Mine Water and the Environment (2019) 38:378–384
https://doi.org/10.1007/s10230-018-0568-3

TECHNICAL ARTICLE

Geochemical Fractionation of Stream Sediments Impacted by Pb-Zn Mining Wastes: Missouri, USA

Miles A. Pearson[1] · **Richard N. Biagioni**[1] · **Mélida Gutiérrez**[2]

Received: 9 April 2018 / Accepted: 9 November 2018 / Published online: 20 November 2018

Abstract

Stream sediments affected by historic mining in Aurora, Missouri, were digested via sequential extraction to determine the amount of Zn, Pb, and Cd bound to each of five geochemical phases: exchangeable, carbonate, Fe-Mn oxides, organic matter, and residual. The metal bound to the exchangeable and carbonate phases represents an approximation of the metal that is bioavailable, and thus a source of toxicity to aquatic biota and a contamination risk to the aquifer underneath. The bioavailable fraction was found to increase with total metal content, comprising an average of 19% of the total Zn, 13% of the Pb, and 14% of the Cd. In general, Pb was preferentially bound to the residual fraction, Zn to the Fe-Mn oxides fraction, and Cd to the organic fraction. As a result of metals binding to different chemical fractions, each of these metals will mobilize differently if/as environmental conditions change and chemical weathering progresses. The most mobile of the three metals was Cd and the least mobile Pb. The concentration pattern for each metal downstream reflects their relative mobility.

Keywords Abandoned mine wastes · Lead · Sediment · Sequential extraction · Zinc

Introduction

Abandoned mine wastes represent a potential hazard to their surrounding environment long after a mine closes (Hudson-Edwards et al. 2011; Stefanowicz et al. 2014). Wastes from lead (Pb) and zinc (Zn) mining operations disposed of in tailings (chat piles), settling ponds, and as smelter fallout, are a common occurrence in the tri-state mining district (TSMD) of Kansas, Oklahoma, and Missouri in the U.S. (Johnson et al. 2016) and in many other former Pb-Zn mining regions (Gutiérrez et al. 2016a).

Pb and Zn contained in mine wastes as sulfides progressively transform into secondary minerals once exposed to oxidizing conditions (Concas et al. 2006; Schaider et al. 2014). Runoff in contact with mine wastes transports Pb and Zn into nearby streams, often carrying associated elements such as cadmium (Cd), iron (Fe), manganese (Mn), copper (Cu), and thallium (Tl) (Liu et al. 2017; Musilova et al. 2016; Stefanowicz et al. 2014), where they either settle or attach to the solid phases of the stream sediment and can remain there for a long time. Under alkaline conditions, these metals pose little threat to the environment as they remain mostly immobile. However, both Cd and Tl, which are toxic even at trace concentrations, have a higher mobility and may be present in pore water or in the water column at concentrations high enough as to be toxic to aquatic biota (Kennou et al. 2015; Liu et al. 2017).

Environmental and mineralogical changes in the sediment may cause metals to be released into the surrounding water depending of the type of substrate, metal concentration, and other parameters such as temperature, pH, and Eh (Roig et al. 2015; Wojtkowska et al. 2016). Knowing the amount of metal that could be released over a range of possible conditions is vital for determining the proper containment and the effectiveness of reclamation strategies (Brown et al. 2014; Schaider et al. 2014).

Mining in the TSMD approximately stopped in the 1950s. Subsequent remediation, mostly phytostabilization, has since been applied to parts of the TSMD, and although the

---

✉ Mélida Gutiérrez
mgutierrez@missouristate.edu

Miles A. Pearson
miles27@live.missouristate.edu

Richard N. Biagioni
rnbiagioni@missouristate.edu

[1] Chemistry Department, Missouri State University, Springfield, MO 65897, USA

[2] Geography, Geology and Planning, Missouri State University, Springfield, MO 65897, USA

evidence of mining has been almost completely erased from the landscape in the remediated areas, toxic concentrations persist in locations impacted by smelters and where the mining waste (chat piles) once stood (Johnson et al. 2016). Previous work by Gutiérrez et al. (2016b) identified a segment of Chat Creek where median concentration values of 5791 mg/kg Zn, 196 mg/kg Pb, and 34 mg/kg Cd were observed. To put these numbers in context, the probable effect concentrations (PEC) guidelines derived from toxicity tests to aquatic biota for these metals are 459, 128, and 5 mg/kg for Zn, Pb, and Cd, respectively (Macdonald et al. 2000). The metal concentrations in this stream segment were above PEC guidelines and therefore presumably toxic to aquatic organisms.

A valuable piece of information in the characterization of metal-contaminated sediments is the fractionation of these metals into the geochemical phases within the sediment in order to determine the mobility of the metal and to forecast potential variations with time and changing pH and redox conditions. Mobility largely depends on the chemical binding, and therefore, the chemical form of the metal. For example, upon reaching a stream, PbS transforms over time to other mineral forms e.g. $PbCO_3$ (Schaider et al. 2014), $PbSO_4$ (Wojtkowska et al. 2016), and PbO (Cao et al. 2008). In alkaline conditions (pH 7), all these minerals are highly immobile with solubility $PbSO_4 > PbO > PbCO_3$ (Cao et al. 2008), but become more soluble as pH decreases. In this study, a further characterization of the sediments was carried out by conducting sequential extraction to determine the mobility and bioavailability of the Zn, Pb, and Cd.

The objectives of this study were: (1) to further evaluate the state of contamination of streams surrounding the former mining town of Aurora, Missouri, by assessing the mobility of Zn, Pb, and Cd in different geochemical phases in stream sediments, and (2) to identify the conditions under which the metals could remobilize to either interfere with remediation procedures or contaminate the underlying karst aquifer, and (3) to critically address the difficulties encountered through the analytical sequential extraction procedure.

Primary and Secondary Minerals

Pb and Zn are mined primarily from sulfide deposits, where the primary minerals are galena (PbS) and sphalerite (ZnS), with lesser amounts of chalcopyrite ($CuFeS_2$). Cd substitutes for Zn and is present in sphalerite at about 3%. Generally, these sulfide minerals are found emplaced in limestone and/or chert (Gutierrez et al. 2016a). After chemical weathering of primary sulfides, secondary minerals form, including cerussite ($PbCO_3$), anglesite ($PbSO_4$), smithsonite ($ZnCO_3$), hydrozincite ($ZnCO_3 \cdot 3Zn(OH)_2$), hemimorphite ($Zn_4Si_2O_7(OH)_2.H_2O$), and iron and manganese oxides and hydroxides (referred to here as Fe-Mn oxides; Carroll et al. 1998; Hudson-Edwards et al. 1995).

The formation of a particular secondary mineral depends on the environmental conditions, type and amount of minerals present, and time. At near-neutral pH and in the presence of carbonates, PbS weathers to insoluble $PbCO_3$ (Hudson-Edwards et al. 1995), while ZnS oxidizes to form dissolved Zn^{+2}, which readily adsorbs to solid phases such as clays and Fe-Mn oxides (Carroll et al. 1998). Although Fe-Mn oxides are regarded as stable and generally have similar chemical interactions, a difference between them is that Mn oxides dissolve at a higher pH and Eh than Fe oxides (Hudson-Edwards et al. 1995).

Metal Fractionation, Mobility and Bioavailability

Fractionation seeks to measure the amount of metal bound to different geochemical phases of the solid material, in this case sediment, and is obtained after reacting a sediment sample with a series of extractants of increasing strength. The amount of metal released by each extraction depends on a variety of factors, among them metal content, chemical composition of the extractant, temperature, and pH.

The two most common fractionation procedures are the Tessier method (Tessier et al. 1979) and the BCR method (Pueyo et al. 2001), which consist of five and three sequential extractions, respectively. The five sequential extractions comprised in the Tessier method are: (1) easily exchangeable, (2) bound to carbonates (3) bound to Fe-Mn oxide, (4) bound to organic matter and sulfides, and (5) residual. Slight modifications to the Tessier method are common, and are used to fit to a specific problem and/or sampling medium (Schaider et al. 2014; Zimmerman and Weindorf 2010). Common modifications include separating the metal bound to Fe-Mn oxides fraction into two: easily reducible and moderately reducible (Schaider et al. 2009), the use of ammonium acetate instead of sodium acetate as an extractant for the exchangeable fraction (Favas et al. 2014), and using *aqua regia* extraction to approximate total metal content (Wojtkowska et al. 2016).

The BCR method consists of a three-step extraction procedure: (1) exchangeable and carbonate bound, (2) hydroxylamine hydrochloride extraction, and (3) H_2O_2 / $NH_4C_2H_3O_2$ extraction. Modifications to this method are also common (Cappuyns et al. 2007; Pueyo et al. 2001). Although less common, several other sequential extraction procedures have also been used (Zimmerman and Weindorf 2010).

Toxicity is related to the metal fraction that is bioavailable, and in the case of contaminated sediments, organisms that are in direct contact with pore water e.g. benthic invertebrates would be the most affected (Macdonald et al. 2000), but other organisms can also be affected through the food chain (Beyer et al. 2004). In general terms, toxicity for these metals has been reported as Cd > Pb > Zn. Bioavailability is closely associated with mobility, and refers specifically to the fraction of metal that is available to biota.

The TSMD area has been thoroughly studied for the potential impact of metals to aquatic biota (Besser et al. 2015; Macdonald et al. 2000), based on toxicity assay studies using freshwater invertebrates and either pore water concentration or total metal concentration of sediments. Fewer studies however have addressed the fractionation of metals in the TSMD. Notable exceptions include those by Carroll et al. (1998) and Schaider et al. (2009, 2014) who investigated mobility and bioavailability of metals from contaminated stream segments within the TSMD, mainly in Tar Creek, Oklahoma.

Materials and Methods

Study Area

Aurora, Missouri, is one of several historic mining towns scattered throughout the TSMD. The geology and mining history of the TSMD, where ores of Zn (sphalerite) and Pb (galena) were mined for over a century, is described in detail in Johnson et al. (2016). After mining ceased, the town underwent several reclamation stages depending on the available funding, each stage consisting of filling cavities and planting of grass on the leveled, sod-covered ground, a process known as phytostabilization. In a previous study, Gutiérrez et al. (2016b) determined that metal contamination was still present in the Aurora area despite remediation, and was confined to two streams flowing next to the former location of chat piles, Chat Creek and Elm Branch. This study concentrates on these two streams, plus a nearby unnamed ephemeral stream (Fig. 1) used as reference. The total metal content of the unnamed creek is consistently less than in Chat Creek and Elm Branch, and is regarded as representing background concentrations.

Besides the toxicity to aquatic biota, metal contaminated water poses a threat to the Ozark aquifer underneath, which is used as a drinking water supply, and whose fractured limestone makes groundwater vulnerable to contamination. This aquifer consists of thick sequence of Paleozoic and cherty limestones, forming an open aquifer that is highly karstified in its upper part (Richards and Mugel 2008).

Sampling

Sediments of the three streams near or within Aurora's city limits were sampled: Chat Creek, Elm Branch, and the unnamed ephemeral creek that runs parallel to Chat Creek (see Fig. 1). A total of 39 samples were collected from the top 10 cm in 2015 with four additional samples collected in 2016 along a 3.5 km stretch of Chat Creek, 0.5 km of Elm Branch, and 2.0 km of the unnamed creek. The 2016 sampling was scheduled to verify the metal levels of contaminated vs. non-contaminated sites (2 sampling sites each). Eight water samples were collected in 2016 but their metal contents were all below detection limits and so were not included in this analysis.

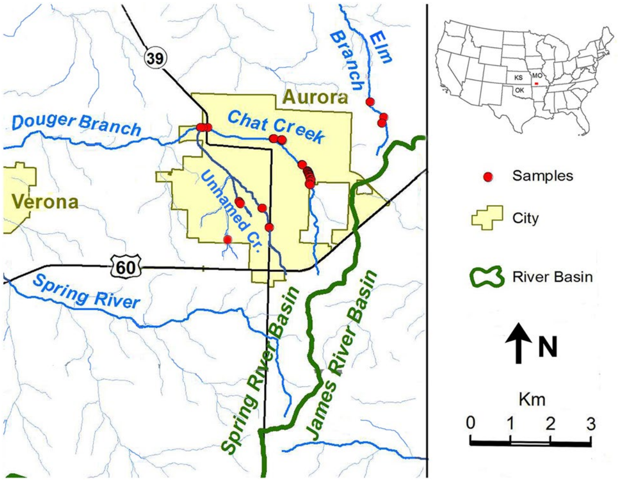

Fig. 1 City of Aurora, Missouri, with location of Chat Creek, Elm Branch, and the unnamed creek, and sediment sampling locations (red dots)

Sediment samples were kept cold during transport to the laboratory, where they were air-dried, disaggregated, and passed through a 1 mm sieve. The pH was determined for a suspension of a 10 g subsample of the dry sediment mixed with at a 1:2 w/w ratio of sediment to water. A 5 g subsample was sent to a commercial laboratory to be analyzed for metal content after *aqua regia* digestion. For this study, the *aqua regia* extraction was considered a close approximation of total metal content. The remaining dried sample underwent sequential extraction following the four first extractions of the Tessier method described below. The residual fraction was estimated as the difference between the total metal content and the sum of the metal extracted in the first four extractions.

Analytical

Approximately 2.0 g of each sediment was weighed out (actual mass recorded) and digested sequentially according to the Tessier method, keeping a 1:10 sediment-extractant ratio in each extraction, as described below and in more detail in Pearson (2017). After each extraction, samples were centrifuged for 30 min, decanted, and filtered through Fisherbrand G4 glass fiber filters. Samples were then analyzed by ICP-AES (Varian Liberty AX-150 Turbo), AAS (Varian SpectrAA 220FS), or ICP-MS (Thermo Scientific iCAP-Q). The first two instruments are housed at Missouri State University, whereas the ICP-MS belongs to the Blackman Water Treatment Plant (City Utilities of Springfield). The

ICP-MS was used for very small concentrations for samples that produced unstable readings in the ICP-AES.

The first fraction was digested by adding 1 M NaOAc to each sample. These samples were further diluted to 10:1 from the original volume of the extracts to minimize interference from high salt content.

To the sediment residues of the first extraction step, 1 M acetic acid/sodium acetate adjusted to pH 5 with glacial acetic acid was added. Samples were agitated continuously for 2 h at room temperature and diluted twofold before metal concentrations were measured with the ICP-AES.

The third fraction, bound to Fe-Mn oxides, was extracted with a 0.04 M $NH_2OH.HCl$ (hydroxylamine hydrochloride) in 25% (v/v) $HC_2H_3O_2$ and placed in a hot water bath (≈96 °C) for 6 h with occasional agitation. Metal concentrations were measured using the ICP-AES.

For the fourth fraction, a solution 0.02 M nitric acid and 30% H_2O_2 adjusted to pH 2 with concentrated nitric acid was added to the residue, placed in a hot water bath (85 °C), and heated with occasional stirring. After 2 h, another 6 mL portion of the extractant solution was added to each sample. Samples were heated for an additional 3 h with occasional stirring. After cooling, 10 mL of 3.2 M NH_4OAc in 20% (v/v) HNO_3 was added to each sample, and samples were diluted to 40 mL and agitated for 30 min. When run on ICP-AES, the instrumental response was inconsistent and unstable for reasons that were not clear. Samples from this fraction were then analyzed by flame AAS, which gave consistent results.

Quality Control

To assure quality control, blank checks, laboratory control checks (LCC), laboratory duplicates (LD), field duplicates (FD), and matrix spikes (MS) were conducted. The average percent error of the LCC for the four fractions was between 5 and 6% for all 3 metals, and thus considered accurate. Every sixth sample was run twice (LD0, with < 10% difference). The largest differences were observed in samples with concentrations approaching the detection limits, where a small difference can account for a large percentage. Similarly congruent results were observed when matrix spikes were applied.

Field duplicates were collected about every 10th sample. Differences within a field duplicate pair gives an idea of natural variation within sediments at about the same geographic location (samples collected 0.5–1.0 m apart). Field duplicates included sample pairs no. 7–8, 16–17, and 44–45. The concentrations for each pair were within an average of 18%, with the exchangeable and carbonate fractions varying less (12% average difference in metal concentration) and the Fe-Mn oxides, organic, and residual fractions slightly more (averaging 30%).

Results and Discussion

The pH of the sediments ranged between 7.06 and 7.64, with an average of 7.47, indicating an absence of acid mine drainage, likely due to the low iron content of the mine tailings in the Missouri part of the TSMD (Schaider et al. 2009). Similar to the heterogeneity of metal content in the chat, stream sediments were highly heterogeneous with respect to their metal content, with up to 18% difference according to field duplicates.

Metal content is shown in Table 1 and Fig. 2. Because of the sharp difference between high and low concentrations observed for all metals (Fig. 2), sediments were separated into two groups for statistical analysis. Low concentrations of visibly non-affected stream segments were considered background concentrations, and were grouped together with sediments with total concentrations < 850 mg/kg Zn, < 200 mg/kg Pb, and < 7 mg/kg Cd. Samples with concentration above background were designated here as *contaminated*. The metals bound to each of the five fractions for each of these two groups are shown in Table 1. The values, reported as average ± standard deviation, offer a broad overview of the metal distribution within the fractions of the contaminated and non-contaminated/background sediments.

Figure 2 shows the concentration and distribution among the five fractions for samples downstream each of Chat Creek, Elm Branch, and the unnamed creek. The unnamed

Table 1 Average ± standard deviation of the concentration of metals recovered during sequential extraction in each of five fractions in sediment samples of contaminated (c) and background (bkg) concentrations

	N	Exchangeable	Carbonate	Fe-Mn oxides	Organic	Residual
Zn_c	42	129 ± 85	1334 ± 1300	2269 ± 946	1529 ± 1405	2682 ± 5202
Zn_{bkg}	8	18 ± 11	155 ± 105	246 ± 67	131 ± 47	182 ± 119
Pb_c	19	17 ± 23	405 ± 507	718 ± 1191	118 ± 134	853 ± 1067
Pb_{bkg}	31	0.3 ± 0.5	8.2 ± 4.3	33.7 ± 10.2	14.3 ± 4.9	68.9 ± 29.4
Cd_c	40	2.3 ± 7.8	4.0 ± 9.7	10.9 ± 5.8	17.9 ± 21.6	21.02 ± 52.3
Cd_{bkg}	10	0.1 ± 0.1	0.4 ± 0.1	0.4 ± 0.1	0.2 ± 0.2	0.8 ± 0.5

N no. samples, includes replicates

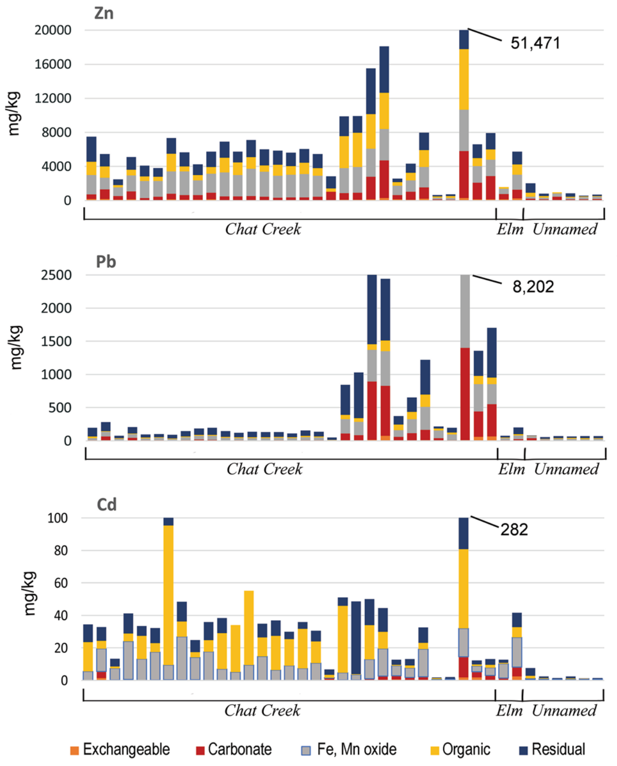

Fig. 2 Zn, Pb, and Cd content in mg/kg in each fraction and for sediment samples downstream for Chat Creek, Elm Branch, and the unnamed Creek. Concentrations for the one sample that surpassed the scale are shown as a numerical value

creek flows parallel to Chat Creek as it traverses the town of Aurora (see Fig. 1). According to historic air photographs, most of the former chat piles had stood between Chat Creek and Elm Branch in the NE part of town (Gutierrez et al. 2016b). The sediment concentrations reflect this fact, with metal concentrations within the segments of Chat Creek and Elm Branch significantly higher than those in the unnamed creek.

Figure 2 also reflects the fact that Pb, Zn, and Cd bind differently to each geochemical fraction, suggesting competition among the metals and mineral phases. Although the results for contaminated (> 200 mg/kg Pb) sediments show that the Pb is preferentially bound to iron oxides and residual fractions, locations with much higher metal content (Fig. 2) indicate that a significant amount of Pb binds to the carbonate fraction. The latter would become available if the pH drops to about 5.5. The average amount of Pb that would be released at that pH would is 44%, compared to 18% Zn and 11% Cd (Table 1).

Also, the sharp contrast between low and high concentrations downstream in Fig. 2 indicates that Pb is largely immobile, a pattern that is less noticeable for Zn and is barely recognizable for Cd. The downstream concentration pattern of Cd was unexpected due to the close relationship of Cd with Zn in the sulfide ore and in the sediments. Carroll et al. (1998) explained this behavior as the result of weathering of sulfides driving both Zn and Cd into solution, followed by a quick, preferential adsorption of Zn onto Fe-Mn oxides, which keeps Cd either in solution or attached to calcite grains. This process occurs under neutral to alkaline pH and low Fe content conditions.

Comparing among metal content in the bioavailable fraction (exchangeable + carbonate), the carbonate-bound metal concentration was about 10 times larger than the exchangeable fraction for Zn and Cd, and 50 times larger for Pb, which means that a small drop in pH would mobilize the Pb first.

Zinc was found in high concentration in the sediments and bound to both the Fe-Mn oxide (≈ 30%) and residual fractions (≈ 20%), as seen in Fig. 2. The Fe-Mn oxide fraction was digested using the reducing agent hydroxyl amine, which implies that a large portion of the Zn stored in the sediments will become mobile under reducing conditions. Thus, the wetland treatment proposed for sediments contaminated with mining wastes would remobilize about 30% of the total Zn if reducing conditions develop in the muddy substrate.

In contrast, Cd seems to blend more uniformly throughout the downstream locations and to preferentially bind to both the organic and residual fractions based on the concentration patterns (Fig. 2). The metal bound to the residual fraction averaged 37% and 34% for Cd and Zn, respectively, and much higher (88%) for Pb (Table 1). The high mobility of Cd, also evident from the downstream pattern, represents a threat to aquatic fauna due to its acute toxicity, and is conducive to a greater uptake of Cd by plants.

The Pearson correlation analysis was only run for 11 samples since Pb was present at background levels in all of the other samples. The correlation coefficients (r) were recorded at $p < 0.01$ and $p < 0.05$ significance (Table 2). The results show that Zn and Pb are correlated in all fractions except exchangeable and that Cd correlates to both Zn and Pb in only the organic and residual fractions. Interestingly, Fe correlated to all of the metals in the residual fraction and Mn to all metals in the organic fraction.

The lack of correlation in the bioavailable fraction (except for Pb-Zn in the carbonate fraction) is understandable due to their differences in mobility, as mentioned above, and, to a lesser degree, to some possible reactions that might have occurred during the extraction procedure. Cappuyns et al. (2007) found that Pb readsorption and precipitation occurred after it mobilized from the carbonate extraction. To quantify these variations, they recommended mineralogical analysis after each extraction and monitoring of the pH.

The phytostabilization remediation applied throughout the area during the past few decades seems to have

Table 2 Correlation coefficients for metals within each fraction, after background concentration samples were removed

	Extractable			Carbonate			Fe-Mn oxides			Organic			Residual		
	Zn	Pb	Cd	Zn	Pb	Cd	Zn	Pb	Cd	Zn	Pb	Cd	Zn	Pb	Cd
Zn	n/a	--	--	n/a	0.89	--	n/a	0.82	--	n/a	0.84	0.93	n/a	0.97	0.99
Pb	--	n/a	--	--	n/a	--	--	n/a	--	--	n/a	0.82	--	n/a	0.95
Cd	--	--	n/a	--	--	n/a	--	--	n/a	--	--	n/a	--	--	n/a
Fe	--	--	--	--	--	--	0.78*	--	--	--	--	--	0.84	0.85	0.85
Mn	--	--	--	--	--	--	0.75*	0.99	--	0.82	0.91	0.92	--	--	--

N = 11 and $p < 0.01$

*significant at $p < 0.05$; – no significant correlation; n/a does not apply

effectively contained metal contamination in the Aurora region, leaving only a few stream segments with high Zn, Pb, and Cd concentrations. In this part of the TSMD, alkaline conditions predominate in the stream sediments (avg. pH 7.47), which confine Pb and Zn to mostly their immobile form, with a gradual release of metal due to chemical weathering from the organic (sulfide) fraction. With its higher mobility, Cd may be incorporated into the water column and, in part, taken up by plants; however, the few plants collected in this study had Cd tissue content below detection levels. Further sampling of plants directly downstream from the more contaminated areas would be necessary to confirm this hypothesis. For other parts of the TSMD with higher iron levels and where chat piles are still standing, treatment and disposal of waste include the potential recovery of metals from the tailings and passive treatment for water contaminated with acid mine drainage (Andrews et al. 2013). Several other techniques to immobilize metals include addition of phosphate or bentonite, which reduces soluble Pb by 60–100% (e.g. Cao et al. 2008).

Conclusions

Fractionation results show significant differences in the amount of Zn, Pb, and Cd that binds to each of the five geochemical phases. The mobile (bioavailable) fraction for all three metals is relatively small; however, this fraction becomes more significant at greater metal concentrations. The most mobile of the three metals was Cd and the least mobile was Pb. The difference in mobility was also evident from the downstream concentration patterns. Chat Creek and Elm Branch sediments contained the highest metal concentrations where chat piles had once stood, whereas the nearby unnamed creek traversing Aurora was consistently low in all three metals and therefore assigned to represent background concentration levels.

Metals mobilize according to the chemical fraction where they are preferentially stored. The downstream scattered pattern for Cd hints at this metal having higher mobility. This high mobility of Cd has been explained as the chemical weathering of sulfide ore mobilizing both Zn and Cd, after which the dissolved Zn rapidly adsorbs to iron oxides, leaving Cd in solution.

Under the prevailing alkaline conditions of the Aurora streams, the greatest threat to aquatic organisms is posed by any Cd that is mobilized. Both Pb and Zn are less mobile, with a significant portion of Pb bound to the carbonate fraction, implying a strong dependence to pH. However, both a reduction of pH and an onset of reducing conditions would be needed to mobilize Zn. The Eh change needed to mobilize metals bound to the Fe-Mn oxide phase could be generated by wetland treatment after a thick build-up of sediments.

The analytical complexity of conducting sequential extraction of samples with a wide range of metal content and mineralogy is time consuming and causes difficulties in the interpretation of results. The counterpart to this hardship is a better understanding of the specific conditions at which metals stored in the sediments may become available; this can be used to devise better strategies to contain toxic wastes, and is thus worth the effort.

Acknowledgements We are grateful to the Blackman Water Treatment Plant Laboratory (City Utilities of Springfield) for running the samples for exchangeable fraction.

References

Andrews WJ, Gavilan Moreno CJ, Nairn RW (2013) Potential recovery of aluminum, titanium, lead and zinc from tailings in the abandoned Picher mining district of Oklahoma. Miner Econ 26:61–69. https://doi.org/10.1007/s13563-013-0031-7

Besser JM, Brumbaugh WG, Ingersoll CG (2015) Characterizing toxicity of metal-contaminated sediments from mining areas. Appl Geochem 57:73–84. https://doi.org/10.1016/j.apgeochem.2014.05.021

Beyer WN, Dalgarn J, Dudding S, French JB, Mateo R, Miesner J, Sileo L, Spann J (2004) Zinc and lead poisoning in wild birds in the Tri-State Mining District (Oklahoma, Kansas, and Missouri). Arch Environ Contam Toxicol 48:108–117. https://doi.org/10.1007/s00244-004-0010-7

Brown S, Mahoney M, Sprenger M (2014) A comparison of the efficacy and ecosystem impact of residual-based and topsoil-based amendments for restoring historic mine tailings in the Tri-State Mining District. Sci Total Environ 485–496:624–632. https://doi.org/10.1016/j.scitotenv.2014.03.029

Cao X, Ma LQ, Singh SP, Zhou Q (2008) Phosphate-induced lead immobilization from different lead minerals in soils under varying pH conditions. Environ Pollut 152:184–192. https://doi.org/10.1016/j.envpol.2006.05.008

Cappuyns V, Sweenen R, Nicleas M (2007) Application of the BCR sequential extraction scheme to dredged pond sediments contaminated by Pb–Zn mining: a combined geochemical and mineralogical approach. J Geochem Explor 93:78–90

Carroll SA, O'Day PA, Piechowski M (1998) Rock-water interactions controlling zinc, cadmium, and lead concentrations in surface waters and sediments, U.S. Tri-State Mining District. 2. Geochemical Interpretation. Environ Sci Technol 32:956–965

Concas A, Ardau C, Cristini A, Zuddas P, Cao G (2006) Mobility of heavy metals from tailings to stream waters in a mining activity contaminated site. Chemosphere 63:244–253. https://doi.org/10.1016/j.chemosphere.2005.08.024

Favas JC, Kumar Sankar S, Rakshit D (2014) Geochemical fractionation of trace elements in stream sediments contaminated by mining activity. Clean Soil Air Water 43:446–455. https://doi.org/10.1002/clen.201200718

Gutiérrez M, Mickus K, Camacho LM (2016a) Abandoned Pb Zn mining wastes and their mobility as proxy to toxicity: a review. Sci Total Environ 565:392–400. https://doi.org/10.1016/j.scitotenv.2016.04.143

Gutiérrez M, Wu S, Rodriguez J, Jones AD, Lockwood B (2016b) Assessing the state of contamination for a historic mining town using sediment chemistry. Arch Environ Contam Toxicol 70:747–756. https://doi.org/10.1007/s00244-016-0265-9

Hudson-Edwards KA, Macklin MG, Curtis CD, Vaughan DJ (1995) Processes of formation and distribution of Pb-, Zn-, Cd-, and Cu-bearing minerals in the Tyne Basin, northeast England: implications for metal-contaminated river systems. Environ Sci Technol 30:72–80

Hudson-Edwards KA, Jamieson HE, Lottermoser BG (2011) Mine wastes: past, present, future. Elements 7:375–380. https://doi.org/10.2113/gselements.7.6.375

Johnson A, Gutiérrez M, Gouzie D, McAlily R (2016) State of remediation and metal toxicity in the Tri-State Mining District, USA. Chemosphere 144:1132–1141. https://doi.org/10.1016/j.chemosphere.2015.09.080

Kennou B, El Meray M, Romane A (2015) Assessment of heavy metal availability (Pb, Cu, Cr, Cd, Zn) and speciation in contaminated soils and sediment of discharge by sequential extraction. Environ Earth Sci 74:5849–5858. https://doi.org/10.1007/s12665-015-4609-y

Liu J, Wang J, Xiao T, Nao Z, Lippold H, Luo X, Yin M, Ren J, Chen Y, Linghu W (2017) Geochemical dispersal of thallium and accompanying metals in sediment profiles from a smelter-impacted area in South China. Appl Gecohem 88B: 239–246 https://doi.org/10.1016/j.apgeochem.2017.05.013

Macdonald DD, Ingersol CG, Berger TA (2000) Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch Environ Contam Toxicol 39:20–31. https://doi.org/10.1007/s002440010075

Musilova J, Arvay J, Vollmannova A, Toth T (2016) Environmental contamination by heavy metals in region with previous mining activity. Bull Environ Contam Toxicol 97:569–575. https://doi.org/10.1007/s00128-016-1907-3

Pearson MA (2017) Geochemical fractionation, speciation, and bioavailability of heavy metals in stream sediments in Aurora, MO. MS thesis, Missouri State University, http://bearworks.missouristate.edu/theses/3119. Accessed 6 Jan 2018

Pueyo M, Rauret G, Lück D, Yli-Halla M, Muntau H, Quevauvillere PH, López-Sánchez JF (2001) Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure. J Environ Monit 3:243–250. https://doi.org/10.1039/b010235k

Richards JM, Mugel DN (2008) Potentiometric Surface of the Ozark Aquifer near Springfield, Missouri, 2006–07. USGS Scientific Investigations map 3003 https://pubs.usgs.gov/sim/3003/pdf/SIM3003.pdf. Accessed 6 Jan 2018

Roig N, Sierra J, Moreno-Garrido I, Nieto E, Perez-Gallego E, Schumacher M, Blasco J (2015) Metal bioavailability in freshwater sediment samples and their influence on ecological status of river basins. Sci Total Environ 503–504:269–278. https://doi.org/10.1016/j.scitotenv.2015.06.107

Schaider LA, Senn DB, Brabander DJ, McCarthy KD, Shine JS (2009) Characterization of zinc, lead, and cadmium in mine waste: implications for transport, exposure, and bioavailability. Environ Sci Technol 41:4164–4171. https://doi.org/10.1021/es0626943

Schaider LA, Senn DB, Estes ER, Brabander DJ, Shine JS (2014) Sources and fates of heavy metals in a mining-impacted stream: temporal variability and the role of iron oxides. Sci Total Environ 490:456–466. https://doi.org/10.1016/j.scitotenv.2014.04.126

Stefanowicz A, Woch MW, Kapusta P (2014) Inconspicuous waste heaps left by historical Zn-Pb mining are hot spots of soil contamination. Geoderma 235–236:1–8. https://doi.org/10.1016/j.geoderma.2014.06.020

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 1:844–851. https://doi.org/10.1021/ac50043a017

Wojtkowska M, Bogacki J, Witeska A (2016) Assessment of the hazard posed by metal forms in water and sediments. Sci Total Environ 551–552:387–392. https://doi.org/10.1016/j.scitotenv.2016.01.073

Zimmerman AJ, Weindorf DC (2010) Heavy metal and trace metal analysis in soil by sequential extraction: a review of procedures. Int J Anal Chem, 2010:387803 https://doi.org/10.1155/2010/387803