} = 2$ with concentrated nitric acid. Samples were vortexed, shaken then added to a hot water bath (85°C), and heated for 2 hours with occasional vortexing. After 2 hours, another 6 mL portion of 30% H_2O_2 ($\text{pH} = 2$ with nitric acid) was added to each sample. Samples were heated for 3 additional hours with occasional vortexing. After cooling, 10 mL of 3.2 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ (ammonium acetate) in 20% (v/v) nitric acid was added to each sample, and samples were diluted to 40 mL. Then, samples

were continuously agitated for 30 minutes. When this fraction was run on ICP-AES, the concentration reading (measured intensity) of the laboratory control checks and samples would dramatically decrease (up to 75 percent) over a short period of time, apparently due to nebulization issues. It was theorized that the high concentration of hydrogen peroxide was likely interfering with nebulization. So, samples from this fraction were analyzed by AAS, which gave consistent intensities and concentrations. This was possible because concentrations were rather high in extract 4, so the lower detection limits of ICP-AES were not necessary. Two different sets of standards were made up, one for zinc and one for lead and cadmium to account for differences in concentrations in samples. Two benefits of using the AAS as opposed to the AES, is that AAS had an autosampler and a sample introduction pump system (SIPS) which made auto-dilutions of samples when necessary.

RESULTS AND DISCUSSION

Quality Control

Any evaluation of data for samples must be carried out with recognition of the limitations to the analytical methodologies employed. The following quality control measures were taken to evaluate the reliability of analysis.

Laboratory Control Checks. The laboratory control checks (LCCs) showed close agreement with the theoretical values. The percent error/difference of the LCC serves as a guide to give a measure of the accuracy of the measurement of samples. Percent error is calculated by the following equation:

$$\% \text{ Error} = \frac{|\text{expected} - \text{observed}|}{\text{expected}} \times 100 \%$$

where expected is the actual value of the LCC that was expected, and observed is the actual value given by the instrument.

The coefficient of variation (CV) was also calculated for the LCC, which serves as a measure of precision. CV is calculated by the following equation:

$$CV = \frac{\sigma}{\mu}$$

where σ is the standard deviation of the LCC and μ is the average of the LCC.

The average percent error of the LCC for the four fractions was between 5 and 6 percent for all 3 metals. Environmental LCC may be considered accurate if their percent error is less than 15-25 percent. Table 2 shows the average percent errors in LCC values for each fraction.

Table 2. Average Percent Error in LCC Values.

| Fraction | Zn | Pb | Cd |
|----------|------|-----|-----|
| 1 | 4.7 | 7.4 | 3.5 |
| 2 | 7.1 | 6.3 | 2.5 |
| 3 | 1.5 | 1.6 | 5.5 |
| 4 | 10.4 | 5.1 | 8.6 |
| Average | 5.9 | 5.1 | 5.0 |

Blanks and Detection Limits. The detection limits were calculated from the blanks by the following equation:

$$D.L. = 3 \times \sigma$$

where σ is the standard deviation of the blanks. The blank averages and detection limits are summarized in Table 3 from Fractions 2 through 4. Fraction 1 was analyzed by ICP-MS, which did not run blank checks in the same manner.

Duplicates. Both lab and field duplicates were run in this analysis. Duplicates can be found in Table 4. The percent difference between the duplicates had some variation. Most of the samples were fairly consistent. The larger percent differences come from samples with very low metal concentrations approaching the detection limits, where

consistent measurements are not expected. In these cases, a few ppb could change percent error by 100 percent.

Table 3. Averages for Blanks and Detection Limits ([M] (mg/L)). Table includes each metal from fractions 2-4. D.L. = detection limit, Std Dev = standard deviation.

| | Fraction 2 | Fraction 3 | Fraction 4 |
|------------|------------|------------|------------|
| Zn Average | 0.1389 | 0.3050 | -0.014 |
| Zn Std Dev | 0.4078 | 0.1137 | 0.025 |
| Zn D.L. | 1.2233 | 0.3411 | 0.074 |
| Pb Average | 0.0011 | 0.0323 | 0.052 |
| Pb Std Dev | 0.0398 | 0.0083 | 0.082 |
| Pb D.L. | 0.1194 | 0.0249 | 0.246 |
| Cd Average | -0.0010 | 0.0021 | -0.009 |
| Cd Std Dev | 0.0010 | 0.0010 | 0.010 |
| Cd D.L. | 0.0029 | 0.0031 | 0.030 |

Matrix Spikes. Analysis of matrix spikes can be found in Table 4. Percent recovery is calculated by the following equation:

$$\% R = \frac{\text{observed value} - \text{background value}}{\text{actual value}} \times 100\%$$

where the observed value is the measured value of the MS measured by the instrument, the background value is the value of the unspiked sample, and the actual value is the value of the MS added by which the sample concentration should have increase. Ideally, percent recovery would be 100 percent.

Table 4. Reproducibility of Lab Duplicates. ND = not detected.

| Sample | Fraction 1 | | | Fraction 2 | | | Fraction 3 | | | Fraction 4 | | |
|-----------|------------|------|-----|------------|-------|------|------------|-------|------|------------|-------|-------|
| | Zn | Pb | Cd | Zn | Pb | Cd | Zn | Pb | Cd | Zn | Pb | Cd |
| 4 | 32.5 | 1.3 | 0.2 | 698.1 | 199.5 | 1.6 | 248.4 | 164.0 | 0.8 | ND | 19.4 | 2.7 |
| 4-LD | 33.6 | 1.3 | 0.2 | 634.7 | 177.4 | 1.8 | 224.7 | 172.5 | 0.9 | ND | 19.8 | 2.6 |
| [Average] | 33.1 | 1.3 | 0.2 | 666.4 | 188.5 | 1.7 | 236.6 | 168.3 | 0.8 | ND | 19.6 | 2.6 |
| % diff. | 3.4 | 5.2 | 3.5 | 9.5 | 11.7 | 8.0 | 10.0 | 5.1 | 6.9 | ND | 2.3 | 3.5 |
| 10 | 4.1 | ND | ND | 15.2 | 0.6 | 0.1 | 12.1 | 1.1 | ND | 3.1 | 0.5 | ND |
| 10-LD | 2.8 | ND | ND | 15.3 | 0.5 | 0.1 | 12.8 | 1.1 | ND | 6.0 | 0.7 | ND |
| [Average] | 1.8 | ND | ND | 13.1 | 0.9 | 0.1 | 11.8 | 0.9 | ND | 4.6 | 0.6 | ND |
| % diff. | 23.8 | ND | ND | 19.8 | 2.7 | 5.3 | 3.1 | 2.2 | ND | 63.1 | 45.4 | ND |
| 13 | 2.1 | 0.1 | ND | 11.8 | 0.9 | 0.1 | 11.6 | 0.9 | ND | 8.2 | 0.3 | ND |
| 13-LD | 1.6 | ND | ND | 14.4 | 0.9 | 0.1 | 12.0 | 0.9 | ND | 7.9 | 0.3 | ND |
| [Average] | 3.4 | ND | ND | 15.3 | 0.5 | 0.1 | 12.4 | 1.1 | ND | 8.0 | 0.3 | ND |
| % diff. | 38.9 | ND | ND | 0.4 | 17.4 | 10.2 | 5.8 | 4.3 | ND | 3.6 | 6.5 | ND |
| 27 | 15.8 | ND | ND | 85.2 | 0.4 | ND | 126.3 | 1.0 | 0.4 | 126.3 | 1.0 | 0.4 |
| 27-LD | 14.7 | ND | ND | 88.2 | 0.4 | ND | 133.5 | 1.0 | 0.5 | 108.3 | 0.7 | 4.4 |
| [Average] | 15.3 | ND | ND | 86.7 | 0.4 | ND | 129.9 | 1.0 | 0.5 | 117.3 | 0.9 | 2.4 |
| % diff. | 6.8 | ND | ND | 3.4 | 0.4 | ND | 5.5 | 8.7 | 10.1 | 15.4 | 43.8 | 164.3 |
| 38 | 39.7 | 1.8 | 4.5 | 433.2 | 18.2 | 5.4 | 134.4 | 9.4 | 0.4 | 134.4 | 9.4 | 0.4 |
| 38-LD | 38.6 | 1.6 | 4.2 | 437.7 | 18.5 | 5.3 | 158.2 | 11.7 | 0.5 | 79.0 | 0.5 | 0.2 |
| [Average] | 39.2 | 1.7 | 4.4 | 435.5 | 18.3 | 5.4 | 146.3 | 10.6 | 0.4 | 106.7 | 4.9 | 0.3 |
| % diff. | 2.8 | 11.6 | 9.0 | 1.0 | 2.0 | 0.8 | 16.3 | 21.9 | 23.8 | 51.9 | 181.7 | 83.3 |
| 17 | 3.9 | ND | ND | 45.7 | 1.1 | ND | 134.5 | 2.4 | 0.4 | 134.5 | 2.4 | 0.4 |
| 17-FD | 5.6 | ND | ND | 39.0 | 1.6 | ND | 140.9 | 2.3 | 0.3 | 72.2 | 1.2 | 1.4 |
| Average | 4.7 | ND | ND | 42.3 | 1.4 | ND | 137.7 | 2.3 | 0.4 | 103.4 | 1.8 | 0.9 |
| % diff. | 37.3 | ND | ND | 15.6 | 30.6 | ND | 4.6 | 5.4 | 31.0 | 60.2 | 67.3 | 106.9 |
| S1 | 2.1 | ND | ND | 0.3 | 0.1 | ND | 24.2 | 0.6 | ND | 0.2 | 0.2 | ND |
| S1-FD | 1.5 | ND | ND | 8.4 | 0.1 | ND | 3.7 | 0.4 | ND | 0.2 | 0.2 | ND |
| Average | 1.8 | ND | ND | 4.4 | 0.1 | ND | 14.0 | 0.5 | ND | 0.2 | 0.2 | ND |
| % diff. | 38.7 | ND | ND | 184.3 | 48.6 | ND | 146.5 | 47.4 | ND | 8.1 | 33.3 | ND |

The percent recovery on the matrix spikes varied widely and some of the percent recovery was rather poor, mostly in the first fraction. However, metal contribution from

the first fraction is rather minor, so this does not significantly reflect the overall interpretation of the data. After digestion, it was realized that the matrix spikes were spiked with too low of a concentration of metals. This can cause a small fluctuation in the instrument to result in an extremely large percent recovery. This is most likely the issue in the high percent recovery in the matrix spikes.

Table 5. Matrix Spikes and Percent Recovery (mg/L). ND = not detected. Avg. = Average.

| | Fraction 1 | | | Fraction 2 | | | Fraction 3 | | | Fraction 4 | | |
|-------|------------|------|------|------------|-------|-----|------------|------|-----|------------|------|-----|
| | Zn | Pb | Cd | Zn | Pb | Cd | Zn | Pb | Cd | Zn | Pb | Cd |
| 15 | 4.2 | ND | ND | 22.6 | 0.8 | 0.1 | 15.0 | 1.3 | ND | 6.7 | 0.5 | ND |
| 15-MS | 148.9 | 85.4 | 20.7 | 94.4 | 95.4 | 7.6 | 48.3 | 37.6 | 3.1 | 59.2 | 66.7 | 5.3 |
| % R | 289 | 171 | 206 | 144 | 189 | 75 | 67 | 73 | 31 | 105 | 133 | 53 |
| 28 | 6.1 | ND | ND | 48.0 | 1.2 | ND | 91.5 | 1.6 | 0.9 | 25.5 | 0.5 | 0.3 |
| 28-MS | 142.3 | 51.7 | 9.2 | 134.8 | 117.6 | 3.8 | 118.2 | 36.5 | 6.7 | 81.8 | 61.4 | 6.3 |
| % R | 272 | 104 | 92 | 174 | 233 | 38 | 53 | 70 | 58 | 113 | 122 | 60 |
| 46 | 17.6 | ND | ND | 76.7 | 1.1 | 0.2 | 32.7 | 1.6 | 0.4 | 9.0 | 0.4 | ND |
| 46-MS | 193.7 | 58.9 | 18.4 | 132.2 | 110.1 | 7.6 | 50.3 | 34.3 | 3.5 | 61.0 | 33.7 | 5.2 |
| % R | 352 | 118 | 184 | 111 | 218 | 75 | 35 | 66 | 30 | 104 | 67 | 51 |
| Avg. | 305 | 131 | 161 | 143 | 213 | 63 | 52 | 69 | 40 | 107 | 107 | 55 |

Sample Results

The average concentrations of zinc, lead, and cadmium in each of the four geochemical fractions are summarized in Table 6. The total metal concentration as determined by the outside lab is given along with action levels determined by the EPA during the Oronogo-Duenweg mining belt site cleanup in Jasper County, MO. The

average total metal concentration in the sediment is below the action level for soil remediation (with the exception of the ALS total for lead). However, several individual fraction concentrations for lead and cadmium exceed these totals, as well as several total concentrations for zinc. The average concentrations for fractions 2 through 4 exceed the actions levels for remediation in tributary sediments.

Table 6. Average Metal Concentration in Geochemical Fractions (mg/kg). ALS total contains the average concentrations of metals as determined by the external laboratory which performed total metal analysis. AL (action levels) are the levels above which media required clean up in the EPAs Oronogo-Duenweg Missouri mining remediation project.

| Metal | Fraction 1 | Fraction 2 | Fraction 3 | Fraction 4 | Total | ALS Total | Soil EPA AL | Sediment EPA AL |
|-------|------------|------------|------------|------------|-------|-----------|-------------|-----------------|
| Zn | 100.8 | 879.3 | 1782 | 1187 | 3949 | 6053 | 6,400 | 250 |
| Pb | 6.0 | 102.4 | 164.4 | 39.8 | 312.6 | 563.1 | 400 | 70 |
| Cd | 1.0 | 2.0 | 8.3 | 11.2 | 22.5 | 32.4 | 40 | 2 |

Among the four fractions, 73.5 percent of zinc, 54.0 percent of lead, 73.4 percent of cadmium were recovered (Table 7). The remainder of the metals is in the residual fraction and likely could be recovered using the fifth extract of the Tessier method, HF-HClO₄, a mixture of hydrofluoric and perchloric acids.

Figures 7, 8, and 9 show the concentration of zinc, lead, and cadmium respectively amongst the four exchangeable fractions. The graphs are ordered relative to the flow of Chat Creek and surrounding streams. Chat Creek shows much higher concentrations of metals than surrounding streams. This shows a significant contribution.

of metals from the former mining operations in Aurora. The highest concentrations of metals are present in fraction 3.

Table 7. Average Percentage of Metals Recovered during Sequential Extraction.

| Metal | Fraction 1 | Fraction 2 | Fraction 3 | Fraction 4 | Total |
|-------|------------|------------|------------|------------|-------|
| Zn | 3 | 17.2 | 33.9 | 19.4 | 73.5 |
| Pb | 0.6 | 12.2 | 30.5 | 10.7 | 54.0 |
| Cd | 3.5 | 9.8 | 30.6 | 29.5 | 73.4 |

Zinc is most readily exchangeable in the Fe-Mn oxide-bound fraction for most sediment samples (Table 7). This fraction was digested using the reducing agent hydroxyl amine. This means that the majority of the zinc in the collected sediments becomes most mobile in reducing environments (e.g. environments with high organic matter). The highest contamination is shown along the main section of chat creek that was sampled near the former chat piles. More specifically, samples along the middle section of Chat Creek that was sampled, showed the highest concentrations of zinc. When compared to the concentration of zinc present in the smaller creeks within Aurora, samples 9-15, it is clear that the contamination along chat creek is significantly higher than natural levels.

Lead, like zinc, shows the highest exchangeability in the Fe-Mn oxide bound fraction (Table 7). The middle section of Chat Creek (samples 1-5 and 43-45) showed high levels of lead that were significantly higher than even the samples slightly upstream in Chat Creek. Lead also appears to show lower percent exchangeability than either zinc and cadmium in both easily exchangeable and bound to organic matter fractions (Table 7). The lower percentage of lead recovery is likely due to its presence as galena, or PbS

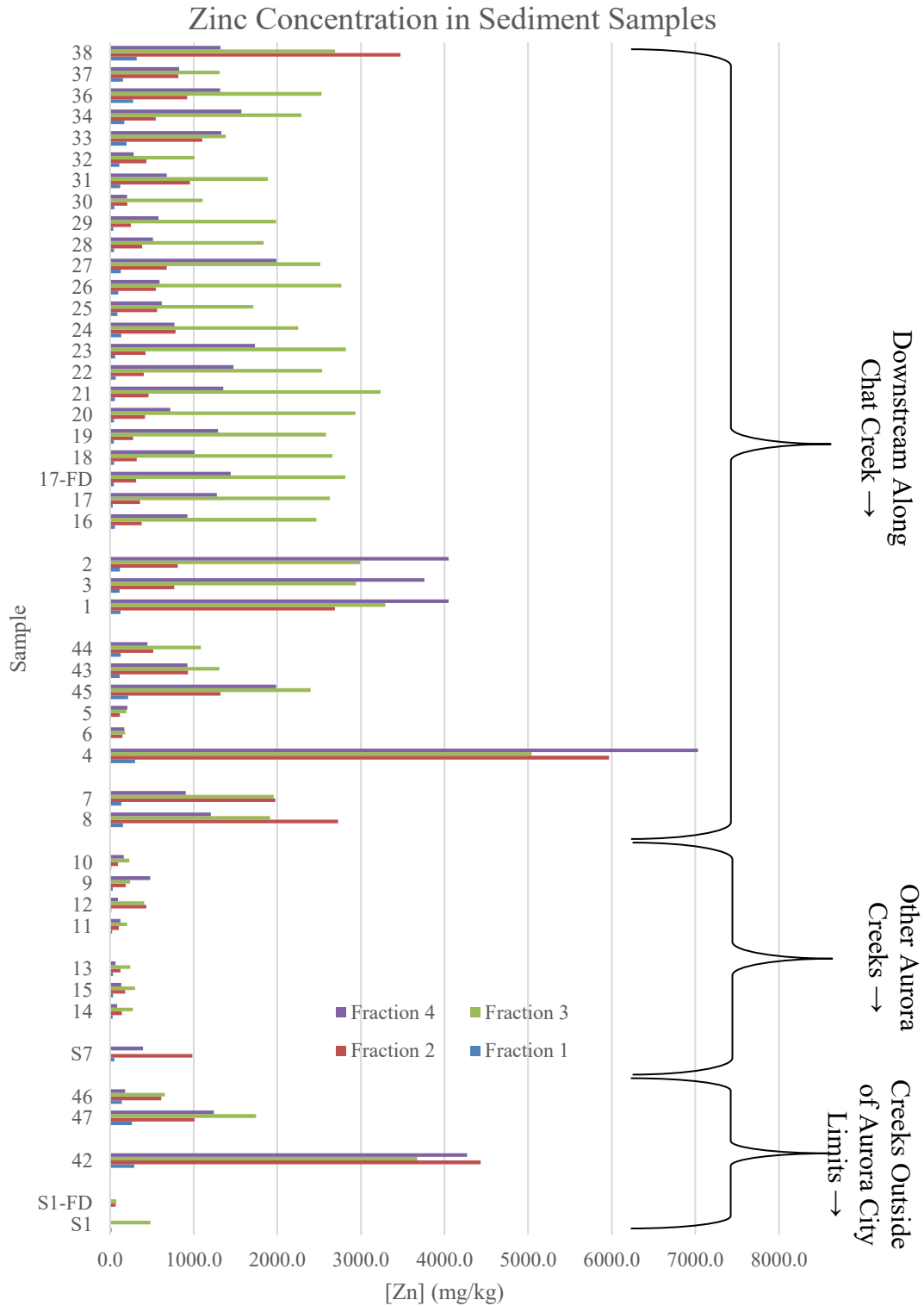


Figure 7. Concentration of zinc in sediment samples by fraction. Samples are represented by numbers on the y-axis and are ordered from upstream to downstream along Chat Creek and other creeks. Graph is segmented by creek areas. Appendix A, contains data used to construct this figure.

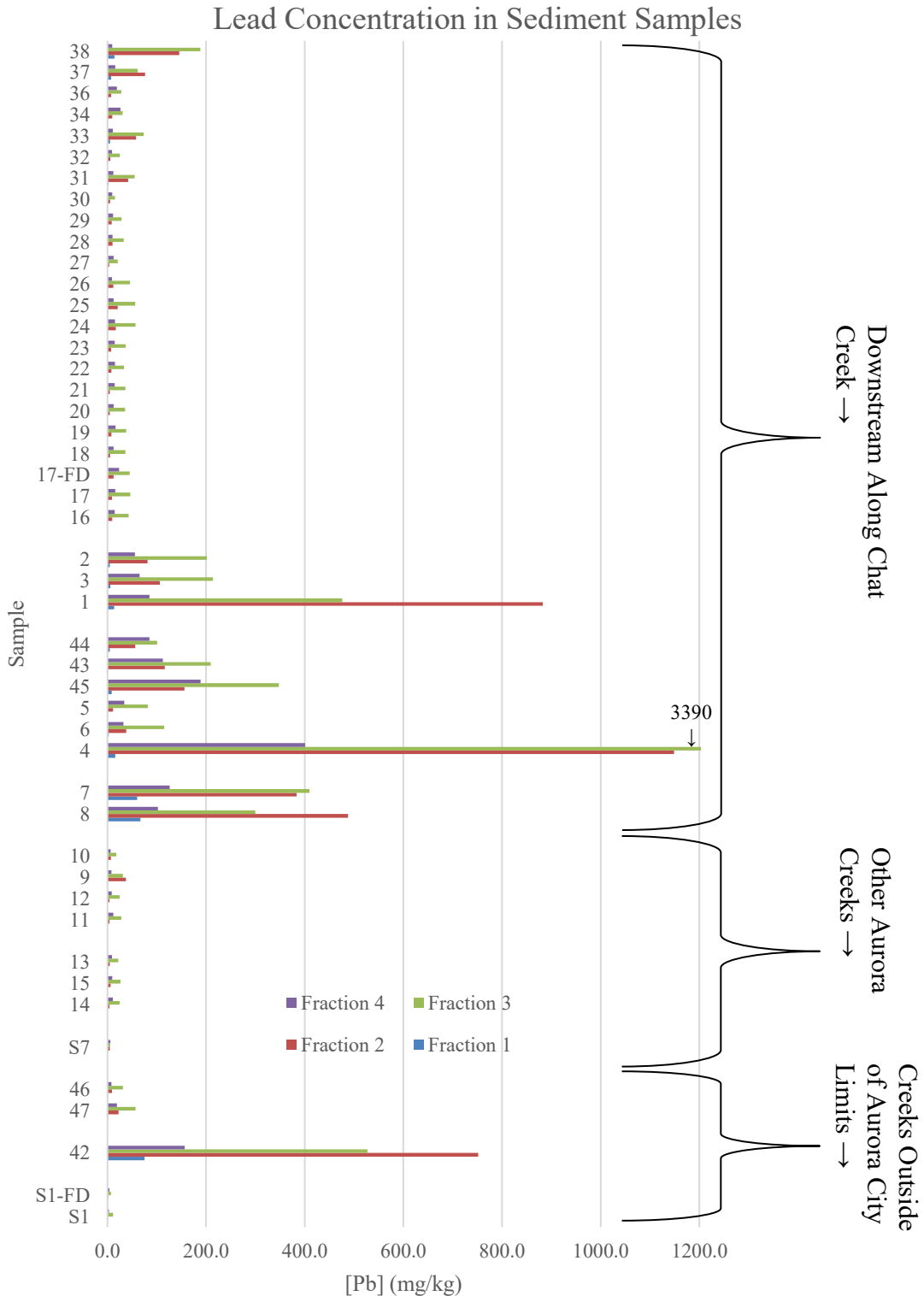


Figure 8. Concentration of lead in sediment samples by fraction. Samples are represented by numbers on the y-axis and are ordered from upstream to downstream along Chat Creek and other creeks. Graph is segmented by creek areas. Appendix B, contains data used to construct this figure.

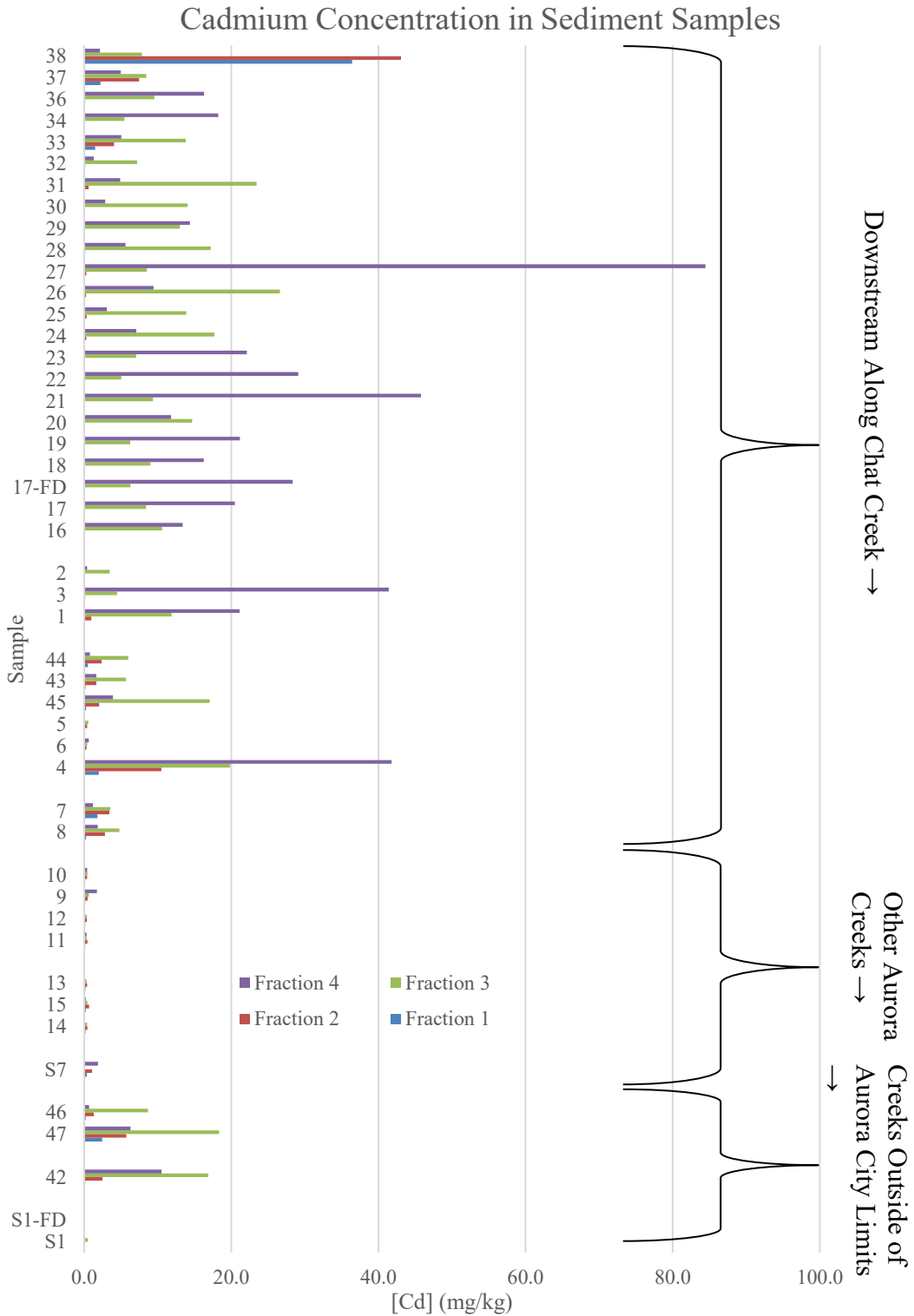


Figure 9. Concentration of cadmium in sediment samples by fraction. Samples are represented by numbers on the y-axis and are ordered from upstream to downstream along Chat Creek and other creeks. Graph is segmented by creek areas. Appendix C, contains data used to construct this figure.

(lead sulfide). Galena is the major ore of lead and is highly insoluble in water.

Cadmium shows a contamination distribution similar to zinc among the sampling sites with the major contamination along the main section of Chat Creek. Along Chat creek, most cadmium shows mobility only in Fe-Mn bound and organic matter bound fractions. Cadmium presence in the other two fractions is mostly minor. The organic matter-bound fraction contains more cadmium than the Fe-Mn oxide-bound fraction, unlike zinc and lead. Cadmium mobility was expected to be higher. However, this was found to be fraction dependent. Cadmium had the greatest mobility in both easily exchangeable and organic matter-bound fractions. Cadmium may still have been more mobile in general and may have been previously washed away from stream sediments. This might explain the low concentrations in the first two fractions.

Correlations. A simple statistical correlation analysis was run on each fraction using Microsoft Excel. The correlation was run to see which metals were indicative of one another. Zinc appeared to have the highest correlation with each of the other two in every fraction with the exception of fraction 3 (Table 8). In fraction 3 (bound to Fe-Mn oxides), the highest correlation exists between zinc and lead (0.59), followed by the lead-cadmium correlation (0.23), then lastly zinc and cadmium (0.18). In the other fractions zinc has the highest correlative values. The highest correlation in all fractions other than fraction 1 is between zinc and lead. Fraction one has the highest correlation between zinc and cadmium (0.49), but only slightly greater than zinc and lead (0.43). The largest correlation overall is between zinc and lead in fraction 2 (Table 8).

Fraction 3 was metals bound to Fe-Mn oxides. Table 9 shows the correlation of zinc, lead, and cadmium with iron and manganese. A very strong correlation exists

between lead and manganese (97 percent). This shows that the majority of lead was indeed bound in manganese oxides. The correlation between manganese and lead is very close to the correlation between manganese and iron, showing that about two-thirds of lead was bound to both iron and manganese oxides together.

In the second fraction, bound to carbonates, the strongest correlation is between calcium and cadmium (57 percent) (Table 9).

Table 8. Correlation of Metals. The correlation of zinc, lead, and cadmium in each of the four geochemical fractions: 1) Easily Exchangeable, 2) Bound to Carbonate, 3) Bound to Fe-Mn Oxides, 4) Bound to Organic Matter.

| | Fraction 1 | | | Fraction 3 | | |
|-----------|------------|-----------|-----------|------------|-----------|-----------|
| | <i>Zn</i> | <i>Pb</i> | <i>Cd</i> | <i>Zn</i> | <i>Pb</i> | <i>Cd</i> |
| <i>Zn</i> | 1.00 | | | 1.00 | | |
| <i>Pb</i> | 0.43 | 1.00 | | 0.59 | 1.00 | |
| <i>Cd</i> | 0.50 | 0.12 | 1.00 | 0.18 | 0.23 | 1.00 |

| | Fraction 2 | | | Fraction 4 | | |
|-----------|------------|-----------|-----------|------------|-----------|-----------|
| | <i>Zn</i> | <i>Pb</i> | <i>Cd</i> | <i>Zn</i> | <i>Pb</i> | <i>Cd</i> |
| <i>Zn</i> | 1.00 | | | 1.00 | | |
| <i>Pb</i> | 0.90 | 1.00 | | 0.65 | 1.00 | |
| <i>Cd</i> | 0.59 | 0.30 | 1.00 | 0.40 | 0.36 | 1.00 |

Table 9. Correlation of Exchangeable Metals in Fraction 2 with Ca and Fraction 3 with Fe and Mn.

| | <i>Zn</i> | <i>Pb</i> | <i>Cd</i> | <i>Mn</i> | <i>Fe</i> |
|-----------|-----------|-----------|-----------|-----------|-----------|
| <i>Mn</i> | 0.37269 | 0.96882 | 0.19007 | 1 | |
| <i>Fe</i> | 0.03984 | 0.67545 | -0.1731 | 0.69838 | 1 |
| <i>Ca</i> | 0.14079 | -0.0813 | 0.57371 | | |

Plant and Water Samples

Plant samples showed elevated levels of metals (Table 10). Sampling sites with both plant and sediment samples are compared in Table 11. Table 10 was grouped by types of plant. Aquatic samples showed significantly higher levels of all three metals. The highest concentration of zinc was 709 ppm in sample S3-B. Sample S4-B had the highest levels of both lead (116 ppm) and cadmium (8.2 ppm). There are two explanations for these elevated levels: 1) these plants have accumulated metals by up taking them from a heavily contaminated environment or 2) sediments were not completely removed from plants during washing and the high metal concentration is a false reading given by measuring the metals in the sediments instead of the plants. Further research would need to be conducted in order to provide a definite conclusion. It should be noted that both of these highest samples were aquatic plants, which were more difficult to fully remove sediments from roots. However, elevated levels also exist in other types of plant samples that were easier to clean. Metal concentrations are generally higher among those taken from Chat Creek. However, not many samples were taken from other creeks and more samples should be taken in order to show a significant correlation. Botanical expertise was lacking in this research and specific plant type bioavailability was unaccounted for and was beyond the scope of this research.

Quality control on plant samples showed that the sample measurements were well above the detection limits (Table 12), and LCC showed that measurements were both accurate and precise (Table 13). MS recovery was low at 57%, but still reasonable (Table 14). Lab duplicates showed good agreement with a low percent difference 14% (Table

Table 10. Concentration of Metals in Dried Plants Samples ([M] (mg/kg)).

| Type | Sample | Zn | Pb | Cd | Creek |
|------------------|---------|-------|------|-------|-------|
| P | S1 | 95.4 | 0.55 | 0.098 | Other |
| P | S4-C | 240.5 | 12.9 | 0.48 | Chat |
| | Average | 168 | 6.73 | 0.29 | |
| G | S2-A | 207 | 5.75 | 0.29 | Chat |
| G | S2-B | 174 | 0.96 | 0.081 | Chat |
| G | S3-C | 117 | 1.24 | 0.13 | Chat |
| G | S4-A | 441 | 31.8 | 1.7 | Chat |
| G | S5-A | 188 | 10.3 | 0.21 | Chat |
| G | S6 | 64.2 | 0.51 | 0.071 | Other |
| G | S7 | 198 | 2.32 | 0.35 | Other |
| | Average | 199 | 7.56 | 0.40 | |
| A | S3-A | 509 | 5.52 | 1.75 | Chat |
| A | S3-B | 709 | 17.0 | 1.70 | Chat |
| A | S4-B | 631 | 116 | 8.15 | Chat |
| A | S5-B | 272 | 13.8 | 0.33 | Chat |
| Digestion Blanks | | | | | |
| | Tea | 23.5 | 0.39 | 0.028 | |
| | Blank | 10.5 | 0.33 | 0.044 | |

* The types of plants are designated “G” for grass, “A” for aquatic plants, and “P” for other types of plants. Samples included roots (and stems for P samples).

15). Cadmium had the poorest results for both MS and LD, which brought down the better results of zinc and lead.

Water samples showed no significant contamination from metals (Table 16). Most water samples were below the detection limits. Samples over the detection limits were only barely above them. Tables 17 and 18 show quality control of analysis.

Table 11. Metal Concentration in Sediment (mg/kg) versus Plant Samples. Comparison of the concentration of plant samples relative to their respective sediments.

| Sample | Sediment Samples | | | Plant Samples | | |
|--------|------------------|------|-----|---------------|-----|-----|
| | Zn | Pb | Cd | Zn | Pb | Cd |
| S1 | 506.1 | 14.6 | 0.2 | 95.0 | 0.6 | 0.1 |
| S7 | 1428.6 | 15.2 | 3.4 | 198.0 | 2.3 | 0.4 |

Table 12. Plant Sample Blanks ([M] (mg/L)).

| Blank | Zn | Pb | Cd |
|---------|--------|--------|---------|
| 1 | 0.005 | 0.007 | 0.0005 |
| 2 | 0.013 | -0.023 | -0.0006 |
| 3 | 0.010 | -0.002 | -0.0010 |
| 4 | -0.058 | -0.004 | -0.0025 |
| 5 | 0.004 | 0.032 | 0.0000 |
| 6 | -0.004 | 0.015 | -0.0009 |
| 7 | 0.213 | 0.023 | 0.0001 |
| Average | 0.026 | 0.007 | -0.0006 |
| Std Dev | 0.086 | 0.018 | 0.0010 |
| D.L. | 0.26 | 0.055 | 0.0030 |

Table 13. Plant Sample Laboratory Control Checks. Prepared/theoretical LCC concentrations are shown in parentheses after metal.

| LCC | [LCC] (mg/L) | | | Percent Difference (%) | | |
|---------|--------------|----------|-----------|------------------------|------|------|
| | Zn (0.2) | Pb (0.2) | Cd (0.01) | Zn | Pb | Cd |
| 1 | 0.196 | 0.220 | 0.0108 | 2.1 | 10.1 | 8.2 |
| 2 | 0.185 | 0.179 | 0.0092 | 7.5 | 10.8 | 7.7 |
| 3 | 0.174 | 0.167 | 0.0094 | 12.9 | 16.3 | 5.6 |
| 4 | 0.130 | 0.187 | 0.0088 | 34.9 | 6.4 | 12.2 |
| 5 | 0.160 | 0.165 | 0.0080 | 20.0 | 17.6 | 19.6 |
| 6 | 0.171 | 0.172 | 0.0080 | 14.4 | 14.0 | 19.7 |
| 7 | 0.228 | 0.191 | 0.0080 | 13.8 | 4.7 | 19.6 |
| Average | 0.18 | 0.18 | 0.01 | 15.1 | 11.4 | 13.2 |
| Std Dev | 0.03 | 0.02 | 0.001 | 10.39 | 4.84 | 6.31 |
| CV | 0.17 | 0.10 | 0.12 | 0.69 | 0.42 | 0.48 |

Table 14. Matrix Spike Recovery of Plant Samples ([M] (mg/L)).

| Sample | Zn | Pb | Cd |
|--------------------------|-------|-------|-------|
| S2-B | 20.70 | 0.12 | 0.012 |
| S2-B-MS | 18.13 | 3.39 | 0.115 |
| % Recovery | 51 | 66 | 20 |
| S4-B | 56.72 | 12.13 | 0.831 |
| S4-B-MS | 60.97 | 17.46 | 1.282 |
| % Recovery | 85 | 107 | 90 |
| S5-A | 18.71 | 1.02 | 0.021 |
| S5-A-MS | 22.92 | 3.56 | 0.150 |
| % Recovery | 84 | 51 | 26 |
| S6 | 6.37 | 0.05 | 0.007 |
| S6-MS | 10.63 | 3.13 | 0.205 |
| % Recovery | 85 | 62 | 40 |
| S8-B | 23.82 | 0.93 | 0.011 |
| S8-B-MS | 24.31 | 4.04 | 0.114 |
| % Recovery | 10 | 62 | 20 |
| Average | 63 | 69 | 39 |
| Total Average % Recovery | | | 57 |

Table 15. Plant Samples Lab Duplicates ([M] (mg/L)).

| Sample | Zn | Pb | Cd |
|----------------------|-------|------|-------|
| S3-C | 12.43 | 0.13 | 0.016 |
| S3-C-LD | 10.99 | 0.12 | 0.010 |
| Average | 11.71 | 0.12 | 0.013 |
| % Difference | 12.3 | 13.2 | 47.9 |
| S4-A | 44.40 | 3.28 | 0.167 |
| S4-A-LD | 45.27 | 3.20 | 0.178 |
| Average | 44.84 | 3.24 | 0.173 |
| % Difference | 1.9 | 2.4 | 6.3 |
| S5-B | 31.42 | 1.41 | 0.031 |
| S5-B-LD | 22.95 | 1.36 | 0.034 |
| Average | 27.19 | 1.38 | 0.033 |
| % Difference | 31.2 | 3.5 | 7.1 |
| S7 | 20.16 | 0.22 | 0.040 |
| S7-LD | 20.01 | 0.25 | 0.030 |
| Average | 20.09 | 0.23 | 0.035 |
| % Difference | 0.7 | 11.9 | 28.5 |
| Average % Difference | | | 14 |

Table 16. Metal Concentration in Water Samples ([M] (mg/L)). ND = not detected.

| Sample | Zn | Pb | Cd |
|---------|--------|--------|--------|
| S2 | 0.7564 | 0.0018 | 0.0028 |
| S3 | 0.3779 | 0.0051 | ND |
| S4 | 0.3888 | ND | 0.0009 |
| S6 | 0.3921 | 0.0036 | ND |
| S8 | 0.0518 | ND | ND |
| Average | 0.3934 | 0.0014 | 0.0005 |
| Std Dev | 0.2494 | 0.0032 | 0.0014 |

Table 17. Water Samples LCC.

| Sample | [M] (mg/L) | | | Percent Difference (%) | | |
|---------|------------|-------|--------|-------------------------------|------|------|
| | Zn | Pb | Cd | Zn | Pb | Cd |
| LCC 1 | 0.217 | 0.2 | 0.0096 | 8.7 | 0.1 | 4.3 |
| LCC 2 | 0.232 | 0.229 | 0.0083 | 16.2 | 14.7 | 17.1 |
| Average | 0.225 | 0.215 | 0.0089 | 12.4 | 7.4 | 10.7 |
| Std Dev | 0.011 | 0.021 | 0.0009 | Total Average % Difference | | 10.2 |
| CV | 0.047 | 0.097 | 0.102 | | | |

Table 18. Water Samples Blanks ([M] (mg/L)).

| Sample | Zn | Pb | Cd |
|---------------|---------|---------|---------|
| Blank Check 1 | -0.0009 | -0.0001 | -0.0001 |
| Blank Check 2 | -0.0024 | 0.0018 | -0.0009 |
| Average | -0.0016 | 0.0009 | -0.0005 |
| Std Dev | 0.0010 | 0.0013 | 0.0006 |
| D.L. | 0.0031 | 0.0040 | 0.0019 |

CONCLUSION

Significant contamination still exists along Chat Creek. Relative to other creeks in and around Aurora, Chat Creek shows elevated levels of zinc, lead, and cadmium from the former mining operations within the town. Former mining holes and chat piles are in close proximity to the elevated levels of metals along Chat Creek.

The majority of sediment samples show greatest exchangeability within Fe-Mn oxide and organic matter bound fractions. Zinc and lead have the largest mobility in the Fe-Mn oxide bound fractions, leading to the greatest mobility and bioavailability of these two metals under reducing conditions. Cadmium has the largest exchangeability in the organic matter-bound fraction, making cadmium most mobile and bioavailable under oxidizing conditions. Easily exchangeable and carbonate bound fractions contain a much lower percentage of metal contamination than the other two. Metals released under these conditions would be in much lower amounts than the other two fractions.

Plant samples taken from Chat Creek showed slightly higher concentrations of metals than samples from other creeks. However, few samples were taken and it was difficult to remove all sediment from plant roots. So, there is not enough evidence to confidently state the bioavailability of metals regarding analysis of plant samples. Water samples did not show elevated metal contamination during analysis.

Three instruments were used in this analysis. ICP-MS was used in the analysis of metals concentrations from fraction 1, which contained the lowest concentrations. Fractions 2 and 3 were analyzed on ICP-AES. Fraction 4 was analyzed on AAS due to nebulization issues on ICP-AES.

This research provides a large data set on which further research can build. Future research that could help to further develop this research could be the analysis of iron, manganese, and calcium in these sediment fractions. Measurement of these metals could increase the significance of correlation between zinc, lead, and cadmium in fractions two and three.

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APPENDICES

Appendix A

Zinc Concentration in Geochemical Fractions (mg/kg). Percentages (%) of total metal content from previous outside analysis are shown in parenthesis. Percentages above 100 are believed to be due to contamination or heterogeneity of low contaminant samples. ND = not detected.

| Sample | Fraction 1 | Fraction 2 | Fraction 3 | Fraction 4 | Total |
|--------|-------------|---------------|--------------|--------------|--------------|
| 1 | 123.4 (0.8) | 2689 (17.4) | 3291 (21.2) | 4050 (26.1) | 10154 (65.5) |
| 2 | 117.1 (1.2) | 809.3 (8.2) | 2993 (30.2) | 4050 (40.9) | 7969 (80.4) |
| 3 | 115.1 (1.2) | 765.9 (7.8) | 2941 (29.8) | 3760 (38.1) | 7581 (76.7) |
| 4 | 297.4 (0.6) | 5968 (11.6) | 5041 (9.8) | 7034 (13.6) | 18348 (35.5) |
| 4-LD | 261.6 (0.5) | 5618 (10.9) | 4998 (9.7) | Error | NA |
| 4-LD-2 | 268.1 (0.5) | 5059 (9.8) | 4478 (8.7) | Error | NA |
| 5 | 1.6 (0.2) | 116.3 (16.3) | 194.3 (27.2) | 206.3 (28.9) | 518.5 (72.6) |
| 6 | 3.1 (0.5) | 147.9 (22.7) | 178.5 (27.4) | 170.2 (26.1) | 499.8 (76.8) |
| 7 | 133.9 (2) | 1975.3 (29.8) | 1957 (29.6) | 905.6 (13.7) | 4972 (75.1) |
| 8 | 153 (1.9) | 2728 (34.5) | 1915 (24.2) | 1204 (15.2) | 5999 (75.8) |
| 9 | 29.7 (1.5) | 185.5 (9.2) | 237.8 (11.8) | 479.9 (23.9) | 932.9 (46.4) |
| 10 | 16.3 (2.1) | 93.6 (11.9) | 230.1 (29.2) | 162 (20.5) | 502.1 (63.6) |
| 10-LD | 12.8 (1.6) | 113.6 (14.4) | 236 (29.9) | 155.5 (19.7) | 517.9 (65.6) |
| 11 | 24.9 (2.9) | 104 (12.3) | 202.2 (23.9) | 124.6 (14.7) | 455.7 (53.8) |
| 12 | 13.7 (2.8) | 432.4 (87) | 407 (81.9) | 93.5 (18.8) | 946.7 (191) |
| 13 | 33 (5.6) | 122.1 (20.8) | 242.2 (41.2) | 62.9 (10.7) | 460.2 (78.3) |
| 13-LD | 22.2 (4) | 122 (21.9) | 255.5 (45.8) | 120.4 (21.6) | 520.1 (93.2) |
| 14 | 32.4 (4.8) | 140.5 (20.8) | 270.5 (40) | 82.3 (12.2) | 525.8 (77.7) |
| 15 | 32.9 (3.8) | 178.8 (20.6) | 296.6 (34.2) | 132.8 (15.3) | 641.1 (73.9) |
| 16 | 56.5 (1) | 377.1 (6.9) | 2467 (45.3) | 925.1 (17) | 3826 (70.2) |
| 17 | 30.2 (0.5) | 356.8 (5.9) | 2628 (43.4) | 1277 (21.1) | 4293 (70.8) |
| 17-FD | 45 (0.7) | 311.9 (5.1) | 2814 (46.4) | 1443 (23.8) | 4614 (76.1) |
| 18 | 46.7 (0.8) | 319.3 (5.7) | 2658 (47.2) | 1009 (17.9) | 4033 (71.6) |
| 19 | 44.4 (0.8) | 273.6 (4.7) | 2583 (44.1) | 1291 (22.1) | 4192 (71.7) |
| 20 | 48.9 (0.8) | 417.7 (7) | 2936 (48.8) | 720.6 (12) | 4123 (68.6) |
| 21 | 57.1 (0.8) | 458.1 (6.5) | 3236 (45.6) | 1353 (19.1) | 5104 (71.9) |
| 22 | 69.1 (1.2) | 403.3 (7.1) | 2537 (44.4) | 1476 (25.8) | 4485 (78.4) |
| 23 | 61.7 (0.9) | 423.3 (6.1) | 2820 (40.9) | 1731 (25.1) | 5036 (73) |
| 24 | 133.9 (2.3) | 782.4 (13.7) | 2250 (39.3) | 768.3 (13.4) | 3935 (68.7) |

Appendix A continued on next page.

Appendix A continued

| Sample | Fraction 1 | Fraction 2 | Fraction 3 | Fraction 4 | Total |
|---------|-------------|--------------|--------------|--------------|--------------|
| 25 | 88.1 (2.1) | 560.4 (13.2) | 1711 (40.3) | 616.8 (14.5) | 2976 (70.2) |
| 26 | 97.3 (1.7) | 549.8 (9.7) | 2768 (49.1) | 590.5 (10.5) | 4006 (71) |
| 27 | 125.7 (1.7) | 678.5 (9.2) | 2514 (34.3) | 1990 (27.1) | 5308 (72.3) |
| 27-LD | 118 (1.6) | 705.8 (9.6) | 2672 (36.4) | 2166 (29.5) | 5662 (77.1) |
| 28 | 48.9 (1.3) | 385.3 (10.1) | 1838 (48) | 512 (13.4) | 2784 (72.7) |
| 29 | 37.7 (0.9) | 248.2 (6.1) | 1986 (48.6) | 578.2 (14.1) | 2850 (69.7) |
| 31 | 119.8 (2.3) | 952.5 (18.7) | 1886 (37.0) | 678.1 (13.3) | 3636 (71.3) |
| 32 | 110.5 (4.4) | 431.7 (17.3) | 1010 (40.6) | 280.3 (11.3) | 1833 (73.6) |
| 33 | 194.6 (3.6) | 1103 (20.3) | 1383 (25.4) | 1330 (24.5) | 4012 (73.7) |
| 34 | 170.5 (2.3) | 543.9 (7.3) | 2291 (30.5) | 1572 (21.0) | 4577 (61.0) |
| 36 | 276.0 (3.7) | 921.5 (12.4) | 2529 (34.1) | 1318 (17.8) | 5044 (68.0) |
| 37 | 154.5 (3.6) | 815.5 (19.1) | 1311 (30.8) | 825.5 (19.4) | 3107 (72.9) |
| 38 | 318.3 (2.7) | 3471 (28.9) | 2692 (22.4) | 1320 (11.0) | 7802 (65.0) |
| 38-LD | 307.5 (2.6) | 3485 (29.0) | 3150 (26.3) | 1573 (13.1) | 8516 (71.0) |
| 42 | 287.0 (1.6) | 4433 (24.5) | 3674 (20.3) | 4271 (23.6) | 12665 (70.0) |
| 43 | 113.8 (2.6) | 932.1 (21.5) | 1307 (30.2) | 925.5 (21.4) | 3278 (75.7) |
| 44 | 126.6 (5.0) | 516.5 (20.3) | 1085 (42.5) | 447.1 (17.5) | 2175 (85.3) |
| 45 | 215.3 (2.7) | 1321 (16.6) | 2399 (30.2) | 1986 (25.0) | 5921 (74.5) |
| 46 | 140.0 (6.7) | 611.3 (29.4) | 652.5 (31.4) | 179.3 (8.6) | 1583 (76.1) |
| 47 | 263.0 (4.6) | 1011 (17.6) | 1746 (30.5) | 1241 (21.7) | 4261 (74.4) |
| S1 | 17.1 (29.4) | 2.7 (4.7) | 481.7 (831) | 4.6 (7.9) | 506.1 (873) |
| S1-FD | 11.6 (9.7) | 67.3 (56.6) | 74.7 (62.8) | 4.2 (3.6) | 157.9 (133) |
| S7 | 50.1 (1.8) | 983.8 (34.5) | ND (0.0) | 394.8 (13.9) | 1429 (50.1) |
| Average | 108.1 (2.8) | 1065 (16.7) | 1878 (50.8) | 1549 (18.6) | 4600 (89.3) |

Appendix B

Lead Concentration in Geochemical Fractions (mg/kg). Percentages (%) of total metal content from previous outside analysis are shown in parenthesis. ND = not detected.

| Sample | Fraction 1 | Fraction 2 | Fraction 3 | Fraction 4 | Total |
|--------|------------|--------------|--------------|-------------|--------------|
| 1 | 13.7 (0.4) | 882.4 (25.6) | 475.9 (13.8) | 84.9 (2.5) | 1457 (42.2) |
| 2 | 4.5 (0.4) | 81.4 (7.9) | 201.7 (19.6) | 55.5 (5.4) | 343.1 (33.3) |
| 3 | 5.7 (0.7) | 106.0 (12.5) | 213.7 (25.3) | 65.2 (7.7) | 390.6 (46.2) |
| 4 | 15.6 (0.2) | 1149 (14.0) | 3390 (41.3) | 400.4 (4.9) | 4955 (60.4) |
| 4-LD | 10.3 (0.1) | 1606 (19.6) | 3300 (40.2) | 389.5 (4.8) | 5305 (64.7) |
| 4-LD-2 | 10.7 (0.1) | 1414 (17.2) | 3438 (41.9) | 394.8 (4.8) | 5257 (64.1) |
| 5 | 0.7 (0.3) | 11.4 (5.8) | 81.5 (41.8) | 34.1 (17.5) | 127.7 (65.5) |
| 6 | 2.3 (1.0) | 38.0 (17.5) | 115.1 (53.0) | 32.2 (14.8) | 187.6 (86.4) |
| 7 | 60.0 (4.4) | 383.2 (28.3) | 409.2 (30.2) | 126.1 (9.3) | 978.6 (72.2) |
| 8 | 66.7 (3.9) | 487.9 (28.7) | 299.6 (17.6) | 102.2 (6.0) | 956.5 (56.3) |
| 9 | 0.5 (0.6) | 37.2 (46.5) | 31.1 (38.9) | 8.2 (10.3) | 77.0 (96.3) |
| 10 | 0.5 (0.9) | 7.1 (13.4) | 18.0 (34.0) | 6.3 (12.0) | 32.0 (60.3) |
| 10-LD | ND (0.0) | 6.9 (13.0) | 17.6 (33.1) | 5.9 (11.2) | 30.2 (57.3) |
| 11 | ND (0.0) | 4.0 (6.1) | 28.2 (42.7) | 12.0 (18.1) | 43.1 (66.9) |
| 12 | ND (0.0) | 4.4 (6.2) | 24.8 (35.4) | 8.4 (12.0) | 37.4 (53.6) |
| 13 | ND (0.0) | 4.5 (6.8) | 22.0 (33.4) | 9.2 (14.0) | 34.9 (54.2) |
| 13-LD | 0.1 (0.1) | 3.7 (5.2) | 21.0 (29.2) | 14.6 (20.2) | 39.4 (54.7) |
| 14 | ND (0.0) | 3.9 (5.4) | 24.4 (33.9) | 11.0 (15.2) | 38.8 (54.5) |
| 15 | ND (0.0) | 6.5 (8.3) | 26.2 (33.2) | 9.7 (12.3) | 42.1 (53.7) |
| 16 | ND (0.0) | 9.5 (6.9) | 42.7 (31.0) | 14.7 (10.6) | 66.6 (48.5) |
| 17 | ND (0.0) | 8.9 (5.7) | 46.4 (29.6) | 15.6 (10.0) | 70.6 (45.2) |
| 17-FD | ND (0.0) | 12.4 (7.9) | 45.0 (28.6) | 23.6 (15.0) | 81.0 (51.6) |
| 18 | ND (0.0) | 5.5 (4.8) | 36.1 (32.0) | 12.6 (11.1) | 53.7 (48.0) |
| 19 | ND (0.0) | 8.1 (6.3) | 37.7 (29.2) | 16.1 (12.5) | 61.8 (48.0) |
| 20 | ND (0.0) | 4.8 (3.8) | 35.6 (27.8) | 12.4 (9.7) | 52.6 (41.3) |
| 21 | 0.2 (0.1) | 4.5 (3.3) | 36.2 (26.6) | 14.6 (10.7) | 55.4 (40.7) |
| 22 | ND (0.0) | 7.8 (6.5) | 33.7 (28.1) | 15.5 (12.9) | 56.3 (47.4) |
| 23 | ND (0.0) | 7.3 (4.9) | 36.8 (24.9) | 14.4 (9.8) | 58.1 (39.5) |
| 24 | 0.2 (0.1) | 17.1 (8.7) | 56.9 (29.0) | 14.9 (7.6) | 89.2 (45.5) |
| 25 | 0.1 (0.1) | 20.7 (11.2) | 56.2 (30.5) | 12.4 (6.7) | 89.3 (48.6) |
| 26 | ND (0.0) | 11.6 (7.8) | 45.7 (30.9) | 9.2 (6.2) | 66.0 (44.9) |
| 27 | ND (0.0) | 3.5 (4.0) | 20.8 (23.4) | 12.3 (13.9) | 36.3 (41.2) |
| 27-LD | ND (0.0) | 3.5 (4.0) | 19.2 (21.6) | 13.4 (15.1) | 35.7 (40.6) |
| 28 | ND (0.0) | 9.9 (9.7) | 32.8 (32.1) | 10.4 (10.2) | 52.9 (52.1) |

Appendix B continued on next page.

Appendix B continued.

| Sample | Fraction 1 | Fraction 2 | Fraction 3 | Fraction 4 | Total |
|---------|------------|--------------|--------------|--------------|--------------|
| 29 | 0.3 (0.3) | 8.5 (9.1) | 28.4 (30.2) | 11.4 (12.2) | 48.6 (51.7) |
| 30 | 0.1 (0.2) | 5.3 (11.6) | 15.0 (32.7) | 9.6 (20.9) | 30.1 (65.4) |
| 31 | 2.1 (1.0) | 41.8 (20.4) | 55.0 (26.8) | 11.9 (5.8) | 110.8 (54.1) |
| 32 | ND (0.0) | 5.7 (7.4) | 24.9 (32.8) | 9.0 (11.9) | 39.6 (52.1) |
| 33 | 5.0 (1.8) | 57.9 (20.5) | 73.2 (26.0) | 10.9 (3.9) | 147.1 (52.2) |
| 34 | 0.9 (0.4) | 9.7 (4.9) | 30.6 (15.6) | 26.2 (13.3) | 67.3 (34.3) |
| 36 | 0.4 (0.3) | 7.5 (4.2) | 28.0 (15.8) | 19.3 (10.9) | 55.3 (31.2) |
| 37 | 7.6 (2.8) | 76.4 (27.8) | 61.4 (22.3) | 16.0 (5.8) | 161.5 (58.7) |
| 38 | 14.3 (2.2) | 145.4 (22.3) | 188.2 (28.9) | 9.8 (1.5) | 357.8 (55.0) |
| 38-LD | 12.6 (1.9) | 147.5 (22.7) | 233.2 (35.8) | 9.0 (1.4) | 402.2 (61.8) |
| 42 | 74.9 (3.1) | 751.6 (30.8) | 527.1 (21.6) | 156.8 (6.4) | 1510 (61.9) |
| 43 | 0.5 (0.1) | 115.9 (17.8) | 209.6 (32.1) | 112.5 (17.3) | 438.5 (67.3) |
| 44 | 4.4 (1.2) | 56.2 (15.2) | 100.5 (27.1) | 84.9 (22.9) | 246.0 (66.3) |
| 45 | 8.5 (0.7) | 156.0 (12.8) | 347.6 (28.5) | 188.5 (15.5) | 700.7 (57.4) |
| 46 | 0.3 (0.3) | 9.2 (11.9) | 31.5 (40.9) | 7.8 (10.1) | 48.7 (63.2) |
| 47 | 1.2 (0.6) | 22.4 (11.2) | 56.6 (28.4) | 19.1 (9.6) | 99.2 (49.8) |
| S1 | ND (0.0) | 0.7 (4.9) | 11.4 (81.1) | 3.0 (21.3) | 14.6 (107.3) |
| S1-FD | ND (0.0) | 1.1 (5.4) | 7.0 (33.5) | 4.2 (20.0) | 12.0 (58.9) |
| S7 | ND (0.0) | 4.5 (9.3) | 5.2 (10.9) | 6.0 (12.5) | 15.2 (32.8) |
| Average | 6.0 (0.6) | 150.9 (12.3) | 278.4 (30.8) | 50.9 (11.1) | 486.1 (54.9) |

Appendix C

Cadmium Concentration in Geochemical Fractions (mg/kg). Percentages (%) of total metal content from previous outside analysis are shown in parenthesis. Percentages above 100 are believed to be due to contamination or heterogeneity of low contaminant samples. ND = not detected.

| Sample | Fraction 1 | Fraction 2 | Fraction 3 | Fraction 4 | Total |
|--------|------------|------------|-------------|-------------|--------------|
| 1 | ND (0.0) | 1.0 (1.9) | 11.9 (23.8) | 21.1 (42.3) | 34.0 (68.1) |
| 2 | ND (0.0) | 0.1 (0.2) | 3.4 (7.0) | 0.4 (0.8) | 3.9 (8.0) |
| 3 | ND (0.0) | 0.1 (0.3) | 4.5 (8.8) | 41.4 (81.7) | 46.0 (90.8) |
| 4 | 2.0 (0.7) | 10.5 (3.7) | 19.8 (7.1) | 41.8 (14.9) | 74.1 (26.4) |
| 4-LD | 1.8 (0.6) | 13.1 (4.7) | 16.0 (5.7) | 53.4 (19.0) | 84.2 (30.0) |
| 4-LD-2 | 1.8 (0.6) | 14.1 (5.0) | 16.9 (6.0) | 51.1 (18.2) | 83.9 (29.9) |
| 5 | 0.1 (2.7) | 0.4 (17.9) | 0.5 (24.9) | ND (-4.5) | 0.9 (41.0) |
| 6 | 0.1 (4.0) | 0.3 (18.8) | 0.4 (21.3) | 0.6 (34.3) | 1.4 (78.3) |
| 7 | 1.8 (14.4) | 3.4 (27.7) | 3.5 (28.6) | 1.2 (9.7) | 10.0 (80.4) |
| 8 | 0.2 (1.7) | 2.8 (21.7) | 4.8 (36.7) | 1.8 (14.0) | 9.6 (74.2) |
| 9 | 0.1 (1.5) | 0.5 (5.9) | 0.6 (8.0) | 1.7 (21.8) | 2.9 (37.3) |
| 10 | 0.1 (4.8) | 0.4 (16.1) | 0.4 (17.0) | 0.4 (15.9) | 1.3 (53.8) |
| 10-LD | 0.1 (3.3) | 0.4 (16.9) | 0.4 (16.3) | 0.4 (17.4) | 1.3 (53.9) |
| 11 | 0.1 (4.6) | 0.4 (16.3) | 0.3 (12.6) | 0.3 (12.3) | 1.2 (45.8) |
| 12 | 0.1 (10.8) | 0.4 (30.8) | 0.4 (29.3) | 0.1 (8.2) | 0.9 (79.1) |
| 13 | 0.2 (12.8) | 0.4 (29.2) | 0.3 (23.4) | ND (-2.9) | 0.9 (62.4) |
| 13-LD | 0.2 (12.3) | 0.5 (32.2) | 0.3 (24.7) | 0.3 (21.4) | 1.3 (90.5) |
| 14 | 0.2 (12.3) | 0.4 (29.5) | 0.4 (26.8) | 0.0 (1.3) | 1.0 (70.0) |
| 15 | 0.2 (10.5) | 0.7 (32.2) | 0.4 (21.0) | 0.2 (9.4) | 1.5 (73.2) |
| 16 | ND (0.0) | ND (0.1) | 10.6 (34.8) | 13.4 (43.9) | 24.0 (78.8) |
| 17 | ND (0.0) | ND (0.0) | 8.4 (23.4) | 20.5 (57.1) | 28.9 (80.6) |
| 17-FD | ND (0.0) | ND (0.0) | 6.3 (17.5) | 28.3 (78.9) | 34.6 (96.4) |
| 18 | ND (0.0) | ND (0.0) | 9.0 (30.1) | 16.3 (54.4) | 25.2 (84.5) |
| 19 | ND (0.0) | ND (0.1) | 6.3 (17.7) | 21.2 (59.9) | 27.5 (77.8) |
| 20 | ND (0.0) | ND (0.0) | 14.7 (42.4) | 11.8 (34.1) | 26.5 (76.5) |
| 21 | ND (0.0) | ND (0.0) | 9.3 (22.7) | 45.8 (111) | 55.1 (134) |
| 22 | ND (0.0) | ND (0.0) | 5.0 (14.7) | 29.1 (85.3) | 34.1 (100.1) |
| 23 | ND (0.0) | ND (0.1) | 7.0 (18.3) | 22.1 (57.4) | 29.2 (75.8) |
| 24 | ND (0.1) | 0.3 (0.8) | 17.7 (49.3) | 7.1 (19.7) | 25.1 (69.9) |
| 25 | ND (0.0) | 0.3 (1.3) | 13.9 (55.9) | 3.1 (12.4) | 17.3 (69.6) |
| 26 | ND (0.0) | 0.2 (0.5) | 26.6 (55.0) | 9.4 (19.5) | 36.3 (74.9) |
| 27 | ND (0.0) | 0.3 (0.3) | 8.5 (8.5) | 84.5 (84.5) | 93.3 (93.3) |

Appendix C continued on next page

Appendix C continued.

| Sample | Fraction 1 | Fraction 2 | Fraction 3 | Fraction 4 | Total |
|---------|-------------|-------------|-------------|-------------|-------------|
| 27-LD | ND (0.0) | 0.4 (0.4) | 9.5 (9.5) | 87.4 (87.4) | 97.3 (97.3) |
| 28 | ND (0.0) | 0.1 (0.4) | 17.2 (53.3) | 5.6 (17.4) | 22.9 (71.0) |
| 29 | ND (0.0) | ND (0.0) | 13.0 (39.0) | 14.4 (43.1) | 27.3 (82.1) |
| 30 | ND (0.0) | ND (0.2) | 14.1 (68.9) | 2.9 (14.0) | 16.9 (83.2) |
| 31 | ND (0.0) | 0.6 (1.4) | 23.4 (56.7) | 4.9 (11.8) | 28.9 (70.0) |
| 32 | ND (0.0) | 0.1 (1.0) | 7.2 (54.1) | 1.3 (9.8) | 8.6 (64.8) |
| 33 | 1.5 (4.5) | 4.1 (12.4) | 13.8 (42.0) | 5.0 (15.3) | 24.4 (74.2) |
| 34 | ND (0.0) | ND (0.0) | 5.4 (15.7) | 18.2 (52.7) | 23.7 (68.4) |
| 36 | ND (0.1) | 0.1 (0.4) | 9.6 (25.1) | 16.3 (42.9) | 26.0 (68.5) |
| 37 | 2.2 (7.5) | 7.5 (25.3) | 8.4 (28.6) | 5.0 (16.8) | 23.1 (78.2) |
| 38 | 36.4 (44.2) | 43.1 (52.3) | 7.8 (9.5) | 2.1 (2.6) | 89.5 (109) |
| 38-LD | 33.1 (40.2) | 42.5 (51.5) | 9.9 (12.0) | 3.2 (3.9) | 88.6 (108) |
| 42 | 0.1 (0.3) | 2.5 (5.6) | 16.9 (38.0) | 10.5 (23.7) | 30.0 (67.5) |
| 43 | 0.2 (1.4) | 1.6 (12.6) | 5.7 (43.7) | 1.6 (12.6) | 9.2 (70.4) |
| 44 | 0.5 (4.2) | 2.4 (18.9) | 6.0 (47.5) | 0.8 (6.3) | 9.7 (76.8) |
| 45 | 0.3 (0.8) | 2.0 (6.2) | 17.0 (52.1) | 3.9 (11.9) | 23.2 (71.0) |
| 46 | 0.2 (1.5) | 1.3 (10.4) | 8.7 (68.9) | 0.7 (5.4) | 10.9 (86.2) |
| 47 | 2.4 (5.8) | 5.7 (13.7) | 18.3 (43.9) | 6.3 (15.1) | 32.7 (78.5) |
| S1 | ND (0.0) | ND (0.0) | 0.5 (0.0) | ND (0.0) | 0.2 (0.0) |
| S1-FD | ND (0.0) | ND (0.0) | ND (0.0) | ND (0.0) | ND (0.0) |
| S7 | 0.4 (7.6) | 1.1 (23.7) | 0.1 (1.5) | 1.9 (40.6) | 3.4 (73.4) |
| Average | 1.6 (4.2) | 3.1 (10.8) | 8.3 (28.4) | 13.6 (29.2) | 26.7 (72.6) |