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Assessing Bioavailability, Metal Fractionation, Magnetic Susceptibility, and Organic Matter Interactivity in Mine-Waste Contaminated Sediments in Turkey Creek, Joplin, Missouri

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ASSESSING BIOAVAILABILITY, METAL FRACTIONATION, MAGNETIC SUSCEPTIBILITY, AND ORGANIC MATTER INTERACTIVITY IN MINE-WASTE CONTAMINATED SEDIMENTS IN TURKEY CREEK, JOPLIN, MISSOURI

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Zachary Collette

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ABSTRACT

Joplin, Missouri, part of the Tri-State Mining District (TSMD), has a long history of mining that resulted in mine waste piles proximal to the mines throughout the area. A local lead smelter also resulted in smelter fallout in Joplin. Mine waste pile runoff and local smelter fallout resulted in contamination of sediments, soils, and waterways. In the 1990s, remediation of residential soils and play areas began after blood lead levels in children were much higher than the national average. Soon afterwards, the chat piles were removed and used for beneficial reuse purposes. In May of 2011, an EF5 tornado devastated the town of Joplin, and spread contaminated soils across the area yet again. This study investigates relationships between total metal concentration; it's bioavailable fraction (exchangeable and carbonate-bound phases), potentially bioavailable fractions (reducible phases or metal stored in iron and manganese oxides) and their association to organic matter content, and magnetic susceptibility in sediments from Turkey Creek. Thirty-five samples from Turkey Creek were analyzed for total metal concentrations and bioavailability by assessing the percent of total metal released in the first two extractions according to the BCR sequential extraction scheme. Loss on ignition and magnetic susceptibility were determined to find any relation to either fraction. Fractionation trends were highly variable between sediment samples. 1-45% of Zn, 0-46% of Cd, and 0-11% of Pb occupied exchangeable and carbonatebound fractions, 3-97% of Zn, 2-91% of Cd, and 3-99% of Pb occupied iron and manganese oxide fractions and 2-97% of Zn, 8-94% of Cd, and 0-99% of Pb occupied organic and residual fractions of sediment. A risk assessment code (RAC) (%) was performed for Zn, Pb, and Cd where 17% of samples for Zn were considered very high risk and 23% were considered high risk, and 9% of samples for Cd were considered very high risk and 14% were considered high risk, whereas no Pb samples were considered high risk or very high risk. Total metal concentrations were high for Zn, Cd, and Pb in several samples, exceeding TSMD-specific Probable Effect Concentrations (PECs) in 57% of samples for Zn, 51% of samples for Cd, and 57% of samples for Pb. Further, 57% of samples exceeded the Sum Probable Effect Quotient which evaluates risk to aquatic fauna.

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INTRODUCTION

Heavy metal contamination can have severe ecological and human health effects. High concentrations of heavy metals can be concerning, but they may not directly correlate to toxicity. In order to do harm, heavy metals must be speciated so that they are able to interact with biota. The ability of the metal to interact with biota is termed bioavailability. In order to assess bioavailability, sequential extraction procedures are commonly used to identify the concentration of heavy metals present in fractions of sediment (fractionation) considered to be bioavailable (Rumah et al., 2017).

Fractionation allows us to more accurately predict the behavior of heavy metals in complex natural systems. Investigating the affinity of metals for different fractions is crucial in creating predictive equilibrium models accounting for changes in environmental conditions on metal uptake and/or release (Pagnanelli et al., 2004). Evaluating mobility of heavy metals bound to sediments and their associated response to a variety of conditions is a significant help in understanding the immediate risk the heavy metals pose and in developing an appropriate remediation strategy.

Heavy metals are naturally found in soil and sediment in trace concentrations as a result of weathering of parent materials (Wuana and Okieimen, 2011). However, anthropogenic activities related to mining, refining, smelting, disposal of mine tailings, sewage sludge, wastewater irrigation, coal combustion residuals, spillage of petrochemicals, and atmospheric deposition can cause accumulation of heavy metals beyond background concentrations that can threaten ecology and human health (Wuana and Okieimen, 2011).

One famous region where mine waste contamination is prevalent is the Tri State Mining

District (TSMD). The Tri-State Mining District encompasses roughly 2,500 square miles in southeastern Kansas, southwestern Missouri, and northeastern Oklahoma (USEPA, 2017). The Tri-State Mining District produced 50 percent of the zinc and 10 percent of the lead in the United States throughout 1850-1950 (USEPA, 2017). When mines were no longer profitable, mining ceased, and the waste left behind remained. Underground mine workings then recharged with groundwater and metal-rich groundwater began to discharge naturally (USEPA, 2017). Additionally, standing tailings piles were left to interact with runoff from precipitation, termed mine waste pile runoff, for decades (Schaider et al., 2014). In 1991, residential soil contamination was accepted as a primary source of elevated blood lead levels in children in the TSMD and remediation efforts began (USEPA, 2017). The TSMD will be discussed in greater detail later.

The purpose of this research is to use sequential extractions as a method of evaluating the amount of bioavailable metal and thus toxicity risk of lead, zinc, and cadmium in sediments of Turkey Creek in Missouri, part of the Tri-State Mining District. The specific objectives are (1) to determine the percentage of total metal that is present in the bioavailable fractions of sediment, (2) to assess sequential extraction procedures and general limitations of these procedures, and (3) to determine relationships about bioavailable metal, organic matter, and magnetic susceptibility. These research tools are applied to a segment of Turkey Creek by Joplin, which is located proximal to many old tailings piles, as well as a lead smelter.

BACKGROUND

Study Area

Ore emplacement for the Tri-State Mining District is still contested. However, a widely accepted view is that brine waters driven by the Ouachita fold-thrust belt picked up metals from Precambrian basement rocks and moved upward through faults until they reached the less permeable Cherokee shales and migrated laterally through the Mississippian host rock and mineralized as depicted in Figure 6 (Johnson et al., 2016).
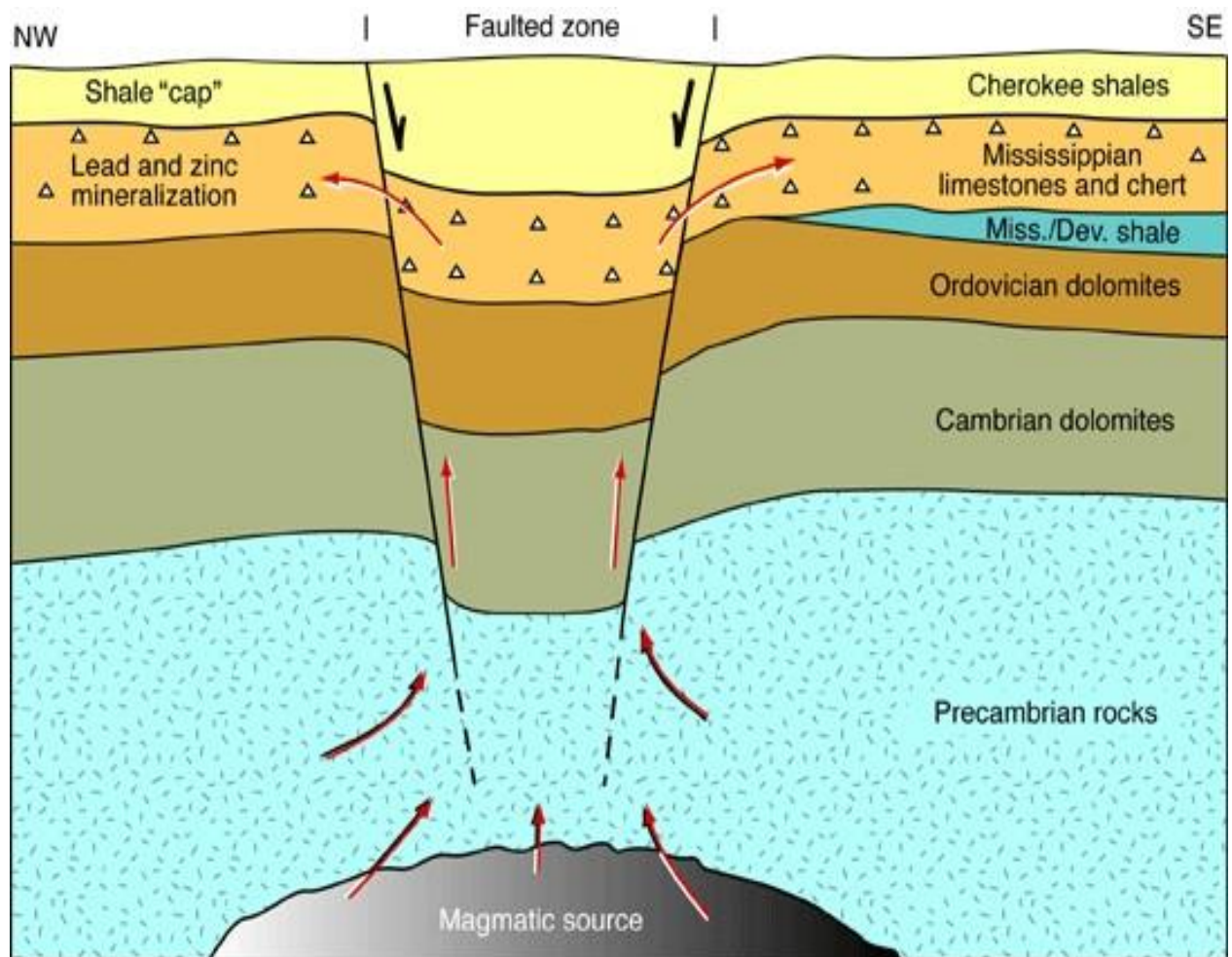
Figure 1 – TSMD ore emplacement depiction (Kansas Geological Survey, 2001).

The lithology of the ore-bearing rock is typical of southeast Missouri where the Missouri portion of the TSMD is located and consists of Mississippian age limestone with chert (Hambleton et al., 1959). The Warsaw and Keokuk formations are the most relevant ore-bearing formations in the Joplin area (Hambleton, et al., 1959). Figure 2 depicts a typical stratigraphic section through this area:

System	Formation	Bed	Thickness	Lithology
PENNSYLVANIAN		Cherokee	0-300'	Shale
		MAYES OR CARTER-VILLE	0-100' Unconformity	Limestone
MISSISSIPPIAN	WARSAW	B bed	0-?	Limestone
		C bed	25-32'	Limestone & chert
		D bed	18-22'	Cotton rock & chert
		E bed	5-8'	Ls. & chert nodules
		F bed	12-15'	Cotton rock & chert
		G bed	10-20'	Thin bedded banded dark grey & brown chert & brown limestone
		H bed	15-20'	
		J bed	0-40' Unconformity	Glauconite speckled ls. with phosphate pebbles, some dark chert nodules
	KEOKUK	K bed	0-40'	Chert nodules in light brown ls.
		L bed	0-35'	Cotton rock & dense chert
		Short Creek Oolite	2-10's	
		M bed	0-70'	Chert nodules in light brown limestone
		N bed	20-30' Chert	Cotton rock chert mostly dense chert
		O bed	8-10'	Banded chert & limestone
		P bed	0-10'	Dense chert
		Q bed	0-10'	Banded chert & limestone
	REEDS SPRING	R bed	50-100'	Dark chert nodules in dark brown limestone
		Fern Glen	50'+	Grey chert nodules in soft grey limestone & green shaly limestone

After J.P. Lyden, 1949

Figure 2 - Stratigraphic column of TSMD-area (Hampleton, et al. 1959).

The Tri-State Mining District

The Tri-State Mining District includes parts of Kansas, Missouri, and Oklahoma. It

encompasses an area of a little more than 3,000 km^2 (Brockie et al., 1968), with lesser satellite

deposits that extend to the east (Figure 3). The TSMD was first mined for lead in the mid-1800s

but soon became a major producer of zinc. Mining activities in the TSMD ended around 1950

(Brockie et al., 1968; Beyer et al., 2004) and then mining wastes laid exposed.
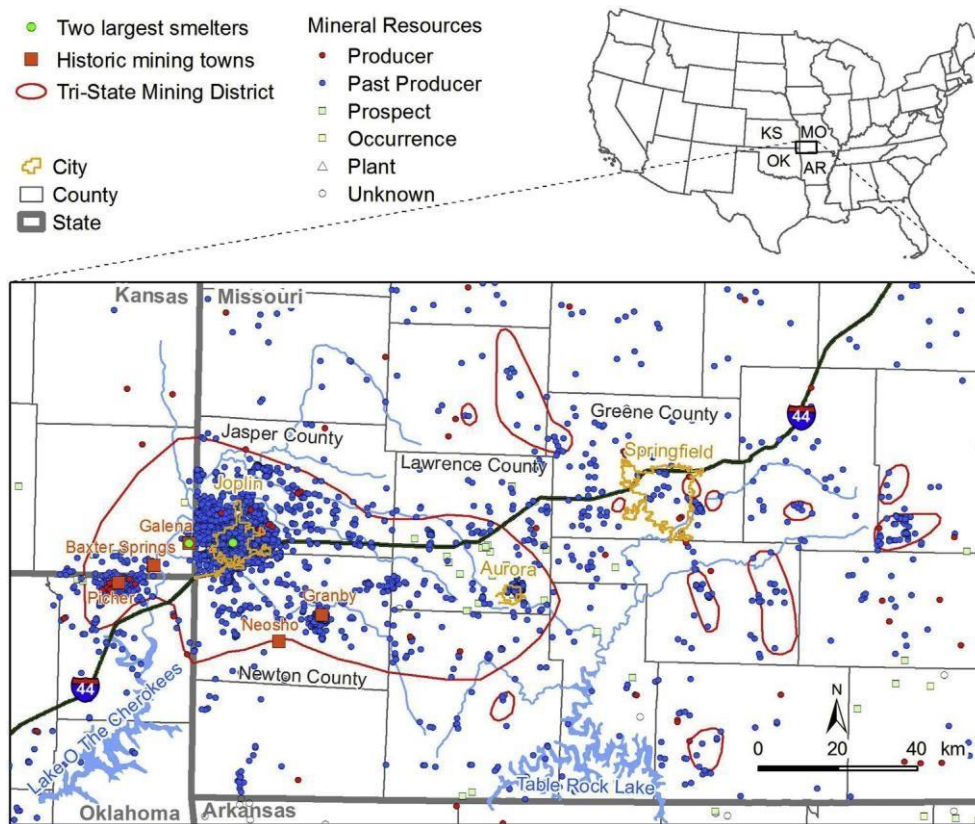
Figure 3 – Extent of the Tri-State Mining District and satellite deposits (red) with Joplin centered among a high concentration of local mines (from Gutierrez et al., 2015).

Joplin, a historic mining town in southwestern Missouri, belongs to the TSMD. Mining

was concentrated in the central and eastern parts of town. Mining and smelting began in Joplin as

early as 1830, peaked from 1900-1950 and continued through the 1970s (USEPA, 2017). Additionally, a lead smelter that operated in town (location depicted in Figure 4) resulted in airborne contamination of lead in dangerous concentrations across residential areas (USEPA, 2017). In 1991, a large-scale health study conducted by various agencies aimed to learn how residents were affected by mine-related contamination (USEPA, 2017). The study showed that approximately 14% of children ages 7 and under at the site had blood lead levels in excess of 10μg/dL (USEPA, 2017). This study prompted the remediation efforts that continue today. Chat piles, a local term for piles of waste rock, were remediated in steps and there are currently no more standing chat piles in Joplin.

Zinc is more abundant in the TSMD ore than lead, but lead is very important for environmental reasons because of its higher toxicity. Cadmium is present in association with zinc (Brockie et al. 1968) and is highly toxic to aquatic life even at small concentrations. These are the three metals of concern within this study area. Turkey Creek was chosen for its proximity to old chat piles and the smelter. Turkey Creek and Tar Creek were found to have the largest concentrations of lead, zinc, and cadmium in gravel-bar sediment samples compared to other TSMD waters such as Center Creek, Shoal, Creek, and Spring River (Smith, 2016). Turkey Creek runs NW from the east side of town through central Joplin until it eventually converges with the Spring River. This makes it an ideal sampling locality to assess if sediments still possess a dangerous amount of mobile heavy metals decades later.
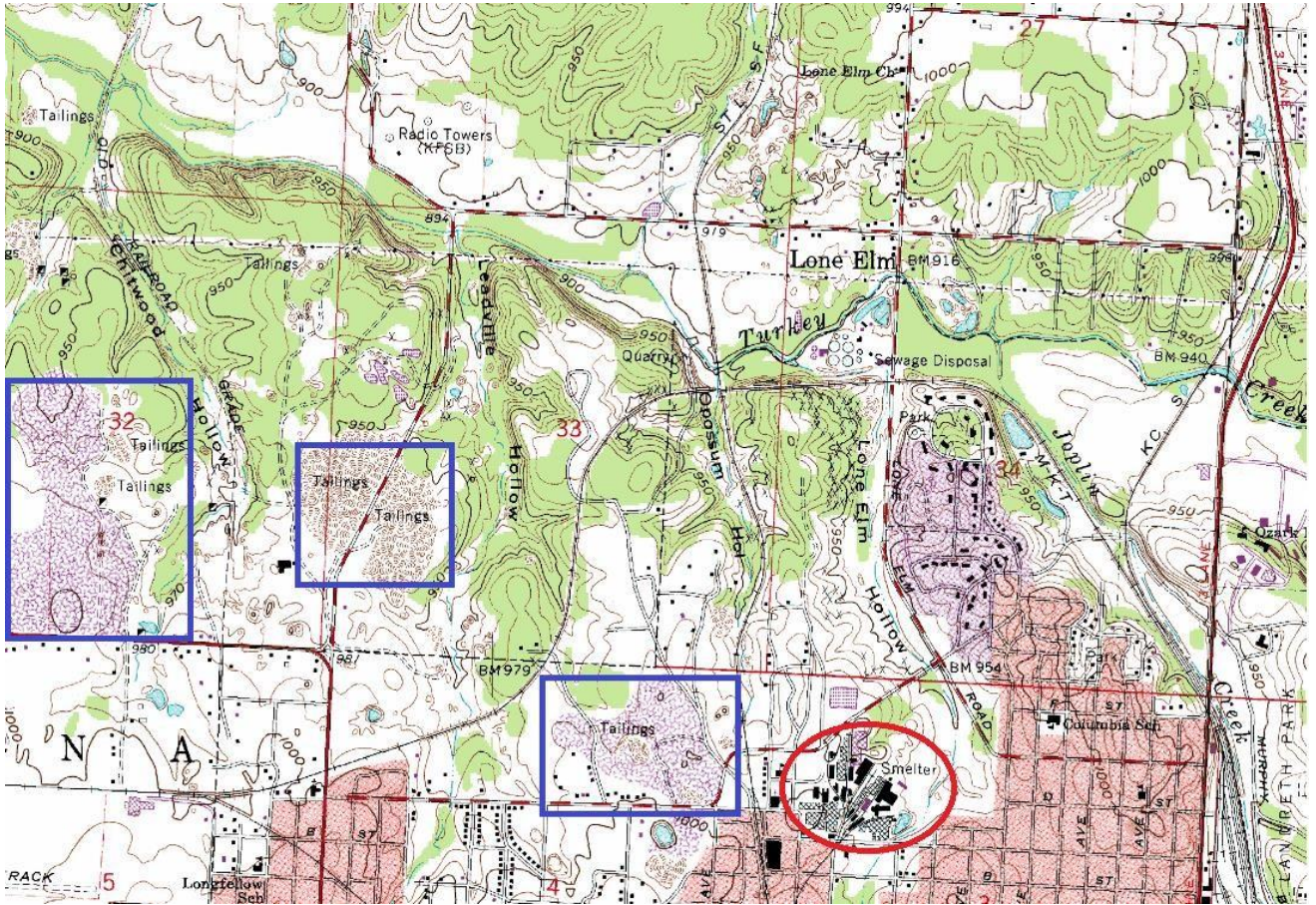
Figure 4 - northern Joplin 1939 topographic map showing the location of the smelter (red circle) and tailings piles (blue rectangles). Turkey Creek runs east to west in the central portion of the map, proximal to the tailings piles and smelter.

Heavy Metal Contamination

Heavy metal elements are defined as having a density of at least 5 times that of water (Tchounwou et al., 2014). Lead and cadmium are heavy metals of interest in the study area due to their toxicity, and because their insolubility, they are extremely persistent in the environment (Tchounwou et al., 2014). Mine waste is often a significant source of heavy metal contamination. Mine waste enters waterways in two ways: direct acid mine drainage from a mine and runoff from mine waste piles (chat, tailings) (Schaider et al., 2014). While mine drainage typically becomes less concentrated as decades pass, mine waste pile runoff retains a relatively constant

concentration of heavy metals. This indicates that mine waste pile runoff should be given priority over mine drainage in mitigation attempts (Schaider et al., 2014).

At one point, around 200 mines were found within the Newton County Mine Tailings Site (USEPA, 2017). During mining, the underground mines at the site were beneath the water table, and consistently refilled with groundwater so that the mines had to be regularly pumped. After cessation of mining, metal-rich waters accumulated within the mines and discharged to nearby waterways. Proximal waterways became acidic and had significant metal loading during this time. The carbonate rocks in the area ultimately buffered the acidity from this effect so that water is only slightly acidic now (USEPA, 2017).

Mine waste pile runoff effects attenuated less over time than mine drainage (Schaider et al., 2014), as rainfall interacts with metal-rich chat piles and carries fine grained material into creeks. This material often aggregates with carbonates, iron oxides, and organic matter and settles out in creek beds. While heavy metals dissolved in water tend to attenuate naturally from continued discharge and interaction with sediments, sediment often acts a sink for heavy metals, termed memory effect (Johnson et al., 2016). This ability to retain heavy metals is why sediments are the focus of this study.

Ecological Effects

Soil microbe abundance and activity was significantly reduced in heavy metal contaminated soils (Kuperman and Carreiro, 1997), and the activity of soil enzymes slows significantly in areas with high heavy metal concentration relative to unpolluted areas (KanzioraCiupa et al., 2016). Soil enzymes are important for maintaining fertility in soils and fostering productivity in ecosystems (Kandziora-Ciupa et al., 2016). Plants in heavy metal

polluted sites exhibit altered metabolism, and lower biomass production (Nagajyoti et al., 2010). Heavy metals have the potential to accumulate faster than they can be broken down in living organisms and continually build up to higher concentrations, especially in higher trophic order organisms (Beyer et al., 2004). This effect, termed biomagnification, occurs so frequently that certain bird species can be bioindicators for heavy metal pollution (Beyer et al., 2004). Birds within the TriState Mining District are among the first free-flying wild birds reported to have severe zinc poisoning (Sileo, et al. 2003). Beyer et al. (2004) found increased concentrations of lead in waterfowl.

Attempts to quantify the amount of heavy metals in sediments that are considered dangerous have been the focus of many studies. A severe effect level (SEL) concentration for chemicals of concern was developed to protect benthic species such as the burrowing mayfly, *hexagenia limbata* and aquatic biota such as fathead minnows, *pimephales promelas* in which harmful effects were expected (Persaud et al., 1993). Similarly, MacDonald et al. (2000) used various published sediment quality guidelines (SQGs) to propose a consensus based SQG for 28 chemicals of concern. They divided the SQGs into two types: threshold effect concentration (TEC) referring to the concentration below which harmful effects are unlikely and probable effect concentration (PEC) referring to the concentration above which harmful effects in species such as *ceriodaphnia dubia*, *daphnia magna*, *H. azteca*, and *C. tentans* are likely (MacDonald et al., 2000). They tested these values to attempt to accurately predict toxicity and reported an 89.6% accuracy for lead, a 90.0% accuracy for zinc, and a 93.7% accuracy for cadmium with a sample size of 347 (MacDonald et al., 2000). Additionally, MacDonald et al. (2009) provided a sum probable effect quotient for cadmium (mg/kg), lead (mg/kg), and zinc (mg/kg) ($\sum PEQ_{Cd,Pb,Zn}$) which is calculated using the following equation:

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

The sediments are considered low risk if they meet these criteria. If the sediments equal or exceed 7.92 they are considered high risk sediments for macroinvertebrate amphipods (MacDonald, et al. 2009).

Human Health Effects

The adverse effects of heavy metals on human health are well documented by organizations such as the World Health Organization (WHO) (Jarup, 2003). The most direct and most prevalent pathway of human exposure is through eating of contaminated plants, fish or other animals, although direct exposure to contaminated sediments and soils is also dangerous (Jarup, 2003). Within the TSMD, lead and cadmium are contaminants of concern due to their high toxicity while zinc is poisonous in sufficient amounts, but is still an essential nutrient. Wild carp, catfish, and crayfish in the Neosho River and Spring River were found to have sufficiently high concentrations of Pb and Cd to represent a potential risk to human consumers (Schmitt et al., 2006).

Lead's ability to mimic calcium in the body and to interact with proteins allows it to interfere with numerous vital processes (Tchounwou et al., 2014). Lead poisoning in children is especially detrimental and results in lower IQs, delayed or impaired neurobehavioral development, growth retardation, poor attention spans and anti-social behaviors (Tchounwou et al., 2014). Brain, kidney, and gastrointestinal damage can occur in acute exposure in adults, but the nervous system is the most sensitive system to lead poisoning (Tchounwou et al., 2014, Wani et al., 2015).

Cadmium is toxic in even lower concentrations than lead, and it is a severe gastrointestinal irritant by ingestion and pulmonary irritant by inhalation. Chronic exposure may lower levels of norepinephrine, serotonin and acetylcholine in the brain (Tchounwou et al., 2014). The mechanisms responsible for cadmium's toxicity are not well understood, although the formation of reactive oxygen species in the body is a current speculation (Tchounwou et al., 2014). Ecological contamination of plants, fish, birds, and unsafe drinking water all contribute to human exposure, though occupational exposure is more common. (Jaishankar et al., 2014)

Zinc is an essential element for humans, meaning it is needed in the diet for proper functioning unlike lead and cadmium. Zinc is present in the TSMD in concentrations far greater than lead and cadmium, and extremely high concentrations of zinc may negatively affect human health. Zinc most often enters the environment through mining (ATSDR, 2005). Recommended Dietary Allowances (RDAs) for zinc are 11mg/day for men and 8mg/day for women (ATSDR, 2005). If large doses of zinc (10-15 times that of the RDA) are ingested, acute effects of cramps, nausea and vomiting can occur. Chronic exposure at these levels may cause anemia, damage to the pancreas, and decrease levels of high-density lipoprotein (HDL) cholesterol. Zinc ingestion equal to 1,000 times the RDA in rats reportedly led to infertility and smaller babies in already pregnant rats (ATSDR, 2005). Consuming too little zinc is often a larger problem than toxic zinc exposure (ATSDR, 2005). However, there is still much evidence that fish and waterfowl within the TSMD are negatively affected by zinc where birds and fish were both found to be poisoned by zinc (Sileo et al. 2003, Beyer et al., 2004, and Schmitt et al., 2007).

Bioavailability of Heavy Metals

Bioavailability of metal refers to the portion of metal that can be incorporated into biota and have an active effect. While high total concentrations of heavy metals such as lead and cadmium in sediments are of concern, total concentration alone does not necessarily correlate to the heavy metals that could interact with biological species. Depending on what mineral heavy metals are bound to, they may stay bound, incorporate into a new mineral, or dissolve under natural conditions given time for the reaction to occur.

Water's pH, redox potential, temperature, the percent of organic matter in sediments, sediment size, and presence of Fe-Mn oxides in sediments are all factors that can influence bioavailability of heavy metals (Schaider et al., 2014). Many studies in the 1970s and prior used concentration as a proxy for toxicity despite knowing the two were not equivalent (Tessier et al, 1979). Since then, many efforts have been made to understand and quantify bioavailability of heavy metals using sequential extractions (Rauret et al., 1999, Silveria et al. 2006, Leleyter and Probst, 1998).

One method of evaluating bioavailability is to employ a risk assessment code (RAC) (%). This is frequently used in conjunction with the BCR method as F1 represents the exchangeable and carbonate-bound fraction, F2 represents the iron and manganese oxide fraction, F3 represents the organic and sulfidic fraction, and F4 represents the residual fraction. After obtaining a percentage, 0-1% is considered no risk, 1-10% is considered low risk, 11-30% is considered medium risk, 31-50% is considered high risk and >50% is considered very high risk.

$$RAC\ (\%) = \left(\frac{F1}{F2 + F3 + F4} \right) \times 100$$

Metal Speciation

Solubility for ZnS, CdS, and PbS tends to be very low/nearly insoluble at 25°C in water. The solubility product constant of ZnS is $\sim 1.0 \times 10^{-13}$, CdS is 1×10^{-28} and PbS is 1.0×10^{-28} (Sillen, et al., 1965). Cadmium occurs widely as a trace metal that has substituted for zinc and is not part of a main ore itself (although a few specimens of the sulfide Greenockite, CdS, were found in the TSMD (Brockie et al., 1968)). All sulfides can be oxidized when exposed to the surface, converting them from PbS, ZnS and CdS to $PbSO_4$, $ZnSO_4$, and $CdSO_4$. Similarly, if carbonate is available, which is the case in the TSMD, these sulfides weather to become carbonates.

Metal sulfides are most stable under reducing conditions (Pearson, 2017). After these sulfides are exposed to oxygen-rich waters, they become unstable (Carroll et al., 1998). Zinc and cadmium respond similarly to pE and pH changes with one key difference – $ZnCO_3$ occurs in a narrow range of conditions (pH $\sim$7.8-8.2 and oxidizing conditions) whereas $CdCO_3$ remains stable into basic conditions (pH 8-11) (Figures 3 and 4) (Pearson, 2017). When 11 > pH > 8.2 Zn occurs as ZnO instead, but Cd will be present as $CdCO_3$ as stated before and will not be found as CdO in any conditions (Figures 5 and 6). This difference aside, Zn and Cd are both free ions at acidic and oxidizing conditions, and they form hydroxides in response to basic and oxidizing conditions.

Zn-C-S-O-H System
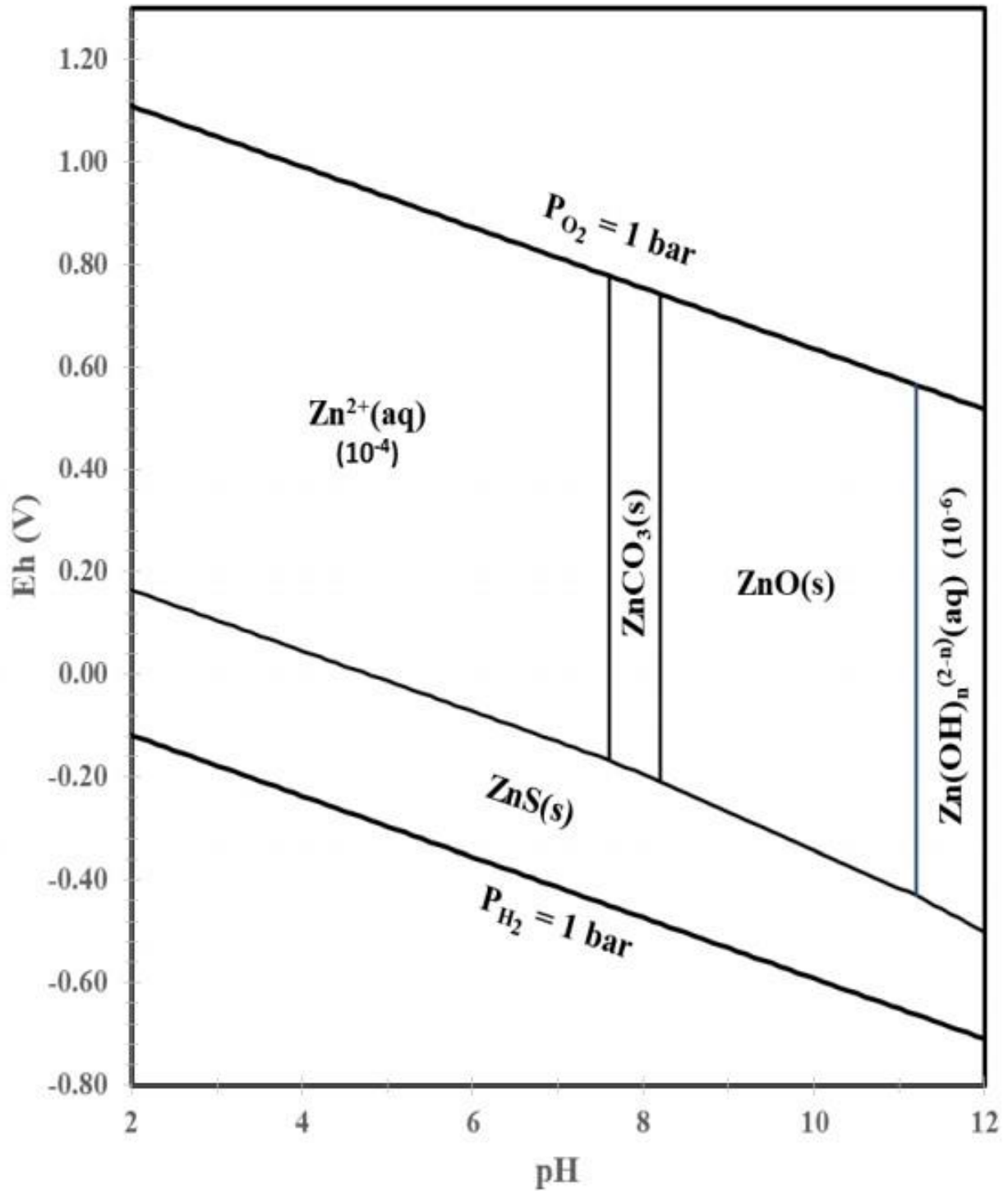
Figure 5 – Eh-pH diagram of Zn-C-S-O-H from Pearson (2017) calculated using free energy of formation values.

Cd-C-S-O-H System
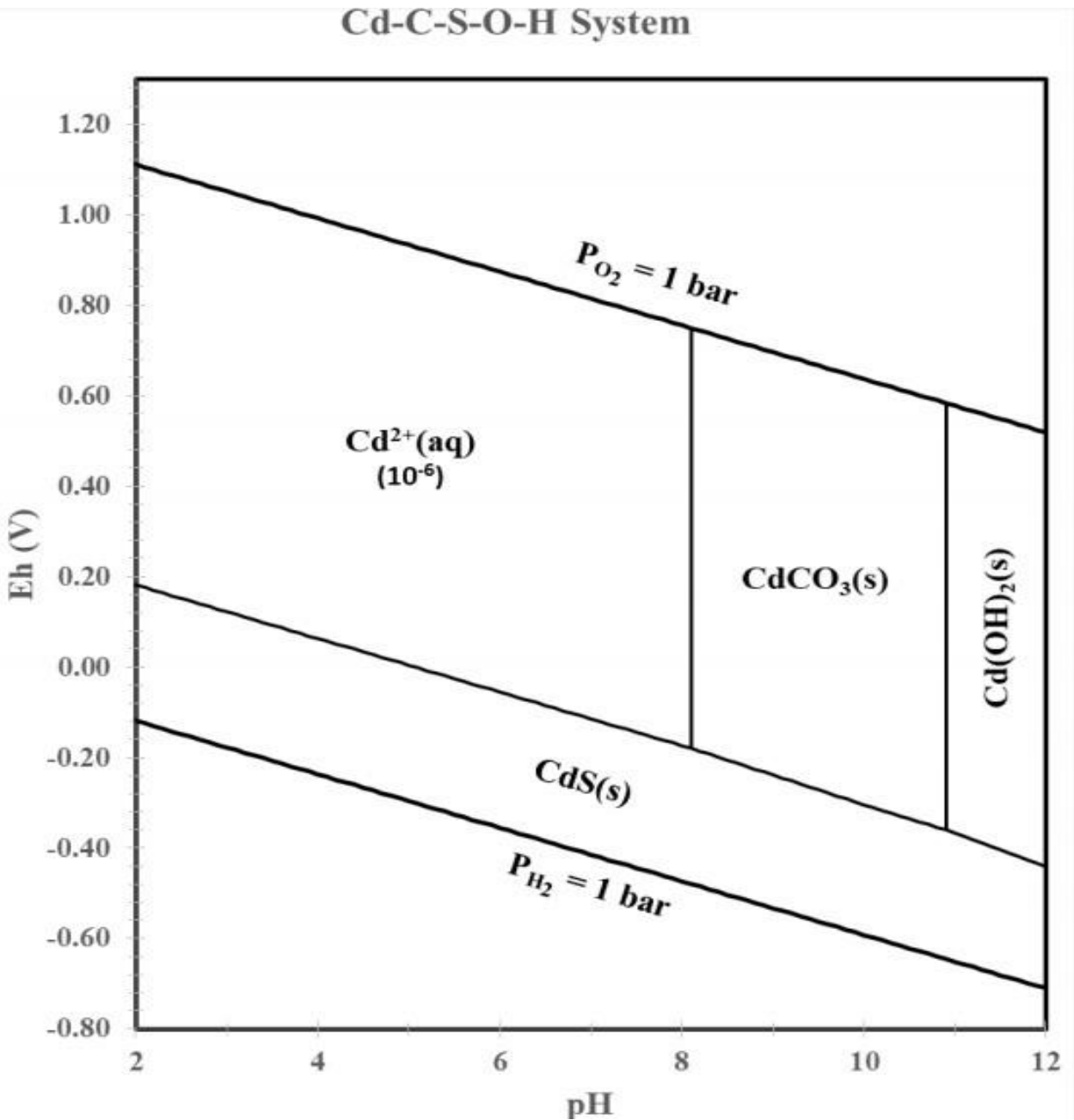
Figure 6 - Eh-pH diagram of Cd-C-S-O-H from Pearson (2017) calculated using free energy of formation values.

Lead speciation is quite different than that of cadmium or zinc. Over a wide range of conditions (~pH 6-11 and Eh -0.3 to -0.9) $PbCO_3$ is the dominant species. Below pH 6 and at

similar Eh PbSO$_4$ is dominant. Pb forms various oxides (PbO, Pb$_3$O$_4$ and PbO$_2$) in response to basic conditions (>11.5 pH) and oxidizing conditions. Regarding these oxides, PbO$_2$ requires the highest Eh to be stable, then Pb3O4, and finally PbO shown in Figure 6 (Pearson, 2017).
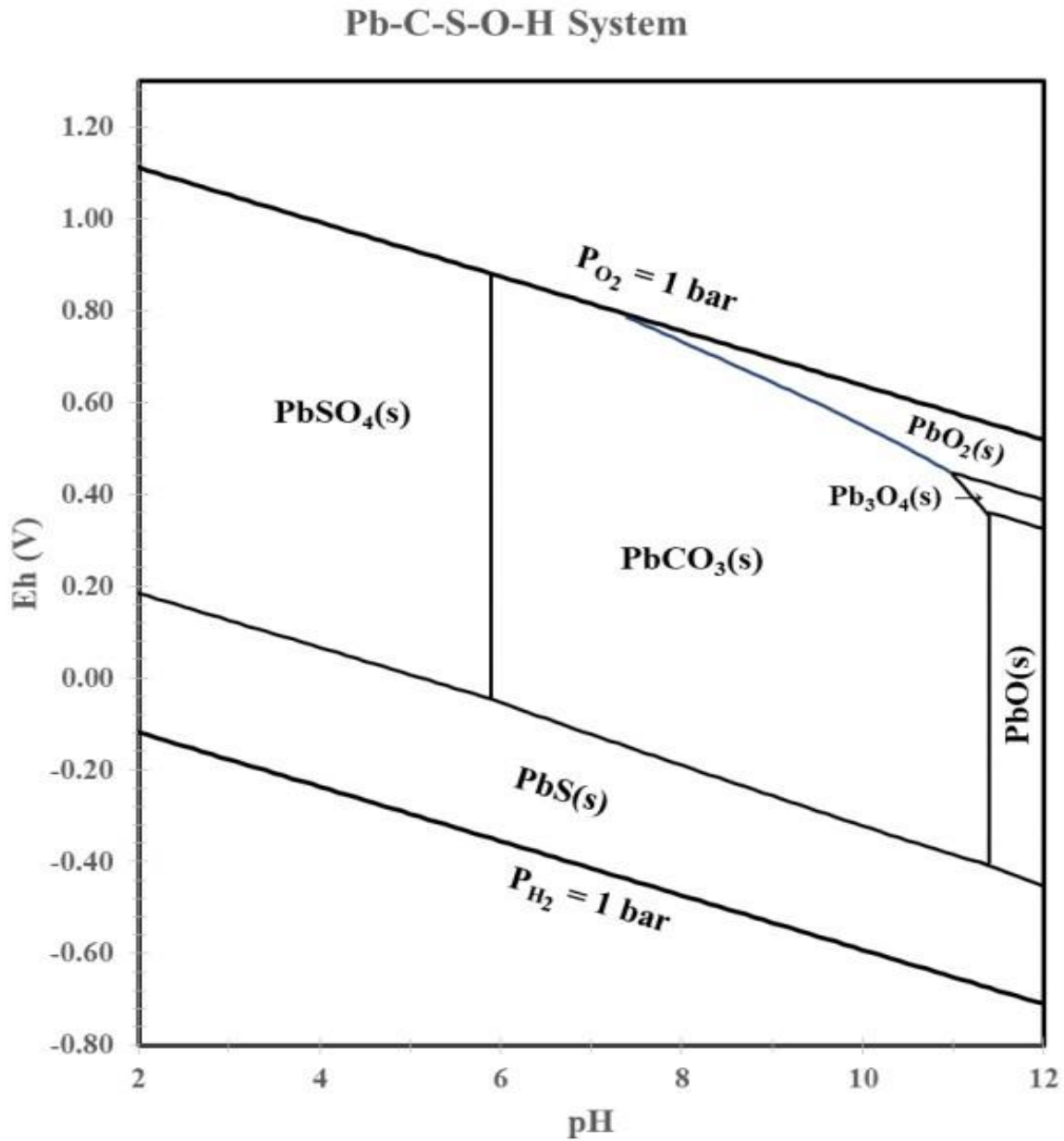
Figure 7 - Eh-pH diagram of Pb-C-S-O-H from Pearson (2017) calculated using free energy of formation values.

Pourbaix diagrams have the limitation of not incorporating interactions of the species with other components of complex natural systems (Pearson, 2017). This leaves out ion sorption, which is an incredibly important mechanism regarding the fate of metals in any watershed. Metals can be removed from the water column by secondary mineral precipitation (e.g. form carbonates or hydroxides), coprecipitation, and sorption into organic matter and iron and manganese oxides (Schaider et al., 2014). Further, iron oxides vary widely in their composition, morphology and physiochemical properties adding another complexity to the situation (Schaider et al., 2014). Organic matter also spans a wide range of compounds, most important being humic substances, and particularly fulvic acid (Linnik, 2013).

The host rock in the TSMD is a Mississippian age carbonate, which contributes to higher alkalinity of the watershed (Carroll et al., 1998). Carrol et al. (1998) found that uptake by iron oxides and carbonates, degassing of CO_2-rich groundwater, iron-catalyzed sulfide dissolution, and uptake and release kinetics are the most important factors governing the fate of lead, zinc and cadmium in the TSMD.

As stated above, TSMD waters should have high alkalinity. This gives the water a natural buffer against pH changes. However, acid mine drainage problems resulting from the formation of sulfuric acid after oxidation of pyrite could result in the destruction of that natural buffer (Schaider et al., 2014). In this watershed, acid mine drainage effects should have attenuated because of remediation attempts decades ago where only contaminated sediment and soils are left. Interactions of the water with the CO_2-rich atmosphere may also contribute to some acidity in the watershed. Biological factors will generally include microbiota utilizing redox reactions as an energy source for metabolism and shifting pE values. Biomass can use excess oxygen in a waterway until conditions become anoxic. Physical factors that can influence water bodies

include temperature and interactions with the atmosphere. Temperature and sunlight can cause stratification in a water body and not allow for the cycling of oxygen, causing an oxidized layer to form closer to the surface and a reduced layer to form close to the bottom sediments. These physical, chemical, and biological factors affect the pE and pH of water which influences fractionation of sediments and which fractions are stable, though there are many more mechanisms and factors to include in a complete review.

Sequential Extractions

Sequential extractions refer to a series of different, but specific, chemical solutions applied to samples so that metals release from a certain fraction of the sample (Zimmerman and Weindorf, 2010). This is meant to be a stepwise procedure showing concentration of metals that are occupying each fraction of the sample, which is more representative of contamination risk than metal concentration alone (Margui et al., 2004). The extractions are meant to relate to specific environmental conditions under which heavy metals may be released from their fractions and thus available for biological uptake.

There are typically five fractions of sediments that heavy metals can be bound: exchangeable, carbonate-bound, Fe-Mn oxide bound, organic matter bound, and residual (Tessier et al., 1979). These fractions are listed in order in which metals are most bioavailable to least bioavailable. The exchangeable fraction can be removed by a change in ionic composition, so a salt solution will easily release these metals (Zimmerman and Weindorf, 2010). The carbonatebound fraction is sensitive to pH changes and will be released under mildly acidic solutions

(Zimmerman and Weindorf, 2010). Fe-Mn oxide bound metals will release their adsorbed heavy metals under reducing conditions (Zimmerman and Weindorf, 2010). Organic bound heavy metals will not release except under strong oxidizing conditions (Zimmerman and Weindorf, 2010). Finally, the residual fraction will only release under strongly acidic conditions capable of dissolving silicate structures (Zimmerman and Weindorf, 2010).

Sequential extraction procedures generally follow this model described by Zimmerman and Weindorf (2010), but many modifications have been implemented. Starting in 1979, Tessier et al. released a five-step sequential extraction procedure to identify the fractionation of trace metals within soils and sediments. In their research, they state that their goal was to move away from using concentration as a proxy for toxicity because of the inaccuracies. Tessier et al.'s (1979) sequential extraction procedure was not perfectly reproducible, but their study gave way to many more studies. In 1999, the European Commission Bureau of Reference (BCR) released a collaborative project to create an accepted sequential extraction procedure that could be widely used so results worldwide would be more comparable (Rauret et al., 1999). The BCR sequential extraction procedure has three steps which combine the exchangeable and carbonate bound fractions into a single step. The BCR sequential extraction procedure has been used successfully in a variety of applications (Zemberyova et al., 2006, Poykio et al., 2013, Margui et al., 2004). Schaider et al. (2014) focusing on Tar Creek within the TSMD, used a more selective procedure involving eight fractions instead of the five originally used by Tessier et al. (1979). The fractions are: water soluble, exchangeable, carbonates, Mn-oxides and carbonates, amorphous Fe and Al oxides, organic matter, crystalline Fe oxides, and residual (Schaider et al., 2014).

Despite the promise that sequential extractions show in separating metal stored in each chemical fraction, they also have limitations. Nonselectivity of the reagents may alter the

surficial chemistry of the sediments tested. This potentially allows released metals to sorb onto the remaining fractions during the process. Model soils used by Shan and Chen (2010) showed that this type of redistribution does occur. Soil properties and the chemical properties of each specific metal affect how much this process occurs (Shan and Chen, 2010).

Ryan et al. (2008) used X-Ray Diffraction (XRD) between each extraction step and found that the octahedral layer of tri-octahedral clays was destroyed from the extraction process. This means that the metals released in the first extraction steps may reattach to a different fraction and be released again later thus skewing the true bioavailability results (Ryan et al., 2008).

Quantifying fractions of heavy metals using sequential extractions will tend to underreport the amount of exchangeable, carbonate-bound and reducible-bound fractions and report too high of values for organic bound and residual metals (Zimmerman and Weindorf, 2010). Coupling sequential extractions with XRD analysis to identify the exact solid components present may be useful in producing a complete understanding of the amounts of metals present and their potential bioavailability (Zimmerman and Weindorf, 2010). XRD analysis can assist in the interpretation of extraction results but can be limited in its ability to do so. Some suggested limitations are the lack of specificity of extraction procedures along with high XRD detection limits and a large amount of amorphous material within samples.

Magnetic Susceptibility

Magnetic susceptibility measures the concentration of magnetic minerals in soil and sediment (Rachwal et al., 2016). Anthropogenic processes such as mining, refining and smelting can lead to an abundance of iron oxides which typically coexist with heavy metals. Heavy metals can either be adsorbed onto the surface of iron oxides or directly incorporated into their structure

(Rachwal et al., 2016). Using magnetic susceptibility as an approximation of contamination by heavy metals has been successful in a variety of studies (Rachwal et al., 2016, Salehi et al., 2013, Lu et al., 2007).

Magnetic susceptibility has been used successfully to pre-concentrate iron-rich sphalerite in other Pb-Zn deposits to reduce loading to the flotation process and reduce grinding costs, reagent consumption, wastewater treatment cost, and tailings treatment cost (Jeong and Kim, 2018). Sphalerite was the major sulfide mineral present in these deposits, and higher iron content correlated with higher magnetic susceptibility and higher-grade ore (Jeong and Kim, 2018).

Loss on Ignition

Total organic content refers to the percent of sediment or soil that is organic matter. Organic matter has a strong affinity for heavy metals and often acts as a natural sink for them. Humic substances that naturally occur from degradation of organic matter form complexes with heavy metals which can decrease the heavy metal's bioavailability (Wright et al., 2012). Measuring the amount of total organic content in sediment samples can provide insight into expected fractionation of heavy metals. The loss-on-ignition method is an easy and inexpensive way to measure organic content in samples (Wright et al., 2012). The general procedure is that samples are oxidized through high temperatures (>550°C), and the mass loss is directly proportional to the organic matter content of the sample (Wright et al., 2012). Sediments of the Tar Creek area of the TSMD were reported to contain about 18-25% organic matter (Schaider et al., 2014).

However, loss on ignition methods can be affected by carbonate loss and thus affect the amount of organic matter reported. Loss on ignition values were compared against Ca

concentrations and correlation was investigated as a means to assess the significance of the influence on carbonate loss on our reported % mass loss values.

Iron Normalization

Studies on metal contamination often do not discriminate among natural and anthropogenic sources (Ho et al., 2012). Metals from both natural and anthropogenic sources accumulate in sediments, and it is difficult to discern if the concentrations are the result of anthropogenic input or biogeochemical processes (Ho et al., 2012). For this reason, different normalization procedures have been used to more accurately portray what represents a natural metal sedimentary load and what represents anthropogenic input. Normalization procedures usually involve two parts: a granulometric approach, and a geochemical correction (Roussiez, et al. 2005).

The granulometric approach involves separating the clay fraction from the rest of the sample (<2µm). However, this is generally laborious and is not practical for many researchers (Roussiez et al., 2005). Instead, the clay and silts fraction are typically combined (<63µm). This is because metals tend to concentrate in fine-grained fractions of sediment. Granulometric normalization may still not correct natural metal variability however, because metal contents and their variability are not just a function of grain-size distribution, but also their composition of primary and secondary minerals (Roussiez et al., 2005). Granulometric normalization should include geochemical normalization to identify variability between size fractionation of samples as well as differences in speciation of the metals.

Geochemical normalization involves using a normalizing element to correct concentrations to highlight anthropogenic input. Several normalizing elements can be chosen, but the choice is important. Normalizing elements should meet three prerequisites to be effective (Roussiez, 2005). The first is that the normalizer should covary proportionally to the naturallyoccurring contents of the metal of interest (Ho et al., 2012). Secondly, the normalizer needs to be insensitive to anthropogenic inputs (Ho et al., 2012). Thirdly, the normalizer needs to be stable and uncompromised by environmental influences such as redox reactions, adsorption/desorption, and other diagenetic processes (Ho et al., 2012). Such elements are considered conservative elements, because they are present in large concentrations naturally over a wide geographic distribution and are less likely to be affected by small variations caused by anthropogenic input (Roussiez, 2005). Aluminum and iron are frequently-used conservative elements, though iron is often used less because of its sensitivity to changes in redox conditions (Ho et al., 2012).

METHODS

Sampling

Sampling was conducted in three separate sampling days, one trip collected 20 samples in Turkey Creek just south of Missouri Southern State University going northwest (downstream) (Fall of 2017). Later, five samples were discarded due to an inadequate amount of fine sediments (<1mm). The second trip (Spring of 2018) began south of Duenweg upstream of the first location and the final trip connected the area between them. On the first trip, two samples were collected every 1/10th of a mile. After this first sampling trip and beginning to work out the lab methodology and assessing how many samples could be evaluated considering limitations such as funding and time, further trips were spaced further to cover a larger spatial extent. On the second and third trips (Spring of 2018), one sample was collected every ¼ mile. Five Turkey Creek samples collected by Jessica Peebles in 2013 were added to this research bringing the total sample number to 35. Figure 8 shows the location of all samples within Turkey Creek. Appendix A includes the latitude and longitude of all samples collected as well as element concentration data.
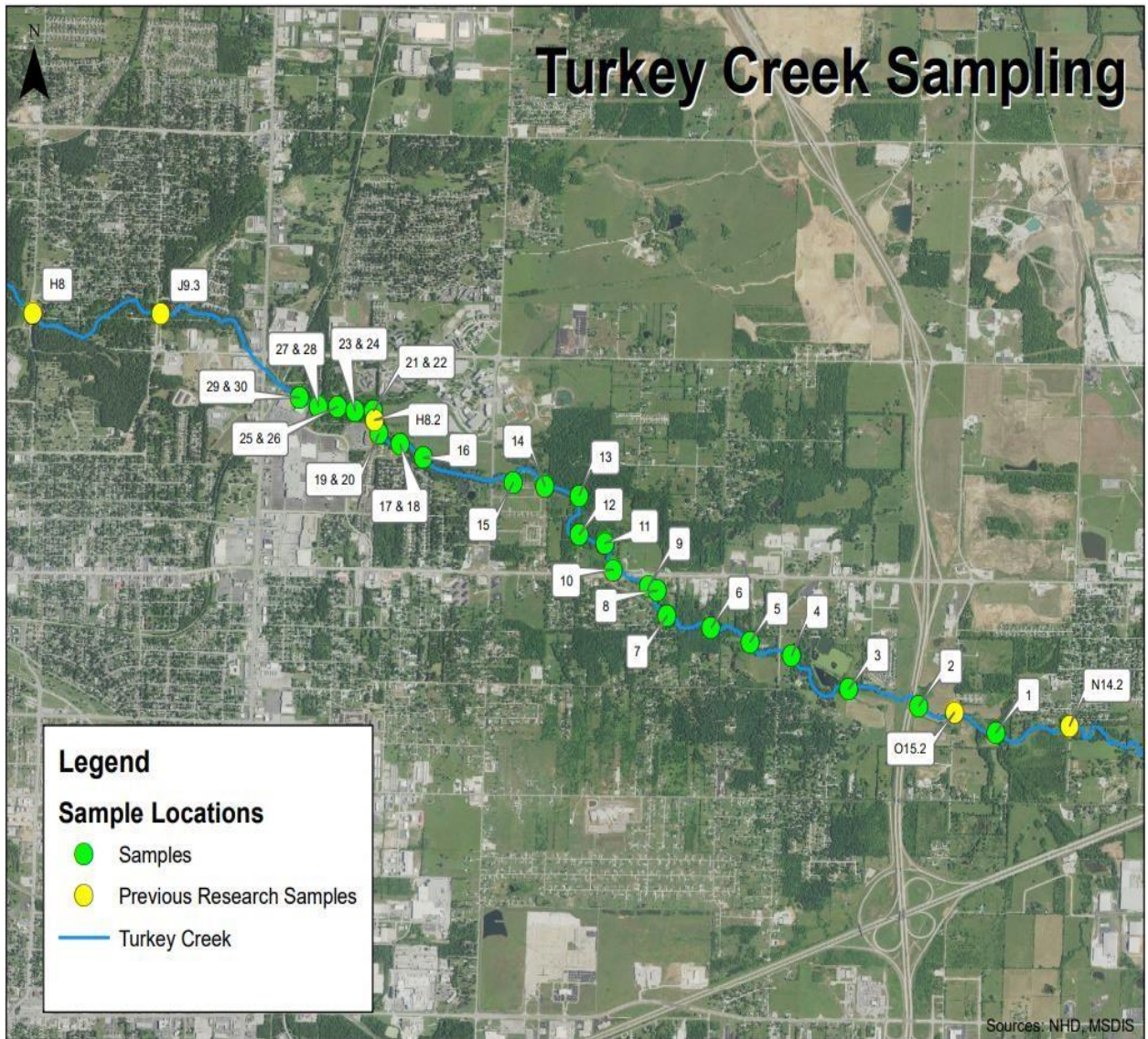
Figure 8 ─Sampling locations within Turkey Creek in the Joplin area. Turkey Creek runs East to West. Inset map: Black square on Missouri State map shows extent of sampling locations.

Lab Methodology

        Sample Treatment. The samples were air dried, disaggregated with pestle and mortar and sieved to 1mm. Grains larger than 1mm were discarded. Some samples were composed of mainly sand and gravel particles with not enough fines for further analysis. A total of 35 samples were then sent to a commercial lab for total metal analyses via acid digestion with aqua regia and ICP-MS.

        Sequential Extractions. Two sequential extraction techniques were carried out in the laboratory as described by Rauret et al. (1999). Glacial acetic acid (0.11 mol L^{-1}) (Solution A) was prepared by mixing 25 mL of glacial acetic acid to about .5L of distilled water in a 1 L graduated flask and made up to volume with distilled water. Then, 250mL of this solution (0.43 mol L^{-1}) was added to a 1 L graduated flask and diluted to volume to bring the molarity to 0.11 mol L^{-1}. This solution was applied to the sediments the day it was made. 40mL of this solution was added to 1g of sediments in 50ml polypropylene centrifuge vials. The centrifuge vials were placed on a manual shaker on their sides in a basket, and the basket was secured to the shaker to prevent leaking. Caps need to be checked for complete tightness to prevent any leaking. The samples were then shaken for 24 hours automatically. The samples were centrifuged at 2500 rpm for 10 minutes and carefully extracted from the centrifuge. The solution was decanted and then filtered using Fisherbrand filter paper, with medium porosity and slow flow rate, into a separate centrifuge vial and all the solutions from the first extraction were stored in the refrigerator.

        The extractions are performed stepwise, so the second extraction was performed on the sediments that have already undergone the first extraction. Hydroxylamine hydrochloride .5M (Solution B) was prepared according to Rauret et al. (1999). The solution was prepared by

dissolving 34.75g of hydroxylamine hydrochloride in 400ml of double-deionized water. Then,

the solution was transferred into a 1L graduated flask. Next, 25ml of 2 mol L^{-1} HNO₃ was added

to the 1L graduated flask containing the dissolved hydroxylamine hydrochloride and then made

up to volume with double deionized water. 40ml of this solution was applied to the sediments

from the previous extraction and set to shake for 24 hours as described above. The following day,

the solution was decanted and filtered as described previously and the sediment was disposed of.

ICP Analysis. There were two uses of the ICP, the first being in Spring of 2018 and the

second being in Spring of 2019. The second run was done on a different ICP than the first, and

different methods were employed. Table 1 below shows the ICP standards used for the

calibration curve in the first ICP run in Spring of 2018.

Table 1 - Standards for 1st ICP run (Spring 2018).

ICP Standards					
Standard #	Zn (ppm)	Fe (ppm)	Mn (ppm)	Pb (ppm)	Cd (ppm)
1	100	100	100	10	10
2	25	25	25	2.5	2.5
3	10	10	10	1	1
4	2.5	2.5	2.5	.25	.25

Four standard solutions containing Zn, Pb, Cd, Fe, Mn were prepared to calibrate the ICP-AES

(Table 1). The first standard was 100ppm of Zn and 10ppm of Pb and Cd. The second standard was

25ppm of Zn and 2.5ppm of Pb and Cd. The third standard was 10ppm of Zn and 1.0ppm of Pb and

Cd. The fourth standard was 2.5ppm of Zn and 0.25ppm of Pb and Cd. Samples were run through

ICP-AES analysis with respect to Zn, Pb, Cd, Mn, and Fe concentrations. Standard 2 was run every 6

samples in the first round of ICP testing (19 samples) for QA/QC. Standard 2 had a Zn, Fe, Mn

concentration of 25 ppm and a Pb and Cd concentration of 2.5 ppm as stated above. These known

values were compared to returned ICP values to calculate % error (Table 2).

Table 2 – Standard 2 actual values compared to ICP values. Values stated are the mean of the three values the ICP reports for each run. Positive values here indicate a value less than the actual, whereas negative values indicates a value more than the actual.

	Laboratory Control Checks % Error			
	Run 1 % Error	**Run 2 % Error**	**Run 3 % Error**	**Average LCC %**
Zn	8.6	5.3	11.9	8.6
Fe	6.8	5.9	12.1	8.3
Mn	10.8	12.0	15.9	12.9
Pb	2.6	1.4	2.2	2.0
Cd	7.8	3.4	7.0	6.1

The percent error calculation shows that the ICP tended to underreport concentrations of Zn,

Fe, Mn, and Cd. Pb concentrations had the lowest percent error and Pb was the only element with

concentrations overreported by up to 2.5%. Detection limits were calculated by running double-DI

water as blanks and multiplying the blank average by 3 (Table 3).

Table 3 - Blank averages, standard deviation, and detection limits for the 1st ICP Run (Spring 2018).

	Detection Limits				
	Zn	**Fe**	**Mn**	**Pb**	**Cd**
Blank Average	0.1652	0.0182	-0.0020	-0.0020	-0.0013
Std Dev	0.0498	0.0356	0.0001	0.0049	0.0006
D.L. (mg/L)	0.1493	0.1068	0.0003	0.0146	0.0019

The second ICP run used different standards for the calibration curve as shown in Table 4

below. These standards were made in the respective extraction solutions (Solutions A and B)

corresponding to the solutions prepared earlier and used for the respective samples for both fractions so that the matrix of the standard was identical to that of the samples.

Table 4 - ICP standards for the 2nd ICP run (Spring 2019).

		ICP Standards			
	Zn	Fe	Mn (ppm)	Cd	Pb
Standard 1	2	2	2	0.2	0.2
Standard 2	5	5	5	0.5	0.5
Standard 3	20	20	20	2	2
Standard 4	50	50	50	5	5

The second ICP run had 4 LCCs run for both extractions for a total of 8, the results of those extractions show less % error in these runs compared to the original ICP run in Spring of 2018. The results are presented in tables 5 and 6 below.

Table 5 - LCCs % error for the 1st extraction samples (Spring 2019).

	Laboratory Control Checks % Error 1st Extraction				
	Run 1 %	Run 2 %	Run 3 %	Run 4 %	Average
Zn	1.0	3.0	5.3	5.3	3.7
Fe	2.6	1.1	0.4	2.3	1.6
Mn	2.7	4.0	5.3	5.2	4.3
Pb	0.2	3.6	3.8	5.4	3.2
Cd	0.8	0.3	0.8	0.1	0.5

Table 6 - LCCs % error for the 2nd extraction samples (Spring 2019).

	Run 5 %	Run 6 %	Run 7 %	Run 8 %	Average
Laboratory Control Checks % Error 2nd Extraction					
Zn	3.9	2.4	4.2	5.8	3.9
Fe	2.4	2.1	0.3	2.5	1.7
Mn	1.7	0.6	1.4	2.6	2.9
Pb	1.8	2.6	2.7	3.6	2.9
Cd	2.1	1.9	1.5	2.2	1.2

The detection limits for the second ICP run were based on the averages of four blanks for both the first extraction and the second extraction. The detection limits, blank averages, and standard deviation of the blanks are in Tables 7 and 8 below.

Table 7 - ICP detection limits for the first extraction samples (Spring 2019).

	Zn	Fe	Mn	Cd	Pb
Extraction 1 Detection Limits					
Blank Average	0.0250	-1.1005	0.06819	0.0042	0.0066
Std Dev	0.0042	0.0053	0.0015	0.0002	0.0002
D.L. (mg/L)	0.6340	0.7933	0.2186	0.0238	0.0372

Table 8 - ICP detection limits for the second extraction samples (Spring 2019).

	Zn	Fe	Mn	Cd	Pb
Extraction 2 Detection Limits					
Blank Average	-0.7096	-0.6900	0.0569	0.0017	-0.0135
Std Dev	0.0037	0.5521	0.0123	0.0001	0.0003
D.L. (mg/L)	0.0214	0.0110	0.0368	0.0004	0.0010

Magnetic Susceptibility. Sediment samples were weighed out to 15g in a sample tray. The meter used was a SM-30. The SM-30 contains a LC circuit with a 6cm diameter and a 1cm thick copper coil that creates a small alternating field. Sensitivity of the instrument is 10^{-7} SI. The

meter was calibrated using an open-air measurement that was checked beforehand for any magnetic interference. The meter operates off a two-step procedure. The first step is taken near the rock (or sediments) and this is termed the pick-up step. The second step is to take a free air measurement termed the compensation step. These values are subtracted from each other and displayed. Careful attention should be payed to inherent magnetic influence in the measuring environment. In this research, it was found that proximity to hinges, nails, lab table surfaces, and cement all influenced the recording. The most consistent measurement came from holding the samples in free-air for the pick-up step and removing the sample for the compensation step. The meter was placed directly above the sediments the same way for each measurement. Three recordings were taken for each sample and the average recording was accepted as the sample value. Samples that no longer contained 15g of sediments were not chosen for magnetic susceptibility as the instrument needs some depth to the sample to function correctly.

Loss on Ignition. Loss-on-ignition was carried out on as many samples as possible. Initial runs were discovered to have run at too low of a temperature (500°C) and only twentythree samples had enough sediment left for this method to be applied. Clean crucibles were dried out at 105°C for 24 hours. The crucibles were then weighed and 10g of sediment were added to them, measuring to the nearest 0.01g. The sediments were placed in the muffler and set at "4", a setting that had been previously tested for the desired temperature, for 16 hours. The heat builds up to 610°C after a few hours. The crucible weights post-ignition were recorded and the loss of sample mass is used as a proxy for the percent of organic matter in each respective sample.

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Data Analysis

The first extraction targets the exchangeable and carbonate-bound fraction and the second extraction targets the Fe and Mn-oxide fraction. The final fraction we report is a combination of both the organic and residual fraction derived from "Total Concentration – Exchangeable/Carbonate-Bound – Iron and Manganese Oxide-Bound = Organic + Residual Fraction". Total metal concentrations were determined via acid digestion from a commercial lab. These results were used to construct bar graphs for the fractionation of the metals according to each sample.

A risk assessment code (RAC) (%) was employed for Zn, Cd, and Pb which compares the exchangeable and carbonate-bound fraction proportionately to all other geochemical fractions to assess bioavailability of the sample. The RAC is calculated by this formula:

$$\text{RAC (\%)} = \left(\frac{\text{F1}}{\text{F2} + \text{F3} + \text{F4}} \right) \times 100$$

where F1 represents the exchangeable and carbonate-bound fractions, F2 represents the iron and manganese oxide fractions, F3 represents the organic and sulfidic fraction, and F4 represents the residual fraction. Note that in this study, F3 and F4 are combined together in one fraction.

Total metal concentrations were compared with Probable Effect Concentrations (PECs) as well as TSMD-Specific PECs and Macdonald et al. (2009)'s Sum Probable Effect Quotient in which sediments are considered low risk if:

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

Sediments that equal or exceed 7.92 are considered high risk to macroinvertebrate amphipods.

Additionally, total metal concentrations correlation with other parameters (Zn, Pb, Cd, Fe, Mn, Al, Co, Ni, Cr, S, P concentrations, and % organic matter and magnetic susceptibility) were investigated. High correlations for each parameter were further represented using a dual-axis figure illustrating concentration trends as samples moved from downstream to upstream. Significance was determined at the $p < .05$ level for important correlations.

RESULTS AND DISCUSSION

Variability

The high variability observed in the metal concentrations of sediment samples may be explained by numerous factors. The historical mining in the Joplin area occurred in many different parts of town. Chat piles were scattered across Newton and Jasper County contributing to mine waste pile runoff that affected different watersheds. Proximity to these chat piles is expected to be correlated to an increase in metal concentrations in sediments. Underground mines were also present throughout the study area. As groundwater filled up in the mines, discharge of metal-rich groundwater contributed to metal loading in nearby waterways. Aside from mine waste pile runoff, and acidic mine drainage, a smelter operated in town. Proximity to this smelter was positively correlated with polluted residential soils and blood-lead levels in children. Remediation of chat piles and metal-polluted soils also affected variability of metal content in sediments. Finally, in 2013 an EF5 tornado went through central Joplin devastating the town and distributing metal-polluted soils across the area yet again.

Sequential Extractions

The sequential extraction results are broken down into the three heavy metals of interest: zinc, cadmium, and lead. Complete fractionation results for all three heavy metals of interest are available in Appendix B.

Zinc Fractionation. The three fractions of Zn had variable concentrations and proportions from sample to sample (Figures 9 and 10). Specific values of each fraction, both in concentration and in percentage can be seen in Table 9 below. The exchangeable/carbonate bound fraction contained from 1-45% of total zinc throughout the samples d iron and manganese oxide fraction contained from 3-79% of total zinc and the organic and residual fraction contained 2-97%.

Due to the high proportion of Zn in the exchangeable and carbonate-bound fraction in some samples, the risk assessment code (RAC) for Zn showed that 6 samples were considered very high risk (> 50%), 8 samples were high risk (31-50%), 6 samples were medium risk (1130%) and all others were low risk or no risk (1-10% and 0-1% respectively) (Figure 11). Proportionally, samples 26 and 29 had the lowest extraction rates for both the exchangeable and carbonate-bound fraction and iron and manganese oxide fraction, yet the highest concentrations. This may be because those samples contained sphalerite (ZnS) which would not be released under these extractions. This area was also proximal to an old tailings pile as discussed further below in the Total Metal Concentration Correlations section.

Schaider et al. (2014) reported that zinc was largely concentrated in the carbonate, Mn oxide, amorphous Fe oxide, and crystalline Fe oxide fractions primarily. The exchangeable, organic, and residual fractions typically contained roughly 10% of the total zinc (Schaider et al., 2014). Our results produced more zinc in both the exchangeable and carbonate-bound fractions and the organic and residual fractions. This may be a difference in the extraction used, the amount of zinc ore (sphalerite – ZnS) present in sediment samples, or difference in size fractionation.

Figure 9 - Zinc concentrations in exchangeable and carbonate-bound, iron and manganese oxide, and organic and residual fractions in Turkey Creek sediments.

Figure 10 - Zinc concentrations in exchangeable and carbonate-bound, iron and manganese oxide, and organic and residual fractions in Turkey Creek sediments expressed as a percentage of total zinc concentration.

Table 9 – Total zinc, extraction 1, extraction 2, and residual fraction concentrations. extraction 1 refers to exchangeable and carbonate-bound fraction, and extraction 2 refers to iron and manganese oxide fraction and residual refers to both the organic and residual fraction.

Sample	Zn Concentration (mg/kg)	Extraction 1 (mg/kg)	% in Extraction 1	Extraction 2 (mg/kg)	% in Extraction 2	Residual Zn (mg/kg)	Residual Zn (%)
N14.2	974	443	45.5	435	44.7	95	9.8
1	1480	177	11.9	430	29.1	873	59.0
2	1210	105	8.7		0.0	1105	91.3
O15.2	2600	612	23.5	990	38.1	998	38.4
3	1050	89	8.5	355	33.8	606	57.7
4	2860	580	203	972	34.0	1308	45.7
5	7180	2091	29.1	2505	34.9	2584	36.0
6	4130	1513	36.6	1373	33.3	1244	30.1
7	585	154	26.4	112	19.1	319	54.5
8	7280	903	12.4	2090	28.7	4287	58.9
9	1830	625	34.1	725	39.6	480	26.2
10	271	34	12.6	56	20.7	181	66.7
11	462	204	44.1	132	28.5	127	27.4
12	854	364	42.7	234	27.3	256	30.0
13	1460	470	32.2	406	27.8	584	40.0
14	2420	1031	42.6	889	36.7	501	20.7
15	1710	550	32.2	583	34.1	577	33.8
16	5070	390	7.7	922	18.2	3757	74.1
17	3570	201	5.6	676	18.9	2692	75.4
18	942	8	0.8	251	26.7	683	72.5
19	2280	113	5.0	90	3.9	2077	91.1
20	902	129	14.3	481	53.3	291	32.3
H8.2	2220	616	27.7	1007	45.4	597	26.9
21	915	178	19.5	720	78.7	16	1.8
22	6950	163	2.4	429	6.2	6357	91.5
23	2490	177	7.1	646	25.9	1667	67.0
24	3280	191	5.8	481	14.7	2608	79.5
25	1920	163	8.5	1014	52.8	743	38.7
26	37100	452	1.2	1848	5.0	34800	93.8
27	2710	225	8.3	409	15.1	2076	76.6
28	2700	247	9.1	484	17.9	1969	72.9
29	35800	214	0.6	974	2.7	34613	96.7
30	8190	197	2.4	1174	14.3	6819	83.3
J9.3	3120	874	28.0	710	22.8	1536	49.2
H8	3820	968	25.3	739	19.3	2114	55.3
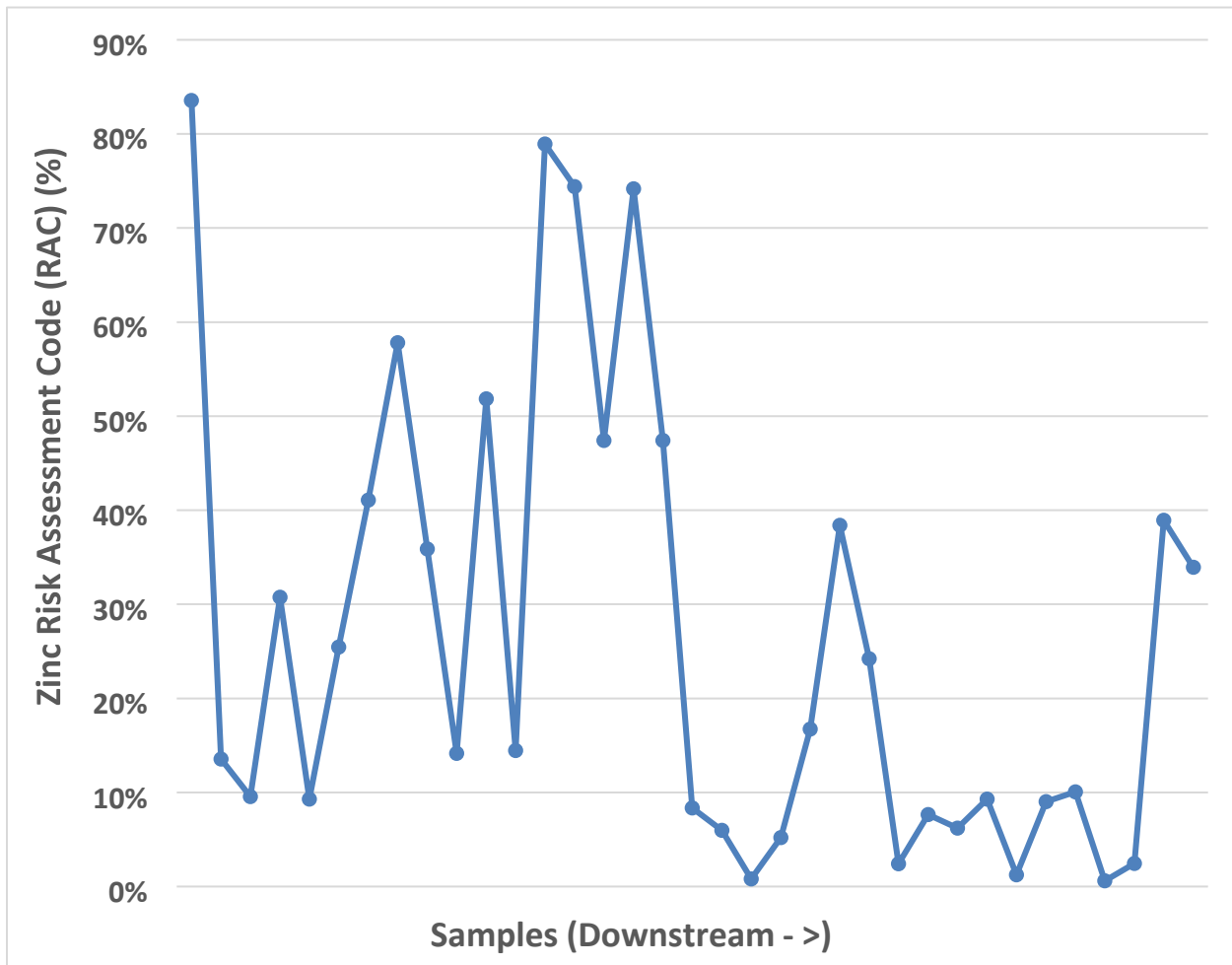
Figure 11 – Risk assessment code (RAC) (%) for zinc. 0-1%: no risk, 1-10: low risk, 11-30%: medium-risk, 31-50%: high risk, and >50%: very-high risk.

Cadmium Fractionation. Cd had similar fractionation to Zn with regards to variability in all three fractions, and sometimes relatively high proportions in the exchangeable and carbonate-bound fractions (Figures 12 and 13). Due to these high proportions, the risk assessment code (RAC) (%) for Cd reported 3 very high risk samples (<50%), 5 high risk samples (31-50%), 9 medium risk samples (11-30%) and the rest were low risk or no risk (1-10% and 0-1% respectively) (Figure 14). Between 2-46% of total Cd resided in exchangeable and carbonate-bound fractions in all samples, while between 2-91% remained in iron and manganese oxide fractions and between 8-94% remained in organic and residual fractions (Table 10).

Cadmium's toxicity makes it a larger concern than zinc when even small concentrations of cadmium are released.

Schaider et al. (2014) reported that cadmium had the highest concentrations (25-50%) contained in the exchangeable and carbonate-bound fraction of the three metals of concern in the study area (Zn, Cd, and Pb). The remaining cadmium was found mostly in manganese oxide, amorphous Fe oxides and crystalline fe oxides fractions with smaller amounts in organic and residual (Schaider et al., 2014). These results are not quite consistent with those findings with larger concentrations found in the organic and residual fractions than Schaider et al. (2014) reported. This may be a function of lack of size fractionation in this study, higher content of sulfides (ZnS and CdS), or the specific extractants used in our extractant scheme.

Figure 12 - Cadmium concentrations in exchangeable and carbonate-bound, iron and manganese oxide, and organic and residual fractions of sediment.
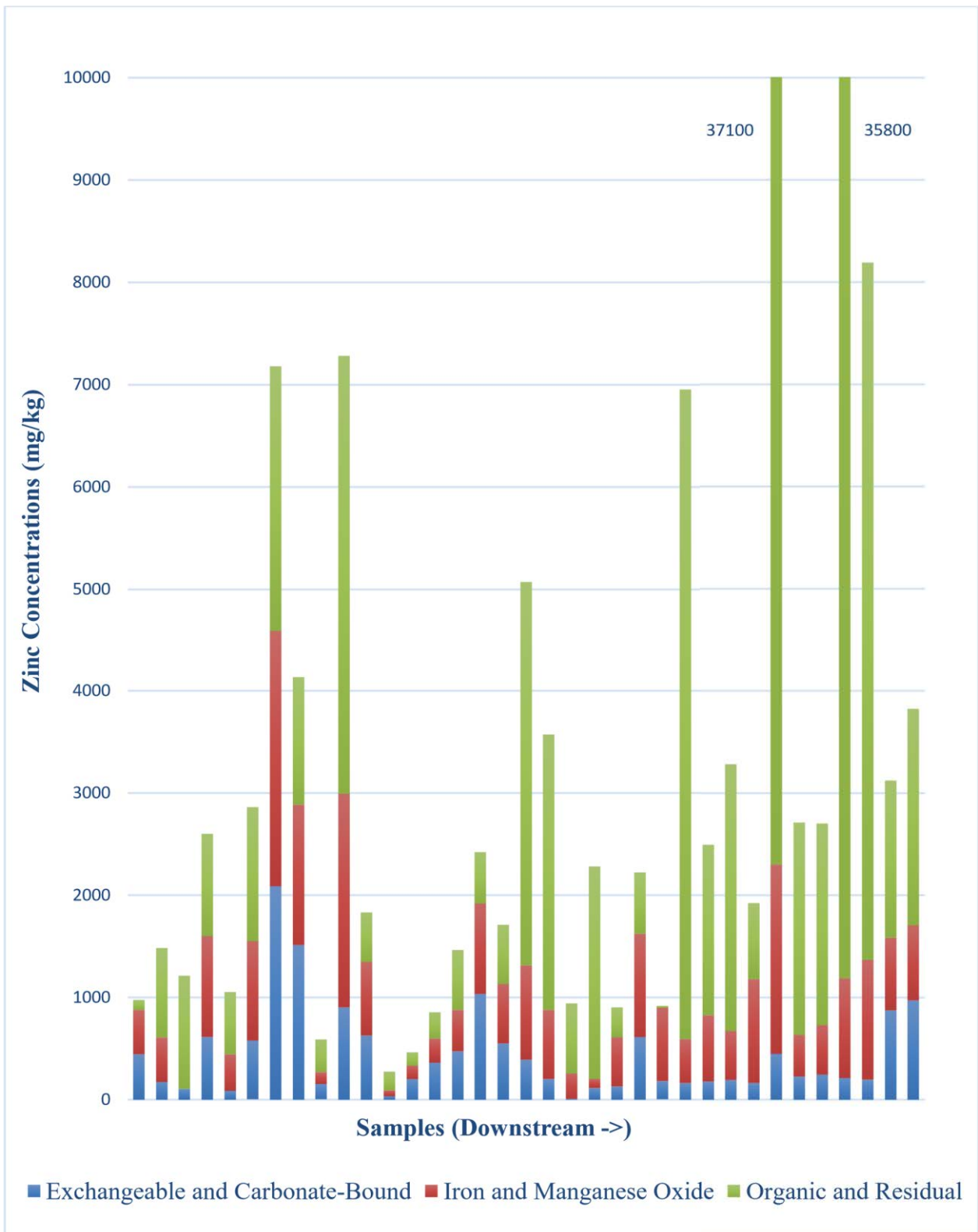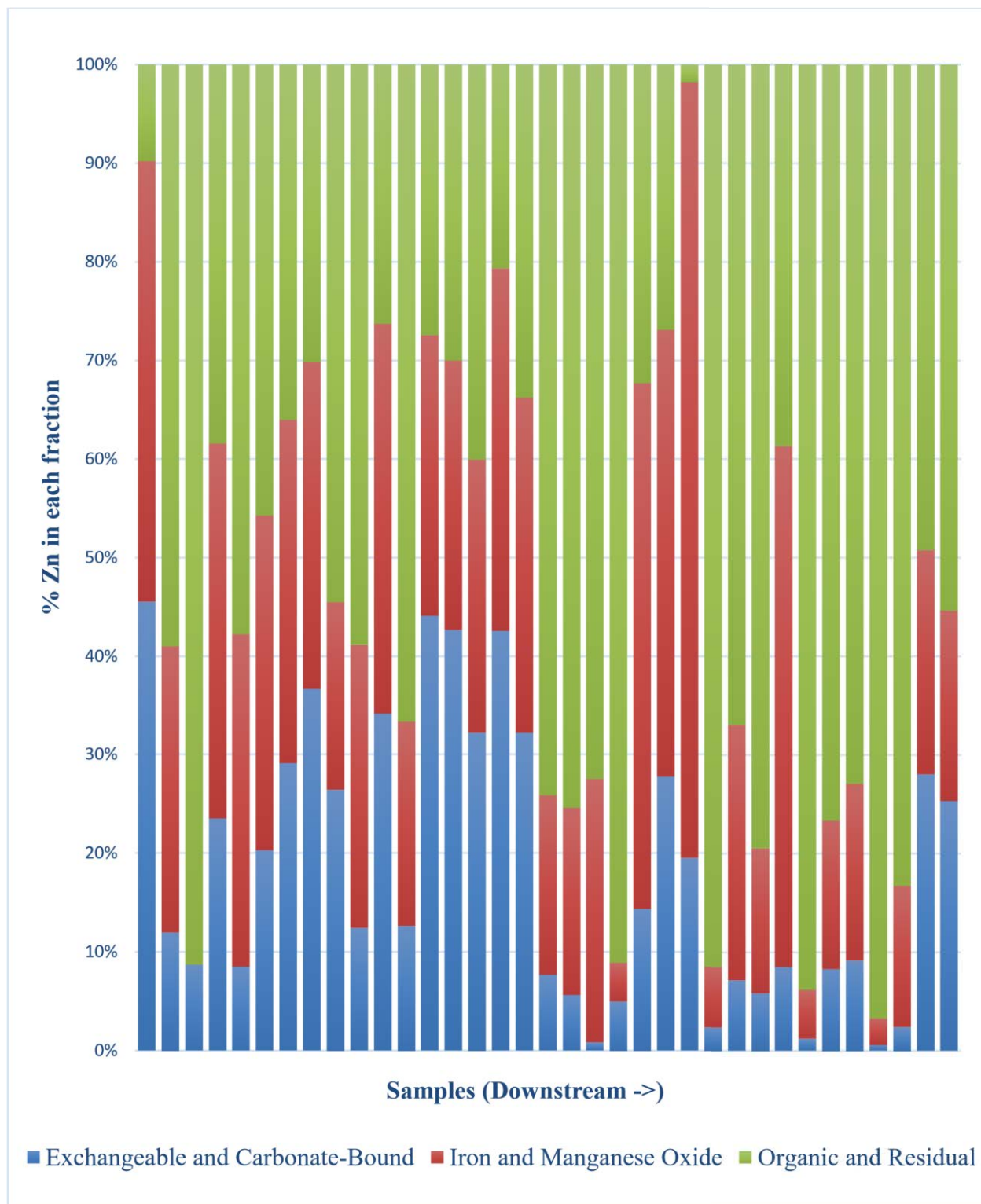
Figure 13 - Cadmium concentrations in exchangeable and carbonate-bound, iron and manganese oxide, and organic and residual fractions of sediment expressed as a percentage of total cadmium concentration.

Table 10 – Total cadmium, extraction 1, extraction 2, and residual fraction concentrations. extraction 1 refers to exchangeable and carbonate-bound fraction, and extraction 2 refers to iron and manganese oxide fraction and residual refers to both the organic and residual fraction.

|							
Cadmium Fractionation Data							
Sample	Cd Concentration (mg/kg)	Extraction 1 (mg/kg)	% in Extraction 1	Extraction 2 (mg/kg)	% in Extraction 2	Residual Cd (mg/kg)	Residual Cd (%)
N14.2	8	1	17.8	1	6.6	6	75.7
1	12	0	2.8	6	48.8	6	48.4
2	8	0	1.6		0.0	8	98.4
O15.2	16	4	26.9	1	4.7	11	68.4
3	6	1	10.3	3	50.6	2	39.1
4	21	3	12.1	17	79.5	2	8.4
5	66	5	7.6	28	42.9	32	49.5
6	21	9	43.4	6	29.3	6	27.3
7	6	1	19.0	1	11.1	4	69.8
8	54	0	0.3	25	46.1	29	53.6
9	11	1	6.3	8	72.3	2	21.4
10	9	4	45.9	1	12.8	4	41.3
11	4	1	17.0	0	6.8	3	76.1
12	6	1	25.4	0	7.0	4	67.5
13	10	2	15.8	1	7.9	8	76.2
14	19	7	35.8	8	42.0	4	22.3
15	12	0	3.7	8	66.5	4	29.8
16	18	2	11.3	4	22.9	12	65.9
17	11	0	1.6	6	52.0	5	46.4
18	4	0	-0.8	1	19.1	4	81.7
19	10	0	0.0	3	33.0	6	67.0
20	4	0	1.1	3	91.0	0	7.9
H8.2	18	6	33.3	6	33.1	6	33.6
21	5	1	16.5	3	69.5	1	14.1
22	21	0	1.6	2	11.1	19	87.3
23	10	0	1.0	4	38.2	6	60.8
24	13	1	7.3	3	23.5	9	69.2
25	11	1	7.0	6	60.9	3	32.1
26	114	1	0.7	8	6.9	105	92.3
27	10	1	7.0	2	20.3	7	72.7
28	11	1	12.1	3	28.7	6	59.2
29	127	0	0.3	4	3.2	123	96.6
30	35	1	1.6	3	9.0	32	89.4
J9.3	17	6	33.3	1	3.3	10	63.3
H8	27	8	30.0	1	2.4	18	67.6

Figure 14 – Risk assessment code (RAC) (%) for cadmium. 0-1%: no risk, 1-10: low risk, 1130%: medium-risk, 31-50%: high risk, and >50%: very-high risk.

Lead Fractionation. Lead resided primarily in the iron and manganese oxide and organic and residual (organic and residual) fractions (Figures 15 and 16). Almost no lead was in the exchangeable or carbonate bound fractions with a maximum extraction percentage of 11% of total lead (Table 11) suggesting that lead is not readily mobile in this watershed without significant changes in pH and eH (acidic and reducing conditions). Lead residing in the iron and manganese oxide fractions was extremely variable ranging from 1-100% of total lead. In certain samples, a drop in both pH and eH (acidic reducing conditions) could mobilize a significant

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amount of lead by dissolving iron oxides. The risk assessment code for lead (RAC) (%) reported 1 sample as medium-risk and all others as low-risk or no-risk (1-10% and 0-1% respectively) due to the low concentrations in the exchangeable and carbonate-bound fractions (Figure 17). Lead's fractionation trends were very different from zinc or cadmium's, both of which, had higher extraction rates in the exchangeable and carbonate-bound fraction and less variability in the extraction rates of the iron and manganese oxide fraction.

Lead concentrations were not well correlated with any other parameters in this study, discussed more below under 4.3 Total Metal Concentrations. Schaider et al. (2014) also found that lead was primarily found in iron oxide, organic, and residual fractions (>90%) and minor amounts were in exchangeable or carbonate-bound fractions. This seems consistent with our findings where lead is concentrated primarily in either iron and manganese oxide, organic, or residual fractions and almost none is concentrated in exchangeable or carbonate-bound fractions.
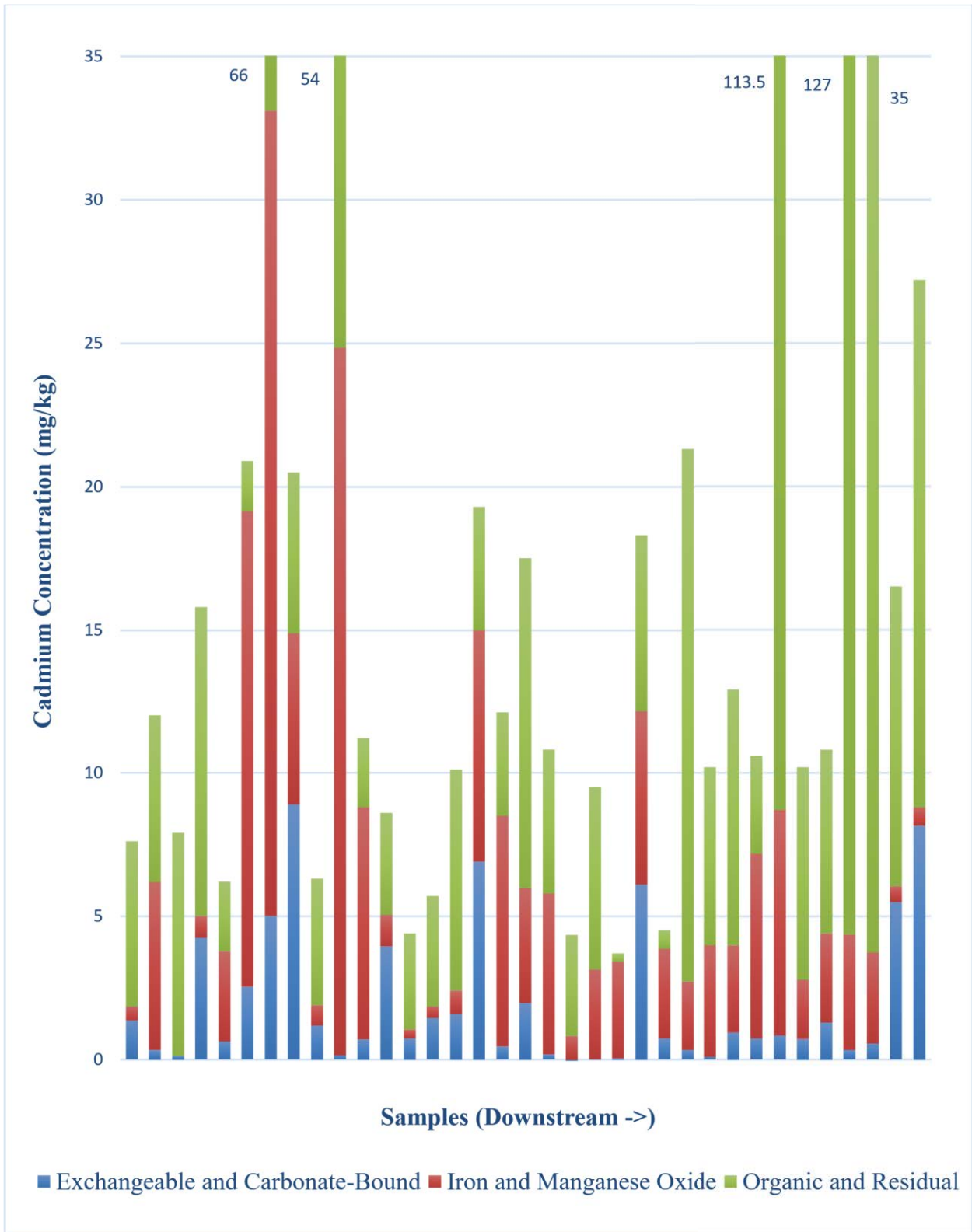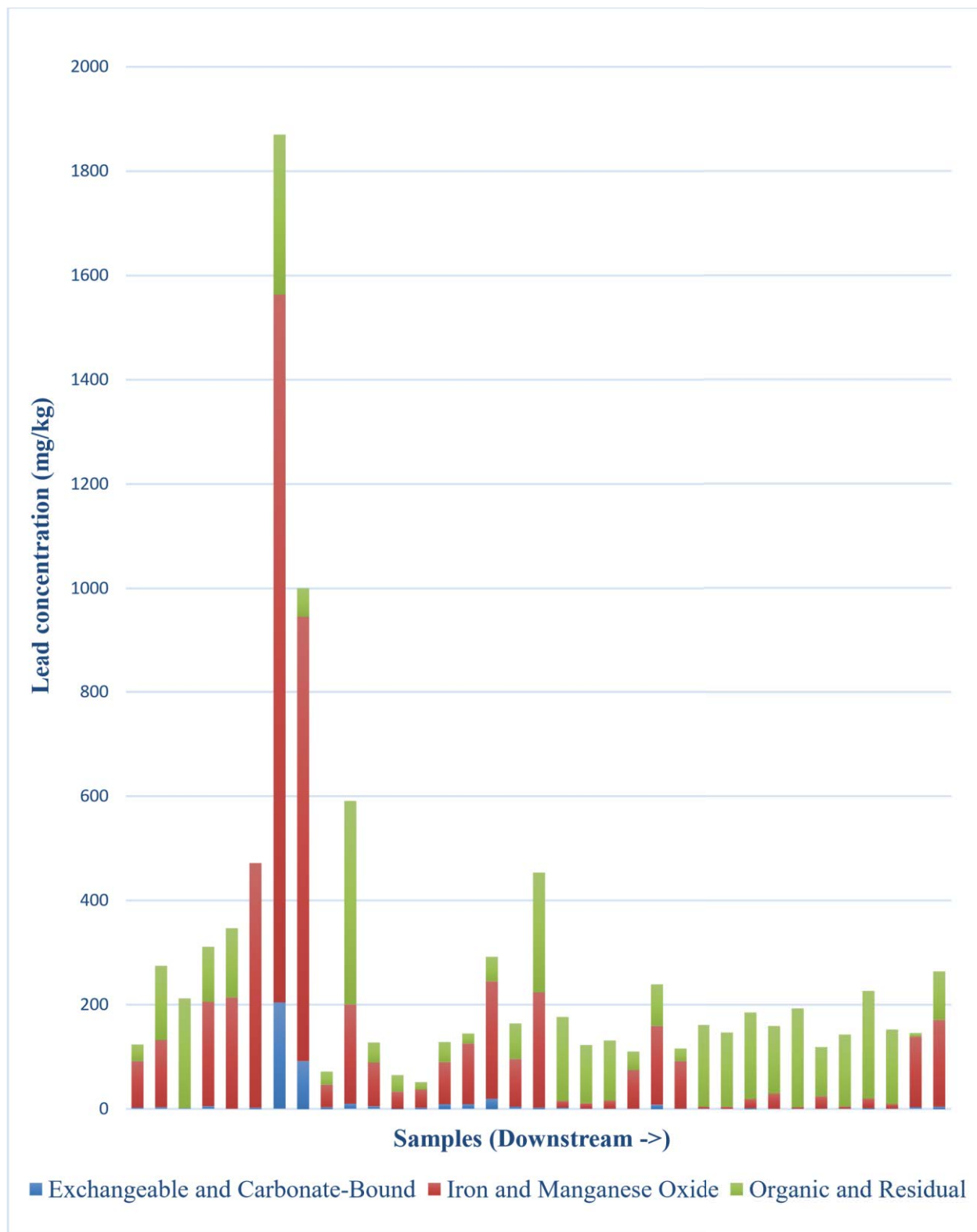
Figure 15 – Lead concentrations in exchangeable and carbonate-bound, iron and manganese oxide, and organic and residual fractions of sediment.
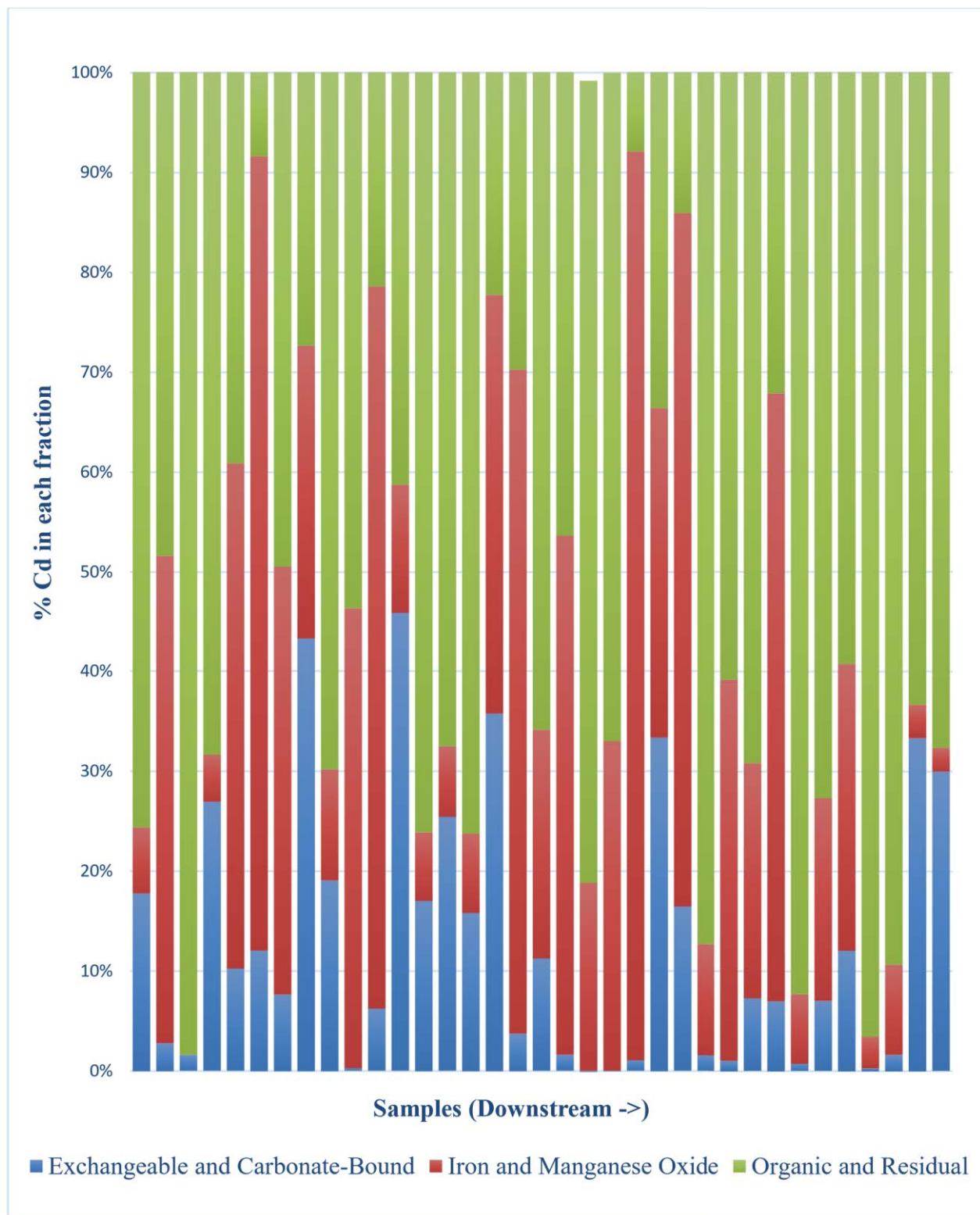
Figure 16 - Lead concentrations in exchangeable and carbonate-bound, iron and manganese oxide, and organic and residual fractions of sediment expressed as a percentage of the total lead concentration.

Table 11 – Total lead, extraction 1, extraction 2, and residual fraction concentrations. extraction 1 refers to exchangeable and carbonate-bound fraction, and extraction 2 refers to iron and manganese oxide fraction and residual refers to both the organic and residual fraction.

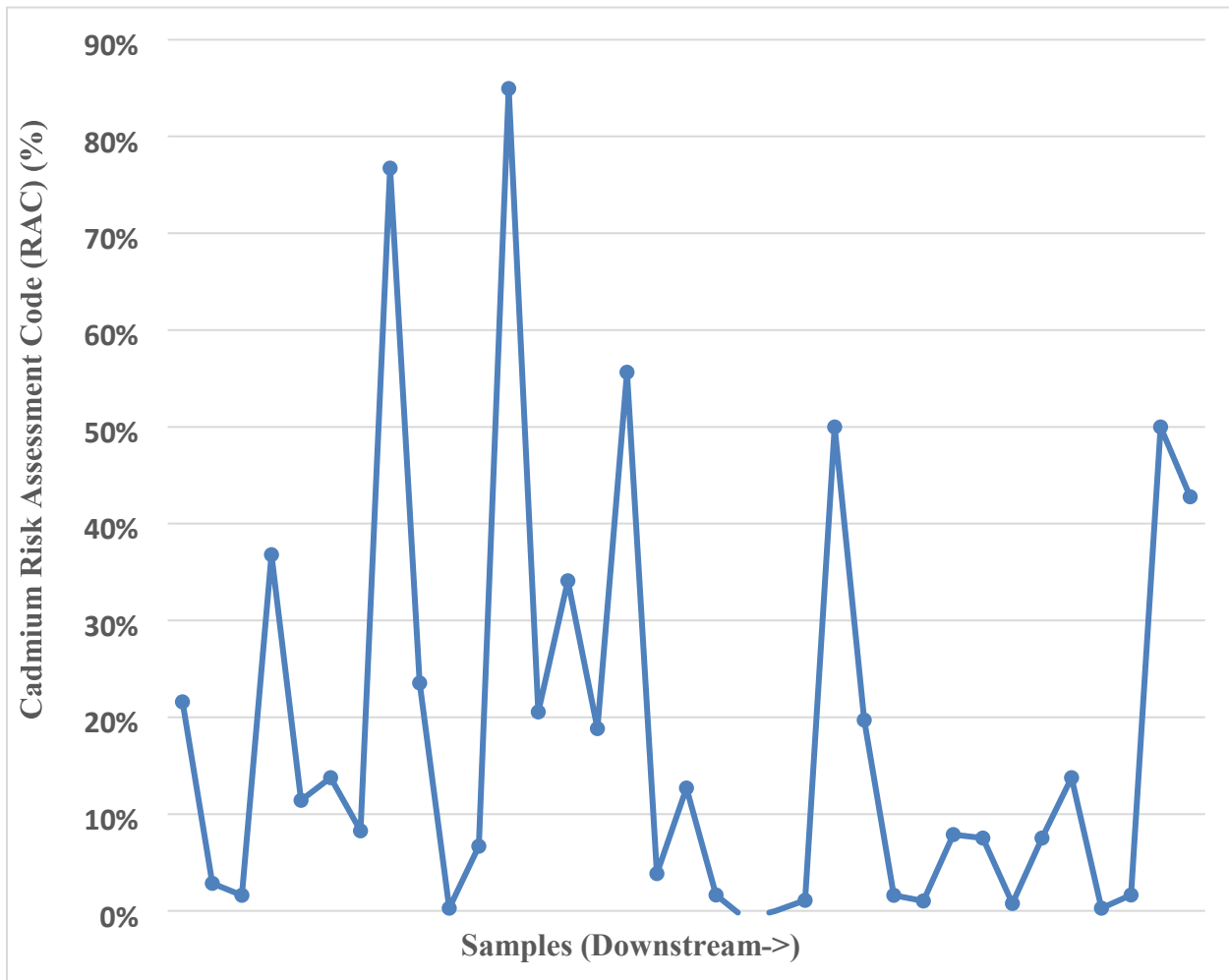|							
Lead Fractionation Data							
Sample	**Pb Concentration (mg/kg)**	**Extraction 1 (mg/kg)**	**% in Extraction 1**	**Extraction 2 (mg/kg)**	**% in Extraction 2**	**Residual Pb (mg/kg)**	**Residual Pb (%)**
N14.2	123	3	2.1	89	72.4	31	25.5
1	274	3	1.0	129	47.2	142	51.7
2	212	1	0.7	0	0.0%	211	99.3
O15.2	311	5	1.5	201	64.5	106	34.0
3	346	0	0.0	213	61.7	133	38.3
4	471	2	0.4	469	99.6	0	0.0
5	1870	205	10.9	1359	72.7	306	16.4
6	1000	91	9.1	854	85.4	54	5.4
7	71	3	4.2	43	60.7	25	35.1
8	590	10	1.7	190	32.2	390	66.1
9	127	5	3.6	85	66.6	38	29.8
10	64	1	1.6	32	49.7	31	48.8
11	51	2	4.0	35	69.0	14	27.0
12	128	10	7.6	80	62.6	38	29.8
13	144	9	6.4	116	80.4	19	13.2
14	291	20	7.0	224	77.1	46	15.9
15	163	5	2.8	91	55.5	68	41.7
16	453	2	0.4	222	48.9	229	50.6
17	176	3	1.5	13	7.2	161	91.3
18	122	1	0.4	10	8.4	111	91.1
19	131	1	0.4	16	11.8	115	87.8
20	110	0	0.4	75	68.0	35	31.7
H8.2	238	8	3.4	151	63.3	79	33.3
21	115	0	0.2	91	79.3	24	20.5
22	161	0	0.0	4	2.8	156	97.2
23	146	1	0.4	3	2.3	142	97.3
24	185	1	0.6	18	9.7	166	89.7
25	159	0	0.1	29	18.5	129	81.3
26	192	0	0.1	3	1.6	189	98.3
27	118	1	0.5	23	19.8	94	79.8
28	142	0	0.1	4	3.1	138	96.9
29	226	1	0.5	19	8.4	206	91.1
30	152	0	0.2	9	6.2	142	93.7
J9.3	145	3	2.3	135	93.4	6	4.3
H8	263	4	1.5	166	63.2	93	35.3
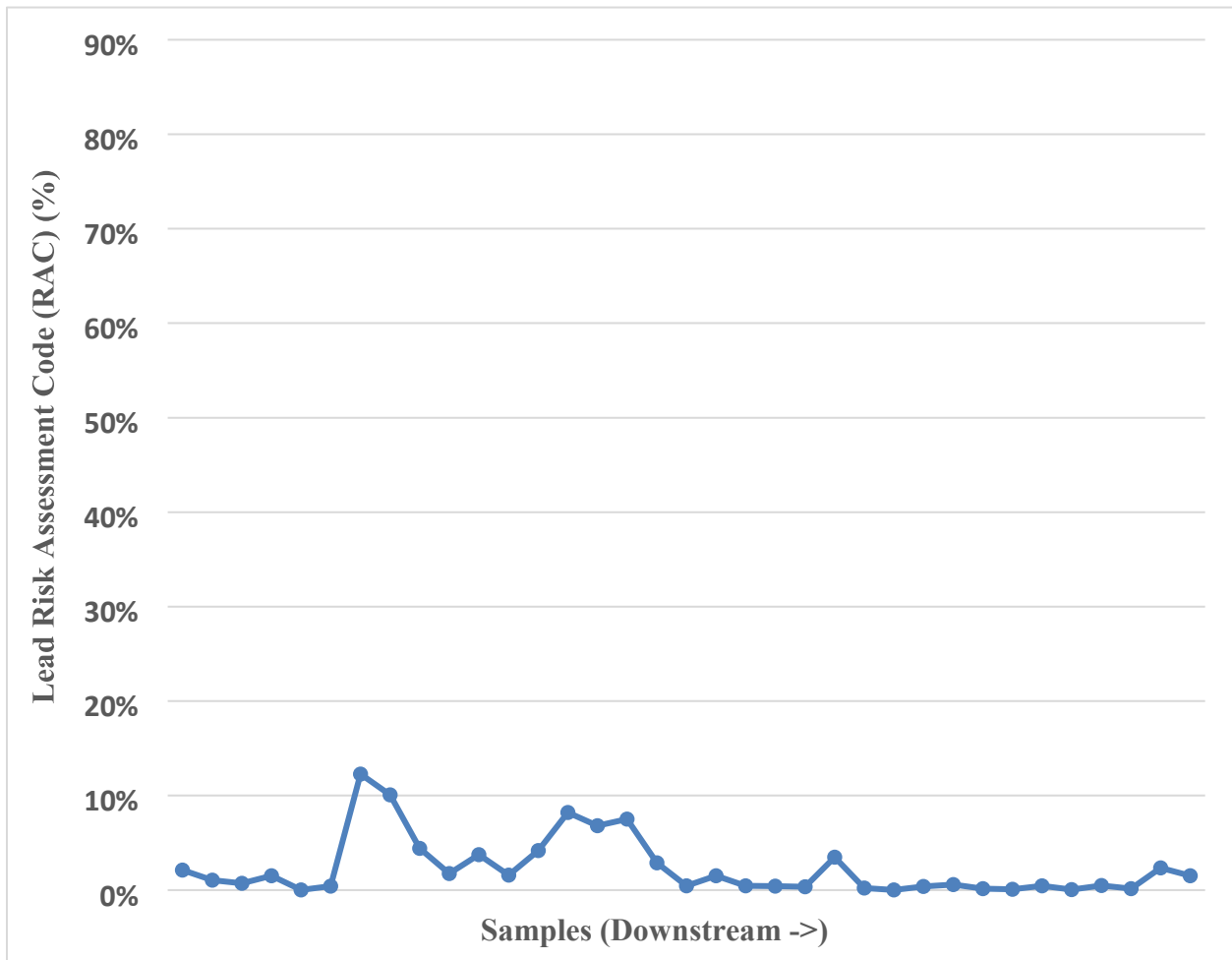
Figure 17 – Risk assessment code (RAC) (%) for lead. 0-1%: no risk, 1-10: low risk, 11-30%: medium-risk, 31-50%: high risk, and >50%: very-high risk.

Total Metal Concentrations

Total metal concentrations for lead, zinc, and cadmium were present in potentially toxic concentrations in some samples throughout the study area. Table 1 shows the total metal concentrations of all three metals of interest starting upstream and moving downstream in sample numbers. These results are compared vs. general probable effect concentrations (PECs) and

TSMD-Specific PECs. Ultimately, each sediment is evaluated using the Dudding Model which calculates sum probable effect concentrations ($\sum$PEQ) from MacDonald et al. (2009) where sediments are considered low risk if ([Cd]/4.98 + [Pb]/128 + [Zn]/459) < 7.92 and high risk if they are $\geq$ 7.92.

The PEC value for zinc is 459ppm, and the TSMD-specific PEC is 2083ppm. Samples reported an average zinc concentration of 4987ppm with 17 exceedances of the TSMD-specific PEC and two outliers at 35,800 ppm and 37,100 ppm. The lowest concentration in the range of samples was 271ppm and the highest concentration was 37,100ppm.

The PEC value for cadmium is 5 ppm, and 11.1 ppm for the TSMD-specific PEC. Samples reported an average cadmium concentration of 22.2 ppm with 15 exceedances of the TSMD-specific PEC and two outliers of 113.5 ppm and 127 ppm. Notably, these samples were the same that reported extremely large values of zinc. The lowest concentration in the range of samples was 3.7ppm and the highest concentration was 127ppm.

The PEC value for lead is 128 ppm, and 150 ppm for the TSMD-specific PEC. Samples reported an average lead concentration of 279.7 ppm with 17 exceedances of the TSMD-specific PEC and two outliers at 1000 ppm and 1870 ppm. Unlike zinc and cadmium, the outliers are not from the same sample, which is consistent concerning the low correlation between lead and the other two metals of interest in terms of concentration and speciation.

A likely explanation of the outliers in samples 26 and 29 are that pieces of sphalerite (ZnS) were included in the sediment samples. Schaider et al. (2007) found similar results, and identified sphalerite using XRD analysis. Cd is also present in trace amounts in sphalerite within the TSMD (Schaider et al., 2007). This explains why almost no Zn or Cd occupied either the

exchangeable/carbonate-bound fractions or the iron-oxide fraction in the sequential extractions because sulfides are included in the organic-matter fraction. Pb concentrations were relatively lower in the same sediments, which is consistent with this explanation.

Fifteen of the sediment samples (50%) were considered high risk evaluated against the Dudding Model from MacDonald et al. (2009) with an average value of 16.87 and a range of 2.28 to 105.16 where ≥ 7.92 is considered 'high risk' to macroinvertebrate amphipods. The dataset of all samples exhibits highly variable concentrations of all three metals of concern. The exceedances of TSMD-specific PECs by all three metals and fifteen exceedances of the $\sum$PEQ suggests that sediments in Turkey Creek pose a risk to macroinvertebrate amphipods.

Table 12 - Total Metal Concentration Data and Sum Probable Effect Quotient (ΣPEQ$_{Zn, Cd, Pb}$).

Sample	Total Zn Concentration (mg/kg)	Total Cd Concentration (mg/kg)	Total Pb Concentration (mg/kg)	Sum Probable Effect Quotient
N14.2	974	7.6	123	4.60
1	1480	12	274	7.77
2	1210	7.9	212	5.87
O15.2	2600	15.8	311	11.25
3	1050	6.2	346	6.23
4	2860	20.9	471	14.09
5	7180	65.5	1870	43.35
6	4130	20.5	1000	20.91
7	585	6.3	71	3.09
8	7280	53.6	590	31.19
9	1830	11.2	127	7.22
10	271	8.6	64	2.81
11	462	4.4	51	2.28
12	854	5.7	128	4.00
13	1460	10.1	144	6.33
14	2420	19.3	291	11.41
15	1710	12.1	163	7.42
16	5070	17.5	453	18.08
17	3570	10.8	176	11.31
18	942	4.3	122	3.87
19	2280	9.5	131	7.89
20	902	3.7	110	3.56
H8.2	2220	18.3	238	10.36
21	915	4.5	115	3.79
22	6950	21.3	161	20.66
23	2490	10.2	146	8.61
24	3280	12.9	185	11.17
25	1920	10.6	159	7.55
26	37100	113.5	192	105.03
27	2710	10.2	118	8.87
28	2700	10.8	142	9.15
29	35800	127	226	105.16
30	8190	35.4	152	26.11
J9.3	3120	16.5	145	11.23
H8	3820	27.2	263	15.82
Average	**4745.9**	**21.9**	**274.9**	16.87
TSMD-Specific	**2083**	**11.1**	**150**	--

Total Metal Concentration Correlations

Total metal concentration correlations are broken down into five sections relating to zinc, cadmium, lead, iron, and manganese concentrations. Appendix C lists all the significant correlations found in this study between all elements of interest, as well as loss on ignition mass values and magnetic susceptibility values.

Zinc correlations. Correlation between zinc concentrations and cadmium concentrations in sediment were significant at the $p<0.01$ level with a correlation coefficient of 0.95 and N=35 (Figure 18). Zinc concentrations were also significantly correlated at the $p<0.01$ level with sulfur concentrations in sediment with a correlation coefficient of 0.97 (Figure 19). Correlations with all other variables were not significant at the $p<0.01$ level, though a correlation with magnetic susceptibility was significant at the $p<0.05$ level with a correlation coefficient of 0.41 and N=35

Zinc's correlation with cadmium is likely a result of cadmium's ability to substitute for one another in minerals like sphalerite due to similar ionic radii and identical charge. Zinc concentrations in this creek will be highest where sphalerite exists, and the same is likely true for cadmium as a trace metal in sphalerite. has been observed in other studies such as Jacob et al. (2013) where it was found that Cd and Zn were more correlated (.70) than any other metal they studied (Al, Be, Bi, Cu, K, Pb, Rb, Se, Tl, Zn).

Zn's strong correlation with sulfur is likely a result of original sulfide minerals (sphalerite –ZnS) still present in sediment throughout Turkey Creek. Another line of evidence for this idea is that samples 26 and 29, which had remarkably high levels of both zinc and cadmium, had simultaneously low concentrations in bioavailable fractions, and was located proximal to a tailings pile according to older topo maps (Figure 20). Low bioavailable fractions would be

consistent with a sulfide mineral, as well as high zinc and cadmium concentrations after a

complete acid digestion. Samples 25 and 30 (collected a few feet away from samples 26 and 29

respectively) had much lower total concentrations of zinc and cadmium, and higher

concentrations in bioavailable fractions of sediment again purporting high sample variability,

which matches well with changes in sample coloration and appearance just a few feet in any

direction within Turkey Creek.
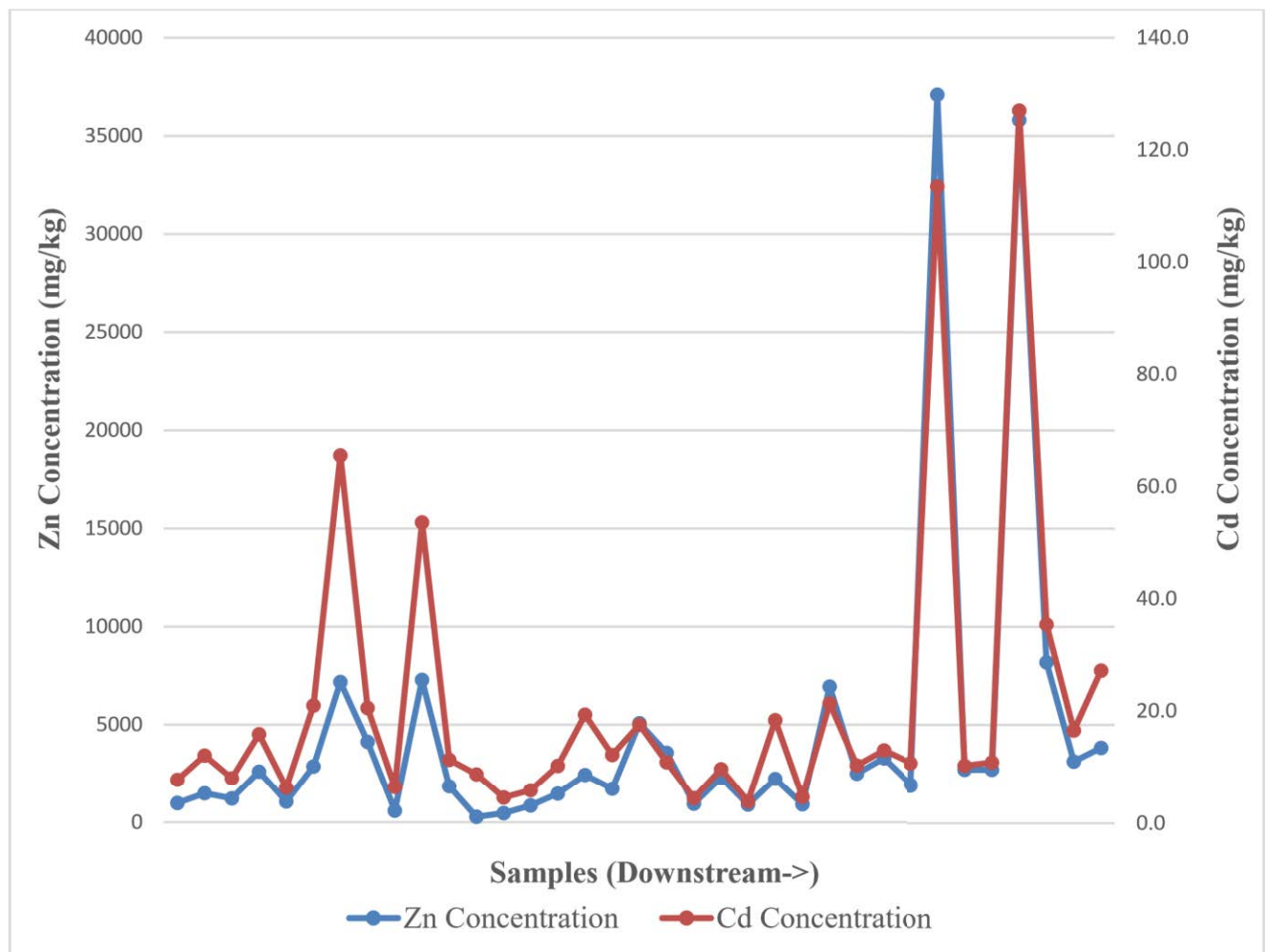
Figure 18 – Total Zn and Cd concentration correlations. The Pearson's correlation coefficient is 0.95 and the correlation is significant at $p < .05$ with N=35.
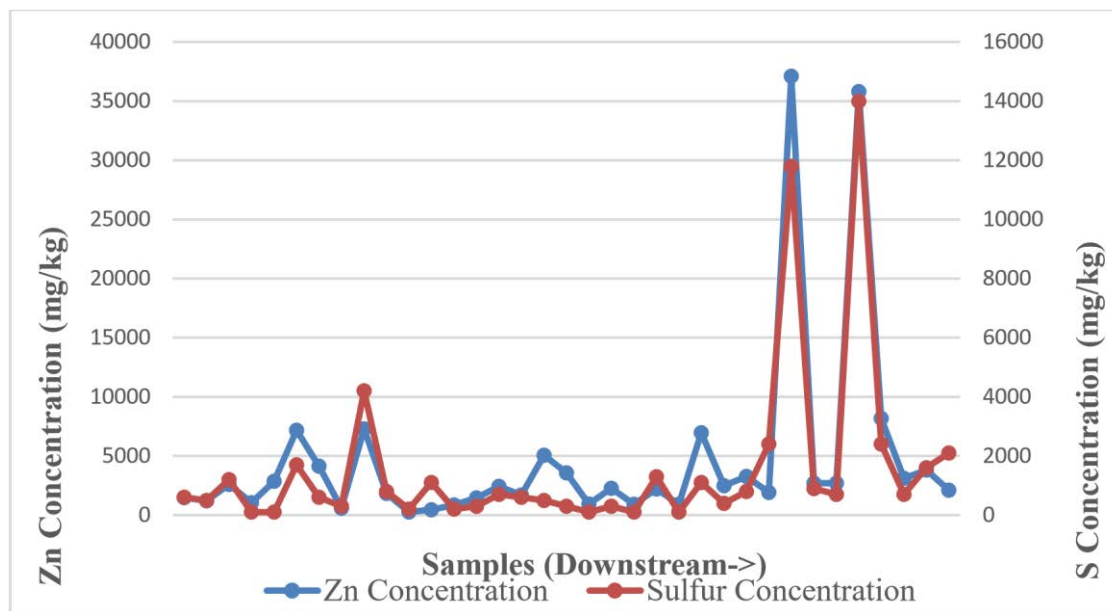
Figure 19 - Total Zn and S Concentration Correlation. The Pearson's correlation coefficient is 0.97 and the correlation is significant at $p < .05$ with N=35.
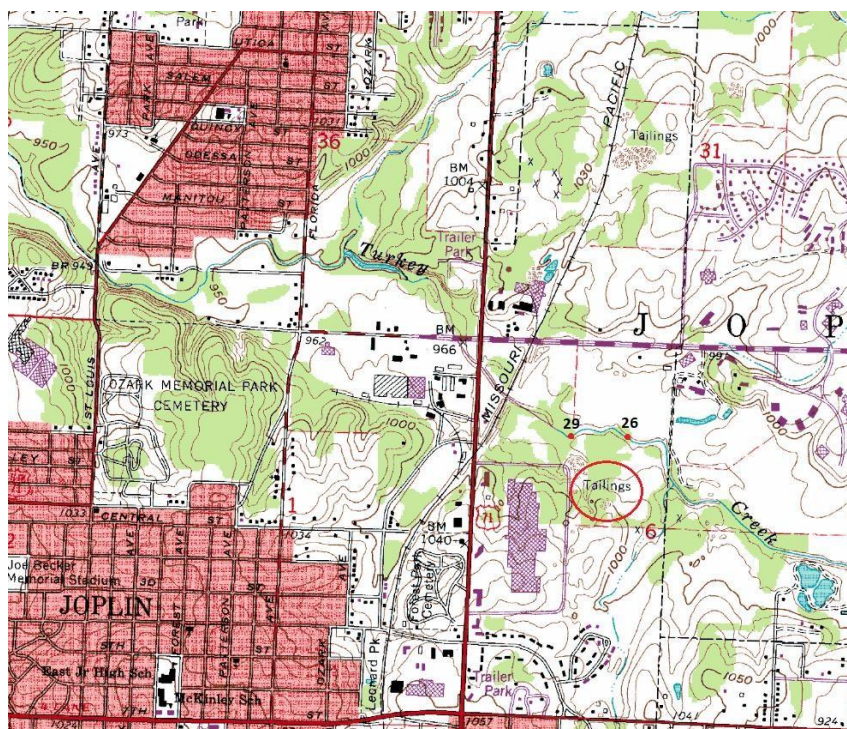
Figure 20 - Tailings pile (from Joplin East 1939 topographic map) located proximal to samples 26 and 29 which had the highest concentrations of zinc and cadmium.

Cadmium Correlations. Cd was correlated most with Zn (0.95) (Figure 18) and S (0.94) (Figure 20) concentrations. Aside from these correlations, Cd was significantly correlated at the $p < .01$ level with magnetic susceptibility with a correlation coefficient of 0.62 at N=23. All other correlations between Cd and other parameters were insiginificant at either the $p < 0.01$ or $p < 0.05$ level. Cd's association with Zn is discussed above and can be seen in Figure 5. Cd's association with S is likely the result of Cd's occupance as a trace metal in sphalerite (ZnS).
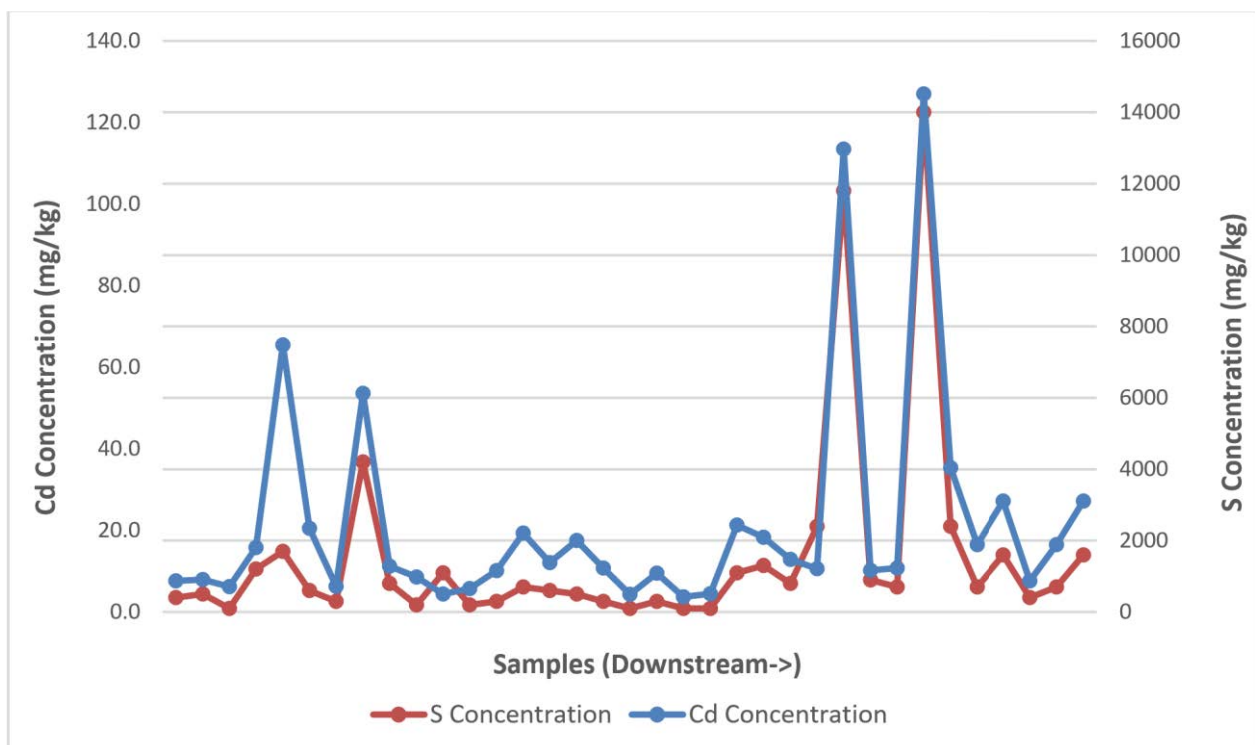
Figure 21 - Total Cd and S concentrations correlation. The Pearson's correlation coefficient is 0.94 and the correlation is significant at $p < .05$ with N=35.

Lead Correlations. Pb was only correlated significantly magnetic susceptibility at the $p < 0.05$ level with an r value of 0.42 and N=23. All other variables were not significantly correlated at the $p < 0.01$ or $p < .05$ level. Pb's lack of association with other elements may be due

to its unique chemical properties and speciation that is unlike other metals of interest in this study.

Iron Correlations. Fe concentrations were strongly correlated with a wider number of variables than Zn, Cd, or Pb. Iron had strong correlations with P (0.92) , Cr (0.92), Co (0.81), and Mn (0.53) all significant at the $p<0.01$ level with N=35. Additionally, iron was significantly correlated with magnetic susceptibility with a correlation coefficient value of 0.81 and significance at the $p<.01$ level with N=23. Iron's correlation with Zn (0.17), Cd (0.18), and Pb (0.17) were almost identical and insignificant.

Iron concentrations may be correlated well with P because iron oxides have an important role in the precipitation and sorption of P (Bortleson and Lee, 1974.) Bortleson and Lee (1974) found that out of 9 sediment cores taken from lake bottoms, 4 had over a 90% correlation coefficient between Fe and P and 7 had over a 90% correlation coefficient between Mn and P with only one core having a higher Fe and P correlation than a Mn and P correlation. Our results indicate a much higher correlation between Fe and P (0.92) than Mn and P (0.40) within Turkey Creek.

Iron concentrations correlation with magnetic susceptibility is expected as iron is considered 'ferromagnetic' and is widely known to have magnetic properties. The correlation not being perfect is likely due to variances in magnetic susceptibility caused by other sources of magnetism (magnetism from other sources in the sediments such as Co and Ni). As discussed later, Co and Ni have strong correlations with magnetic susceptibility in these sediments.

Manganese Correlations. Total Manganese concentrations were primarily correlated with Ni (0.81), Co (0.66), Al (0.65), and Fe concentrations (0.53) significant at the $p<0.01$ level.

Mn was poorly correlated with Zn (0.14), Cd (0.13), and Pb (-0.02). Ni's correlation with manganese suggests that Ni is primarily bound to manganese oxides in Turkey Creek. Mn's correlations with Fe is likely due to their tendency to form oxides in sediments.

Normalization of Zn, Cd, Pb by Fe

Concentrations of zinc, cadmium, and lead in sediments were extremely variable. Normalization by a conservative element, like iron or aluminum, can help identify what part of the sedimentary metal load is natural and what may be anthropogenic. Normalization by iron was effective throughout the 30 samples and their respective heavy metal concentrations with a few exceptions (Figures 22, 23, and 24).

Iron normalization effectively lowers the peaks of all three metals of interest. The natural iron load was high in all sediments with high heavy metal concentrations as well. This suggests that the extremely high zinc and cadmium in samples 26 and 29 may be partially due to a naturally high sedimentary metal load as well as the lead concentration spike in sample 5. Sample 8's peak was not lowered by normalization, so that cadmium, zinc, and lead concentrations were relatively higher in this locality compared to iron concentrations.
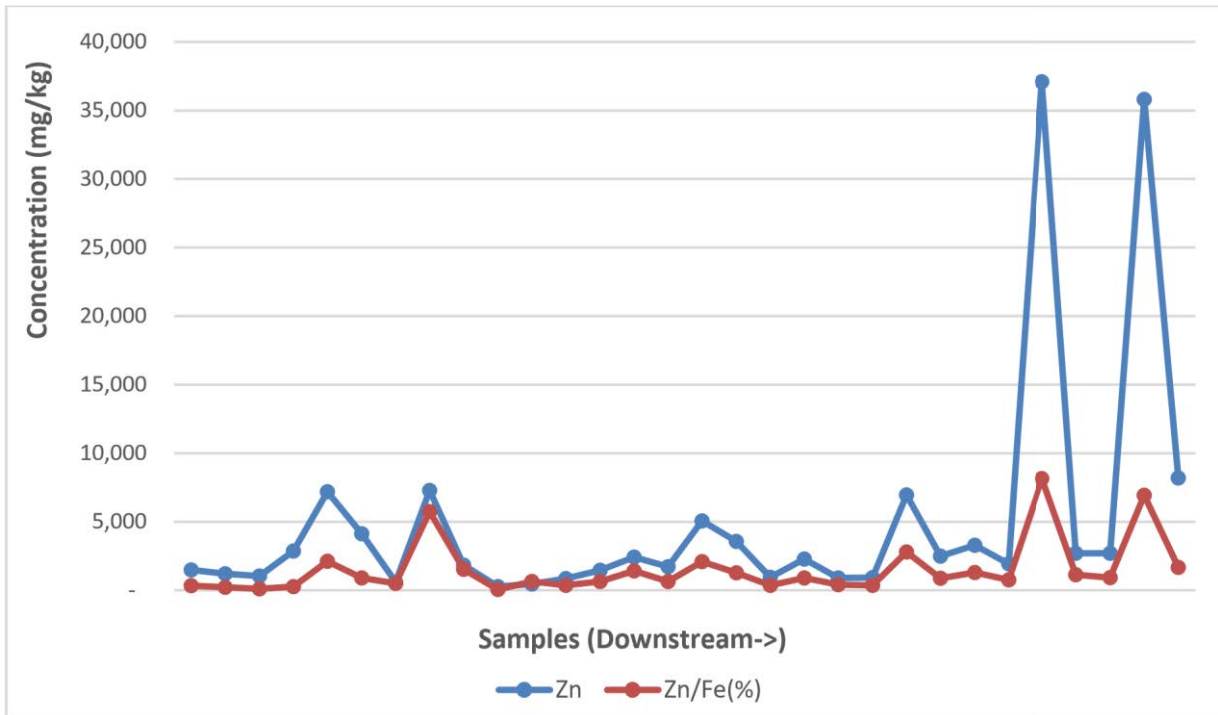
Figure 22 - Zinc concentration divided by percent iron content of samples. Concentration peaks are effectively normalized by iron.
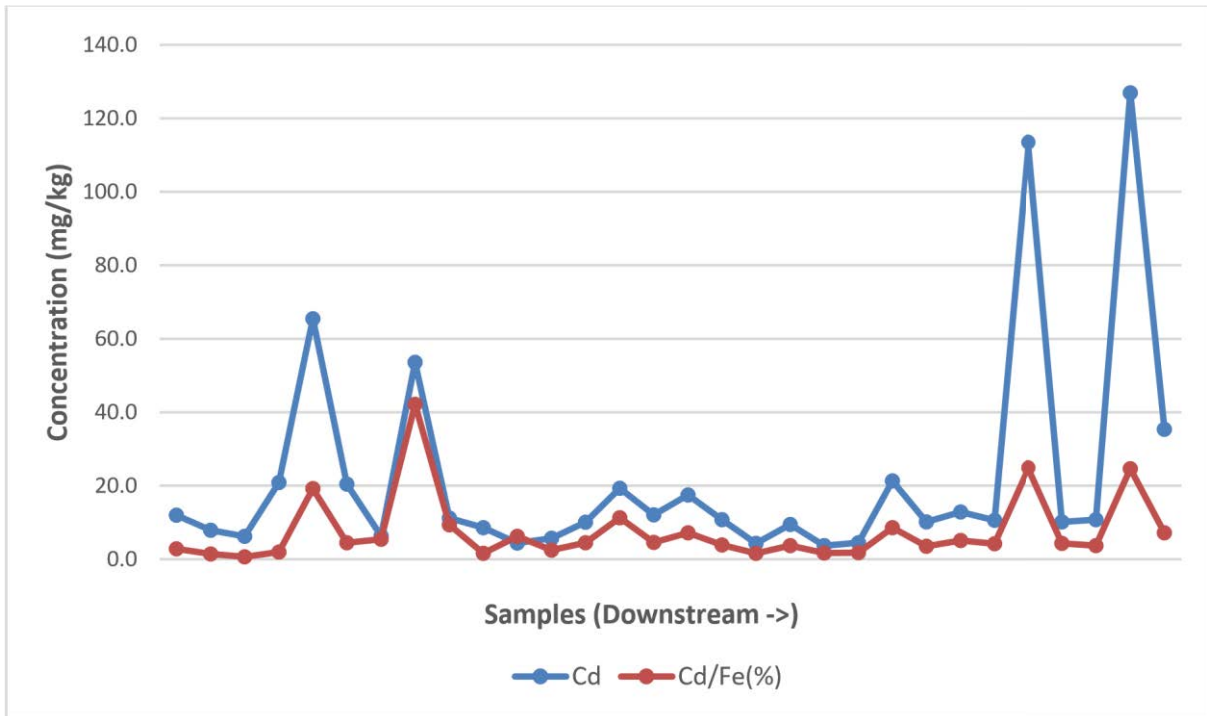
Figure 23 - Cadmium concentration divided by percent iron content of samples. Concentration peaks are effectively normalized by iron.
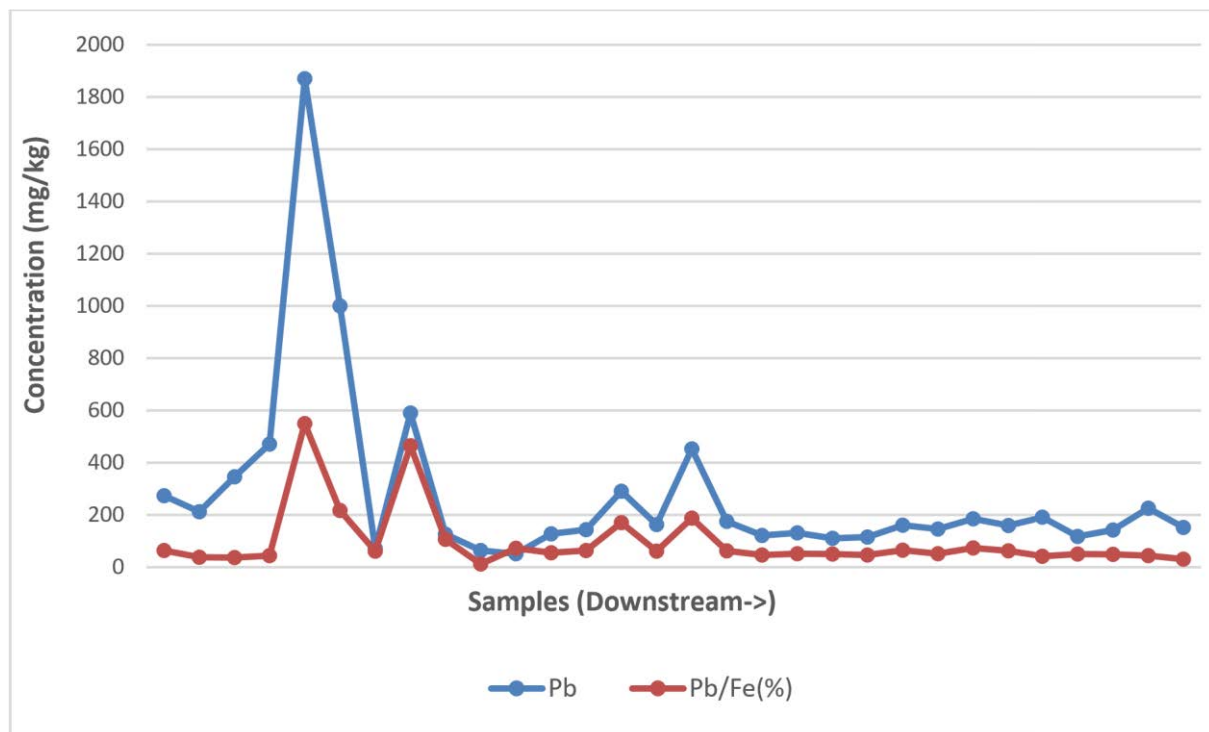
Figure 24 - Lead concentration divided by percent iron content of samples. Concentration peaks are effectively normalized by iron.

Loss on Ignition

Samples lost between 2.3% to 14.2% of original weight of sample indicating high variability in amount of organic content per sample (Table 14). This variability is likely due to the same reasons discussed before in reference to varying total metal concentrations. % organic matter in sediments correlated poorly with Zn (-0.21), Cd (-0.15), and Pb (-0.03) concentrations. Organic matter was most strongly correlated with % Al content at 0.72 which was significant at the $p<0.01$ level with N=23 as well as significantly correlated with Ni concentrations at the $p<0.01$ level. These results indicate generally lower organic matter content than similar studies in the TSMD (Schaider et al., 2014).

Magnetic susceptibility values were compared against Ca concentrations to evaluate carbonate influence on our % mass loss values. The correlation coefficient between these parameters was 0.12 with N=23, and was insignificant even at the $p<0.10$ level, suggesting that carbonate loss likely did not influence our % mass loss values dramatically. The Ca concentration is scaled to represent the exact potential mass loss by the burning of carbonates versus our total mass loss for each sample.

Table 13 - Loss on Ignition Results after 16 hours in the oven with 12 at roughly 610°C.

Loss on Ignition Results				
Sample Number	Sediment Mass (g)	Post-Ignition Sediment Mass (g)	Mass Loss (g)	% Mass Loss
N14.2	10.00	9.23	0.77	7.71
1	10.00	9.34	0.67	6.67
O15.2	10.00	8.58	1.42	14.22
5	10.00	9.53	0.47	4.73
6	10.00	9.58	0.42	4.22
7	10.00	9.63	0.37	3.67
8	10.01	9.23	0.78	7.79
9	10.00	9.49	0.52	5.16
10	10.00	8.67	1.33	13.27
11	10.00	9.52	0.48	4.84
12	10.00	9.75	0.25	2.53
13	10.00	9.54	0.46	4.57
14	10.00	9.40	0.61	6.06
15	10.00	9.43	0.57	5.67
17	10.01	9.65	0.36	3.56
18	10.00	9.53	0.47	4.71
H8.2	10.01	9.04	0.97	9.70
26	10.00	9.57	0.43	4.30
27	10.00	9.77	0.23	2.33
28	10.00	9.54	0.46	4.60
29	10.00	9.66	0.34	3.36
J9.3	10.01	9.57	0.44	4.38
H8	10.00	9.33	0.67	6.73
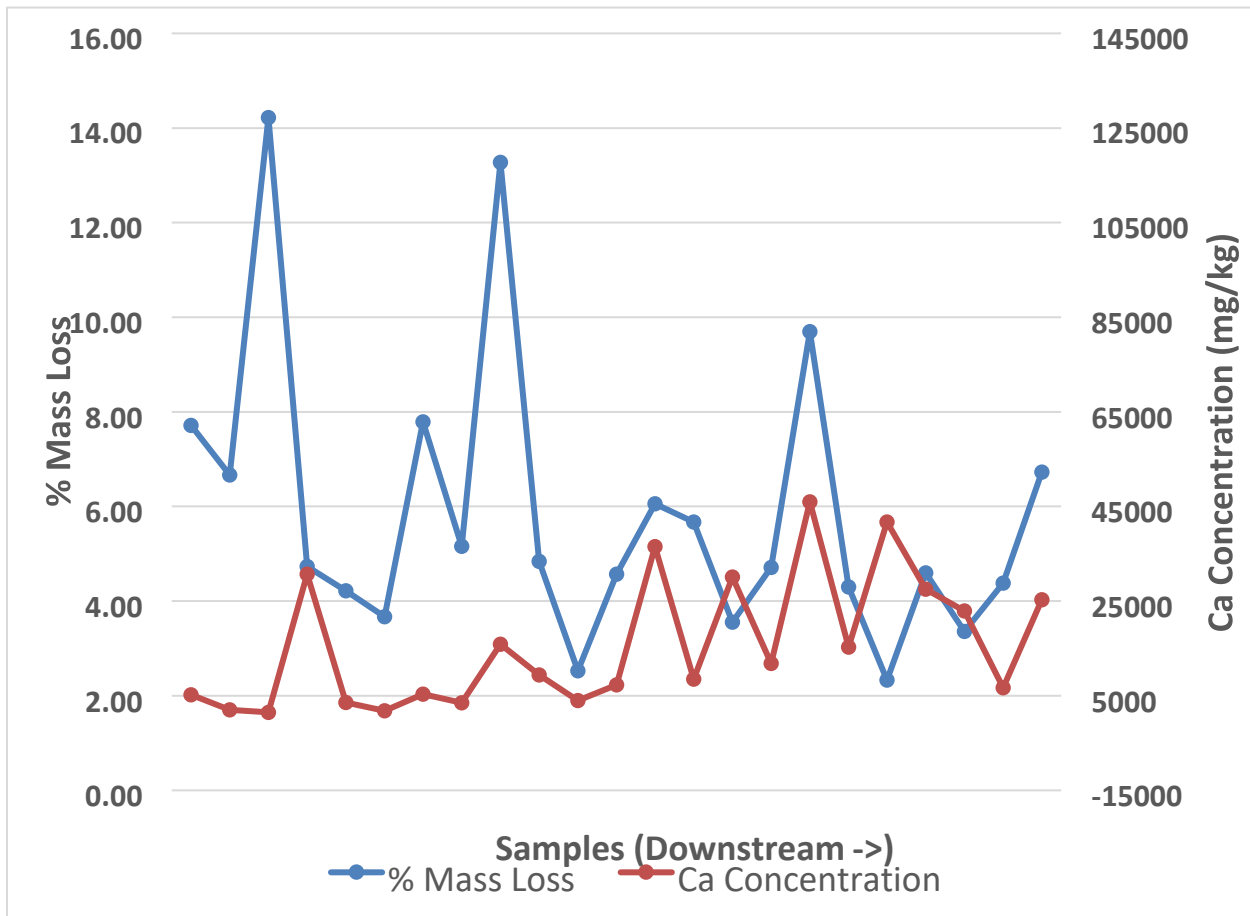
Figure 25 - % Mass loss (LOI) compared to Ca concentrations. Based on molar masses of CaCO3, the figure illustrates the maximum potential influence of carbonate-loss by the loss on ignition method per sample. Pearson's correlation coefficient = 0.12, N=23, P-Value = .58549, not significant at p<.10. This insignificant correlation likely suggests that carbonate-loss did not dramatically influence our loss-on-ignition results.

Magnetic Susceptibility

The average magnetic susceptibility recording was 1×10^{-4}. Correlation between magnetic susceptibility and iron content was favorable with a correlation coefficient of 0.81 and is significant at the p<0.01 level with N=23. The relationship is shown in Figure 26 below. Weaker correlations existed between magnetic susceptibility and Cr concentrations (0.692) P concentrations (0.666), and Cd Concentrations (0.614), Zn (0.579), S (0.550), Co (0.52), all

significant at the p <0.01 level with N=23. Pb concentrations were significantly correlated with magnetic susceptibility at the p<0.05 level with r = 0.43 and N=23. The correlation between magnetic susceptibility and P concentrations is most likely a result of P concentrations' high correlation with Fe content. Cr was also favorably correlated with Fe content and is likely correlated with magnetic susceptibility for that reason.

Magnetic susceptibility's correlation with heavy metals of interest (Zn and Cd significant at the p<0.01 level and Pb significant at the p<0.05 level) may suggest that magnetic susceptibility could be a useful, cost-effective parameter for pre-screening areas of heavy metal contamination as suggested by Rachwal et al., (2017). Jeong and Kim (2018) also were able to effectively use magnetic susceptibility in the mining industry to pre-screen ores for high content of metals of interest, reducing the amount of waste rock produced. Magnetic susceptibility may be useful in TSMD-remediation strategies in a similar fashion.

Table 14 - Magnetic Susceptibility values. Values were determined using SM-30 Meter.

Magnetic Susceptibility		
Sample	Mean Sample Recording	Magnetic Susceptibility
N14.2	0.009	8.67E-05
1	0.022	2.20E-04
O15.2	0.012	1.17E-04
5	0.02	2.00E-04
6	0.026	2.63E-04
7	0.005	5.33E-05
9	0.005	5.00E-05
8	0.006	6.00E-05
10	0.013	1.33E-04
11	0	0.00E+00
12	0.008	8.33E-05
13	0.004	3.67E-05
14	0.004	4.33E-05
15	0.005	5.00E-05
17	0.006	6.33E-05
18	0.006	5.67E-05
H8.2	0.003	3.00E-05
26	0.016	1.60E-04
27	0.009	8.67E-05
28	0.011	1.07E-04
29	0.033	3.30E-04
J9.3	0.01	1.00E-04
H8	0.006	6.00E-05
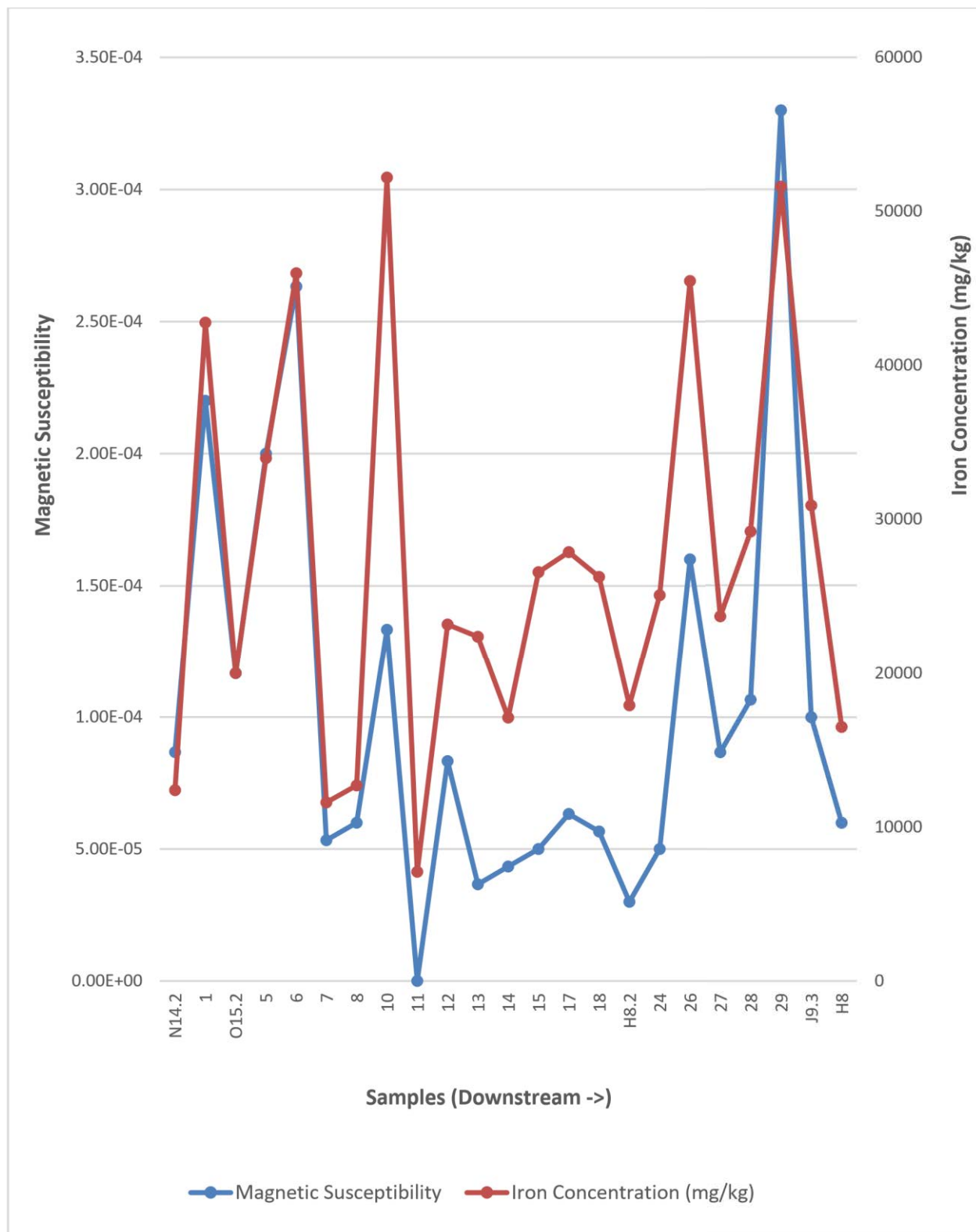
Figure 26 - Magnetic susceptibility values correlated with Fe concentrations. The Pearson's correlation coefficient is 0.82 and is significant at the $p < .01$ level with N=23.

CONCLUSION

This is the first study to my knowledge that has used sequential extractions on sediments within a watershed in the city of Joplin. Our extraction scheme (BCR Method) was different than other studies using sequential extractions within the TSMD as well where Schaider et al. (2014) developed a 8-step procedure to distinguish between iron and manganese oxide fractions and Pearson (2017) used Tessier et al.'s (1979) 5-step procedure. Our results generally showed less Zn and Cd occupying exchangeable and carbonate-bound fractions and iron and manganese oxide fractions than these other two studies. Our Pb fractionation results matched well with Schaider et al. (2014) who found that Pb resided primarily in iron and manganese oxide as well as organic and residual fractions. Although there was a large variability of metal in each fraction, a general trend in mobility was Pb<Zn<Cd based on the metal contained in the bioavailable fraction.

Total metal concentrations of sediments in Turkey Creek may be at sufficient concentrations to be toxic to macroinvertebrate amphipods according to the Dudding Model (MacDonald et al., 2009) where 50% of our sediment samples were considered high risk. The potential for biomagnification exists as indicated by studies that have found wild birds with zinc poisoning within the TSMD (Sileo et al., 2003, Beyer et al., 2004). Our results in terms of total metal concentrations compared to other studies that have evaluated Turkey Creek were comparable (Smith, 2016) where total metal concentrations exceeded established PECs often.

Magnetic susceptibility's correlation with Zn and Cd concentrations significant at the $p<0.01$ level and Pb concentrations significant at the $p<0.05$ level suggest that magnetic susceptibility may be successfully employed as a cost-effective method of pre-screening areas for

heavy metal contamination within the TSMD. Future studies may employ this method as a means of cost and time-effective way of assessing heavy metal contamination, although more research needs to be done to know how well this correlation holds up throughout the TSMD.

The variability exhibited by these sediments was high in spite of remediation that has taken place in the past decade and exposed the toxic levels of metal content still present in some sediments. Future work may focus on assessing variability between concentrations as a function of location where samples taken nearby are assessed against each other statistically. This watershed may be more variable than other locations within the TSMD given the EF5 Tornado, sporadic nature of remediation efforts, as well as vast number of mines with sporadic tailing pile placements. Future work may also consider incorporating freshwater mussels and assessing their survivability within TSMD waters at different locations as they are sensitive to heavy metals as suggested by Johnson et al. (2016).

Our results indicate that while assessing total metal concentration alone, the total heavy metal concentrations in Turkey Creek sediments may pose a risk in at least half of the samples to benthic and aquatic biota per established PECs and the Dudding Model. Our fractionation results suggest that a majority of Zn and Cd is locked up in organic and residual fractions, including sulfides, and around 10-15% of Zn and Cd may occupy exchangeable and carbonate-bound fractions indicating a drop in pH could release dangerous concentrations of cadmium from sediments. Pb will not release in any significant concentration from a pH drop alone as Pb occupied exchangeable and carbonate-bound fractions in trace concentrations. However, Pb may occupy iron and manganese oxide fractions in toxic concentrations so a drop in pH and reducing conditions may produce dangerous water conditions.

Similar studies in the future may consider using microscopic analysis of grains to identify sulfides to match other lines of evidence (large organic fraction, high correlations between Zn, Cd, and S, and proximity to tailings). It may also be useful to employ size fractionation, separating clay, silt, and sand fractions to assess differences in total metal concentrations and metal speciation between these sizes.

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APPENDICES

Appendix A

Sample latitude, longitude, total metal concentrations of Zn, Cd, Pb, Fe, Mn, % mass loss, magnetic susceptibility and total concentrations of S, P, Ca, Al, Co, Ni, and Cr (used for total metal correlations). Total metal is derived by acid digestion via aqua regia and ICP-MS.

Sample	Latitude	Longitude	% Mass Loss	Total Zn (mg/kg)	Total Cd (mg/kg)	Total Pb (mg/kg)
N14.2	37.074	-94.414	7.71	974	7.6	123
1	37.075	-94.422	6.67	1480	12	274
2	37.076	-94.427	ND	1210	7.9	212
O15.2	37.075	-94.423	14.22	2600	15.8	311
3	37.076	-94.433	ND	1050	6.2	346
4	37.078	-94.435	ND	2860	20.9	471
5	37.079	-94.437	4.73	7180	65.5	1870
6	37.080	-94.440	4.22	4130	20.5	1000
7	37.080	-94.444	3.67	585	6.3	71
8	37.083	-94.446	7.79	7280	53.6	590
9	37.083	-94.447	5.16	1830	11.2	127
10	37.084	-94.450	13.27	271	8.6	64
11	37.086	-94.451	4.84	462	4.4	51
12	37.087	-94.453	2.53	854	5.7	128
13	37.089	-94.452	4.57	1460	10.1	144
14	37.090	-94.455	6.06	2420	19.3	291
15	37.090	-94.458	5.67	1710	12.1	163
16	37.092	-94.466	ND	5070	17.5	453
17	37.092	-94.467	3.56	3570	10.8	176
18	37.092	-94.467	4.71	942	4.3	122
19	37.093	-94.468	ND	2280	9.5	131
20	37.093	-94.468	ND	902	3.7	110
H8.2	37.094	-94.468	9.70	2220	18.3	238
21	37.094	-94.468	ND	915	4.5	115
22	37.094	-94.468	ND	6950	21.3	161
23	37.094	-94.470	ND	2490	10.2	146
24	37.094	-94.470	ND	3280	12.9	185
25	37.095	-94.471	ND	1920	10.6	159
26	37.095	-94.471	4.30	37100	113.5	192
27	37.095	-94.472	2.33	2710	10.2	118
28	37.095	-94.472	4.60	2700	10.8	142
29	37.096	-94.474	3.36	35800	127	226
30	37.096	-94.474	ND	8190	35.4	152
J9.3	37.101	-94.485	4.38	3120	16.5	145
H8	37.101	-94.495	6.73	3820	27.2	263

Sample	Magnetic Susceptibility	Total Fe (mg/kg)	Total Mn (mg/kg)	Al (%)	Co (mg/kg)	Ni (mg/kg)	Cr (mg/kg)
N14.2	8.67E-05	12400	602	1.05	8	5	14
1	2.20E-04	42800	554	1.15	20	30	198
2	ND	55400	288	1.1	16	18	258
O15.2	1.17E-04	20000	418	1.05	8	31	26
3	ND	93100	2020	1.08	35	39	438
4	ND	107000	1105	1.09	20	28	509
5	2.00E-04	34000	709	0.66	16	14	83
6	2.63E-04	46000	980	0.57	12	14	169
7	5.33E-05	11600	146	0.92	7	8	15
8	6.00E-05	12700	447	0.86	8	15	15
9	ND	11900	378	0.64	9	10	24
10	1.33E-04	52200	3310	3.19	22	60	43
11	0.00E+00	7100	138	0.71	5	6	13
12	8.33E-05	23200	1040	0.66	10	12	58
13	3.67E-05	22400	997	0.76	12	13	41
14	4.33E-05	17100	820	0.83	10	11	20
15	5.00E-05	26600	852	0.96	12	16	32
16	ND	24200	903	0.6	11	15	65
17	6.33E-05	27900	547	0.52	9	16	77
18	5.67E-05	26300	637	0.73	10	20	75
19	ND	25400	623	0.48	9	13	76
20	ND	21700	546	0.43	10	12	58
H8.2	3.00E-05	17900	853	1.14	14	15	20
21	ND	24600	593	0.46	8	13	69
22	ND	24800	847	0.53	7	14	64
23	ND	28500	899	0.43	10	15	81
24	5.00E-05	25100	803	0.5	12	18	69
25	ND	25200	619	0.62	10	16	47
26	1.60E-04	45500	1155	0.69	13	30	43
27	8.67E-05	23700	677	0.31	8	12	60
28	1.07E-04	29200	739	0.4	10	18	59
29	3.30E-04	51600	1205	0.54	14	27	90
30	ND	49000	1515	0.52	14	36	122
J9.3	1.00E-04	30900	1035	0.69	16	19	78
H8	6.00E-05	16500	919	0.65	10	13	22

Sample	S (%)	P (ppm)	Ca (%)
N14.2	0.04	390	0.52
1	0.06	760	0.2
2	0.05	840	0.15
O15.2	0.12	650	3.07
3	<0.01	1220	0.36
4	<0.01	1300	0.18
5	0.17	580	0.53
6	0.06	650	0.35
7	0.03	110	1.59
8	0.42	260	0.94
9	0.08	210	0.4
10	0.02	510	0.73
11	0.11	130	3.65
12	0.02	340	0.85
13	0.03	300	3.01
14	0.07	320	1.18
15	0.06	440	4.6
16	0.05	410	1.53
17	0.03	430	4.17
18	0.01	470	2.75
19	0.03	410	2.29
20	<0.01	380	0.67
H8.2	0.13	550	2.53
21	0.01	400	0.82
22	0.11	430	0.22
23	0.04	420	0.48
24	0.08	490	1.51
25	0.24	400	0.59
26	1.18	630	0.23
27	0.09	420	0.4
28	0.07	440	0.57
29	1.4	560	0.46
30	0.24	620	1.28
J9.3	0.07	460	1.54
H8	0.16	460	3.34

Appendix B

Geochemical fraction data of Zn, Cd, and Pb (in mg/kg). Extraction 1 refers to the bioavailable fraction (exchangeable and carbonate-bound) and Extraction 2 refers to the potentially bioavailable fraction (reducible fraction, or iron and manganese-oxide fraction).

Sample	Zn Extraction 1	Zn Extraction 2	Cd Extraction 1	Cd Extraction 2	Pb Extraction 1	Pb Extraction 2
N14.2	443	435	1	1	3	89
1	177	430	0	6	3	129
2	105	ND	0	ND	1	ND
O15.2	612	990	4	1	5	201
3	89	355	1	3	0	213
4	580	972	3	17	2	-14
5	2091	2505	5	28	205	1359
6	1513	1373	9	6	91	854
7	154	112	1	1	3	43
8	903	2090	0	25	10	190
9	625	725	1	8	5	85
10	34	56	4	1	1	32
11	204	132	1	0	2	35
12	364	234	1	0	10	80
13	470	406	2	1	9	116
14	1031	889	7	8	20	224
15	550	583	0	8	5	91
16	390	922	2	4	2	222
17	201	676	0	6	3	13
18	8	251	0	1	1	10
19	113	90	0	3	1	16
20	129	481	0	3	0	75
H8.2	616	1007	6	6	8	151
21	178	720	1	3	0	91
22	163	429	0	2	0	4
23	177	646	0	4	1	3
24	191	481	1	3	1	18
25	163	1014	1	6	0	29
26	452	1848	1	8	0	3
27	225	409	1	2	1	23
28	247	484	1	3	0	4
29	214	974	0	4	1	19
30	197	1174	1	3	0	9
J9.3	874	710	6	1	3	135
H8	968	739	8	1	4	166

Appendix C
Significant correlations between total metal concentrations, % organic matter, and magnetic susceptibility. Zn, Cd, Pb, Fe, Mn, % organic matter, and magnetic susceptibility were investigated for correlations between each other as well as their relationships to Al, Co, Ni, S, and P concentrations. Significance was determined at the $p<.01$ level and at the $p<.05$ level.

Significant Correlations				
Correlation	Pearson's Correlation Coefficient (r)	Sample Number (N)	P-value	Significance (p <0.01)
Total Metal Concentration Correlations				
Zn and S Concentrations	0.97	35	<0.00001	At r=0.97 and N=35, the result is significant.
Zn and Cd Concentrations	0.95	35	<0.00001	At r=0.95 and N=35, the result is significant.
Cd and S Concentrations	0.94	35	<0.00001	At r=0.94 and N=35, the result is significant.
Fe and Cr Concentrations	0.92	35	<0.00001	At r=0.92 and N=35, the result is significant.
Fe and P Concentrations	0.92	35	<0.00001	At r=0.92 and N=35, the result is significant.
Fe and Co Correlations	0.81	35	<0.00001	At r=0.81 and N=35, the result is significant.
Fe and Mn Correlations	0.53	35	0.001058	At r=0.53 and N=35, the result is significant.
Mn and Ni Concentrations	0.81	35	<0.00001	At r=0.81 and N=35, the result is significant.
Mn and Co Concentrations	0.66	35	0.000016	At r=0.66 and N=35, the result is significant.
Mn and Al Concentrations	0.65	35	0.000024	At r=0.65 and N=35, the result is significant.
% Organic Matter Correlations				
Mass Loss and Aluminum Content	0.72	23	0.000107	At r=0.72 and N=23, the result is significant.
Mass Loss and Ni Concentrations	0.56	23	0.005455	At r=0.56 and N=23, the result is significant.
Magnetic Susceptibility (MS) Correlations				
MS and Fe Concentrations	0.82	23	<0.00001	At r=0.82 and N=35, the result is significant.
MS and Cr Concentrations	0.71	23	0.00013	At r=0.71 and N=23, the result is significant.
MS and P Concentrations	0.69	23	0.000285	At r=0.69 and N=23, the result is significant.

MS and Cd Concentrations	0.62	23	0.00179	At r=0.62 and N=23, the result is significant.
MS and Zn Concentrations	0.58	23	0.003793	At r=0.58 and N=23, the result is significant.
MS and S Concentrations	0.55	23	0.006549	At r=0.55 and N=23, the result is significant.
MS and Co Concentrations	0.52	23	0.011345	At r=0.52 and N=23, the result is not significant at $p<0.01$, but is significant at $p<0.05$.
MS and Pb Concentrations	0.43	23	0.036584	At r=0.43 and N=23, the result is not significant at $p<0.01$, but is significant at $p<0.05$.