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Article

Mobility of Metals in Sediments Contaminated with Historical Mining Wastes: Example from the Tri-State Mining District, USA

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Abstract: The Tri-State Mining District (TSMD) of Kansas, Missouri, and Oklahoma was a world class zinc (Zn) and lead (Pb) producer. Mining ceased in the 1950s, leaving behind a large amount of mine wastes. Although much of the affected areas have been remediated, stream sediments may still contain toxic levels of these metals. The mobility of the metals was determined for sediment samples from Turkey Creek, Missouri. The median values of the metal content were 2700 mg/kg Zn, 161 mg/kg Pb, and 10.8 mg/kg Cd. These concentrations marginally surpass the sediment quality guidelines that differentiate between toxic and nontoxic conditions. Mobility was determined by sequential extraction of two phases—bioavailable and Fe-oxides. The fraction of the metal available to biota was 7.7% for Zn, 5.0% for Cd, and 0.4% for Pb, whereas the Fe-oxide fraction retained 25% of Zn, 21% of Pb, and 35% Cd. These values roughly agree with the values reported for other areas of the TSMD. Fractionation provides an estimate of the amount of metal available at the present conditions and gives the amount of metal available should the pH and/or Eh vary. The methodology puts an emphasis on ecosystem health and can be applied to other areas where Zn–Pb concentrations in soils and sediments are a concern.

Keywords: abandoned mines; lead; remediation; sequential extraction; zinc

1. Introduction

Wastes (e.g., tailings or chat piles) from abandoned mines remain a contamination threat in many parts of the world [1,2]. Improperly contained wastes from zinc (Zn) and/or lead (Pb) mining leak toxic metals and metalloids into the environment, reaching streams via surface water runoff and subsurface water flow. Areas of mine tailings are a major source of contamination as they continue to release metals even after hundreds of years [3], making remediation a critical component of waste cleanup. However, remediation of abandoned mine wastes is usually expensive and can take decades to complete due to several factors, including political and social challenges and the size and nature of the mine wastes [1]. Due to the potentially high cost of remediation, funds are generally applied to areas showing the most severe contamination first, leaving less contaminated areas for future efforts [4,5].

Metals store in solid phases, e.g., soils and sediments. From the total amount of metal stored, a fraction will be available to biota and thus contribute to the toxicity threat to biota. Mobility reflects the easiness for a metal to be released into water and depends on the chemical bonds by which the metal is attached to different chemical phases in the sediment [6,7].

With time, chemical weathering reactions transform the primary mined minerals of PbS and ZnS into secondary minerals, such as anglesite (PbSO_4), cerussite (PbCO_3), and smithsonite (ZnCO_3) [8,9]. Both the primary and some of the secondary minerals can be insoluble [10] at $\text{pH} > 7$, and hence the metals would not commonly be released into the environment unless under extreme conditions. However, as these reactions progress, the metals become stored into different chemical phases (fractions) of the sediment [8]. Each phase retains the metal with bonds of different strength, and these metals are then released from the solid phases accordingly [10]. The distribution of the metals in each of these chemical phases is referred to as its mobility [6,7,9]. Sequential extraction can be used to determine the mobility of metals by using increasingly stringent solutions to extract the amount of metal present in each of the sediments' chemical phases. From loosely to strongly chemically bound, metals in these chemical phases are separated into exchangeable, carbonate, Mn, Fe oxi-hydroxides, organic (sulfidic), and residual [8,11,12]. The amount of metal bound to the exchangeable and carbonate phases combined is here referred to as bioavailable.

In mobility studies, using stream sediments has marked advantages over water and soil to record chemical changes [6,13]. Metals that accumulate in stream sediments remain undisturbed for a long time, and, by doing so, they can record the contamination history of the area. Sequential extraction is a method that uses chemical extractions to separate the metal content into fractions, with each metal attached to a particular chemical phase with a particular (weak or strong) bond. For example, the bond of metal-iron oxide does not break under slightly acidic conditions but breaks under reducing conditions. Directly related to mobility, the toxicity of chemical species has been linked to critical concentrations that produce a negative effect to sediment-dwelling biota, such as water fleas, amphipods, and midges, that are sensitive to the contamination of specific metals. Critical concentrations include the threshold effect level (TEL) and the probable effect level (PEC). The PEC is the concentration above which adverse effects in organisms are expected to occur [14,15]. These are known as sediment quality guidelines (SQGs) and are used as nonenforceable guidelines to differentiate between toxic and nontoxic sediments [14].

The objectives of this study are: (1) to determine the mobility of Cd, Pb, and Zn in sediments from Turkey Creek, a stream affected by historic mining wastes within the Tri-State Mining District (TSMD) (USA), (2) to compare these results with the mobility and sediment quality guidelines of metals (SQGs) reported for other parts of the TSMD, and (3) to use this information to discuss the effectiveness of past and future remediation efforts with respect to possible variations of the pH and Eh values.

2. Materials and Methods

2.1. Study Area

As an example of metal mobility within a major historic mining district, the TSMD in Kansas, Missouri, and Oklahoma was chosen. The TSMD is located almost entirely within the Ozarks, a highland region in central United States where limestone sinkholes and springs abound. The area has an annual precipitation of 1090 mm with no defined rainy season and monthly average temperatures that vary between 8.4 °C and 20.9 °C [16]. The TSMD was a world class Zn and Pb producer in the 1900s, with mining operations peaking in the 1920s [5,17]. Activities diminished in late 1950s, after the ores became exhausted, and ceased in the early 1960s. Shortly thereafter, mining companies left the area or declared bankruptcy, leaving behind a large amount of mine tailings and contaminated soils (Figure 1) [6,17]. The tailings (locally known as chat piles) comprised the gangue rock limestone and chert that contained small amounts of ore, from which metals could be leached out [5]. These metals tend to accumulate into sediments once they reach a stream, posing a threat to aquatic biota [18] and human health [8]. Besides Zn and Pb, small amounts of other metals can also be released from chat piles, including silver (Ag), cadmium (Cd), copper (Cu), and thallium (Tl) and metalloids such as arsenic (As). Among these, the most mobile metals are Cd and Tl, which are highly toxic to aquatic biota at even trace concentrations [3,19].

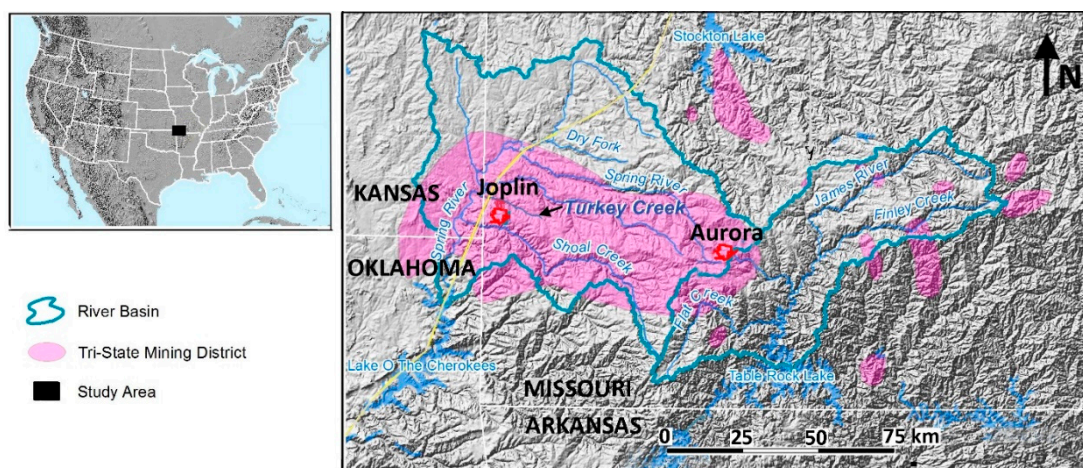


Figure 1. Extent of the Tri-State Mining District (TSMD) shaded in pink, and the locations of Joplin and Aurora, Missouri. Inset shows the TSMD within the United States.

The TSMD ore is a Mississippi Valley-type deposit consisting of mainly galena (PbS) and sphalerite (ZnS), with minor amounts of other minerals, including chalcopyrite (CuFeS_2) [20]. The ore was probably formed as solutions were driven from the formation of the Ouachita Fold and Thrust Belt where deep (>10 km) ocean sediments, heated by the geothermal gradient, leached metals from the host rocks [5]. The fluids were moved upward and toward the north due to the compressional forces forming the Ouachita fold and thrust belt and eventually precipitated the ore when they encountered the chemically receptive Mississippian-aged carbonates of the TSMD [5,20]. These ores were deposited irregularly over a large area, mainly related to regional faulting and basement highs [21]. The ores were first discovered near the surface in the eastern part (Missouri) of the TSMD; later on, richer deposits were found buried deeper in its western part (Oklahoma) [5,17].

Mining towns grew around the main ore bodies as they became discovered [17]. Although originally mined for Pb, Zn became the major mined metal once improvements in metal enrichment methods were used [17]. In the sphalerite ores within the TSMD (also known as black jack or zincblende), Cd commonly replaces Zn up to 5%, and, in a few places, greenockite (CdS) was found [20]. Besides Cd, other associated metals with this ore include Cu, Fe, and Ag in the form of sulfides. Of all the known metals within the TSMD, Cd and Pb are the most toxic to biota and humans [8,15]. This study focused on a 5 km long segment of Turkey Creek near Joplin, Missouri, a stream impacted by chat piles and smelter fallout (Figures 1 and 2). Turkey Creek flows northwest to west and joins the Spring River in Kansas near the Kansas–Missouri border.

2.2. Remediation of the Study Area from the 1980s to Present Time

The major mining operations ceased in the TSMD in the late 1950s leaving a land scarred with shafts and tunnels and a large number of tailing piles (Figure 2a). With time, the ore within the tailing piles released Cd, Pb, and Zn in toxic concentrations, and remediation actions began a few decades after the formation of the tailing piles [5,6,17]. The first remediation methods consisted mainly of filling the mining tunnels and shafts with the chat, followed by phytostabilization [4,6,22]. Remediation has been an ongoing process in some areas (e.g., Joplin, Missouri and Commerce, Oklahoma) within the TSMD, especially in sites where mining was intensive (see Figure 2a,b). In Joplin, a major remediation campaign was undertaken after an F5 tornado hit the area in 2011, causing disturbances of mining wastes and reclaimed soils [23].

The Joplin, Missouri area (including Carthage, Webb City, and Galena, Kansas) has been remediated intermittently for several decades due to the large scale of mining and high metal concentrations that accumulated in the soils and sediments during mining and post-mining activities [22,23]. Limestone, the main host rock in southwest Missouri, provides an alkaline pH

to the subsurface and surface waters, preventing metals from becoming soluble. Therefore, only a small fraction of the metals in the waste incorporates into the water column. However, if the pH drops or the conditions become anoxic, the mobility of metals will increase and a larger portion of dissolved ions will be present in the water, increasing its toxicity [14,15,24]. In addition to measuring the total metal content of sediments, sequential extraction has been conducted in some sites within the TSMD, including the Tar Creek region of Oklahoma [8,24,25] and the Aurora region of Missouri [12], to determine the remaining toxicity and thus the effectiveness of remediation.

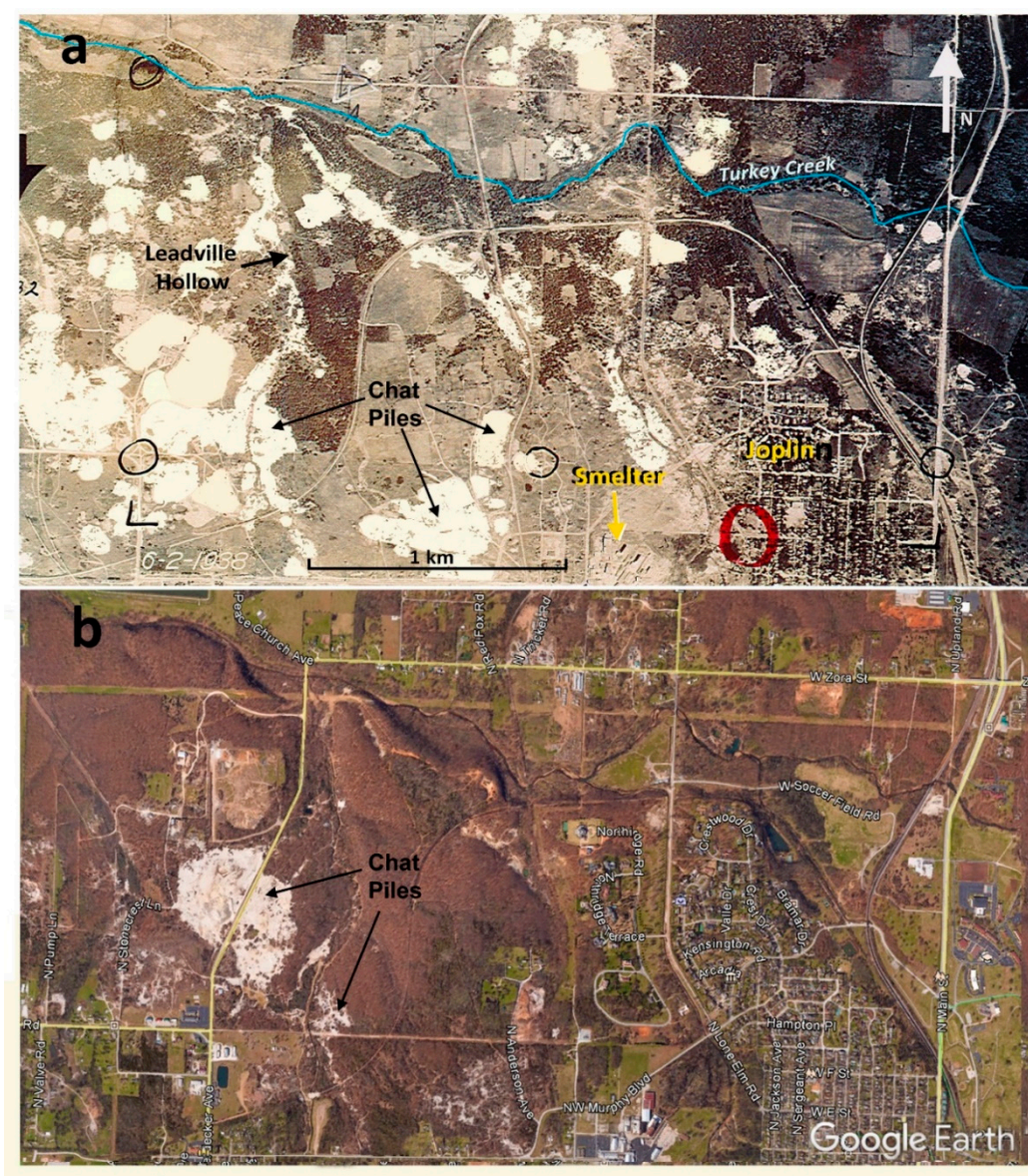


Figure 2. Location of mining wastes (chat piles in white) in a portion of the TSMD near the northern edge of Joplin, Missouri, in (a) 1938 and (b) 2018. Note the reduction of chat piles in 2018 (b) as compared to 1938 (a). Note: The original 1938 photo had some markings (black and red circles); those markings are not related to this study.

2.3. Sampling and Data Collection

Nineteen sediment samples were collected in May 2018 from Turkey Creek. The sampling locations are shown in Figure 3. The pH of the stream water was also measured in the field.

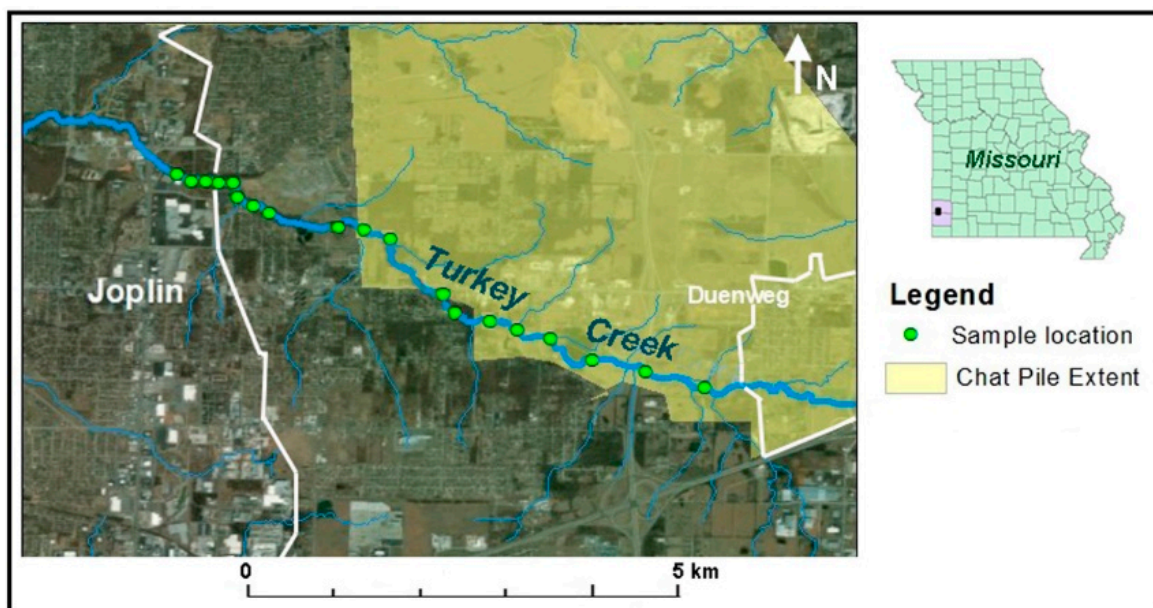


Figure 3. Sampling locations within Turkey Creek, Missouri. Note: This site is 5 km upstream from the area shown in Figure 2.

The sediments were kept cool and transported to a laboratory, where they were air-dried, disaggregated, sieved to 1 mm in size, and stored for further analyses. A subsample of sediments (about 10 g) was sent to a commercial laboratory where the total metal content was determined after extraction with *aqua regia* and using an inductively coupled plasma mass spectrometer (ICP-MS). The amount of metal extracted using *aqua regia* is, in most cases, comparable (in the case of Zn and Pb) or slightly less (in the case of Cd) than the amount extracted by the hydrogen fluoride (HF) acid mixture [26,27]. Therefore, although comparisons of the metal content obtained by these two methods can be made, a distinction is in order, usually by denominating the metal extracted by *aqua regia* as the pseudo-total metal content.

Loss on ignition (LOI) was measured with a subsample of the dried sediment as an approximation of its organic matter content. To determine the LOI, 10.00 g of sediment was placed in a weighed crucible and ignited at 650 °C for six hours in a TEMCO Model 25 muffler (Thermoelectric Mfg, West Chester, PA, USA). Once cooled to room temperature, the crucible was weighed and the loss of weight was determined.

A Community Bureau of Reference (BCR) extraction sequence [28] was conducted to determine the amount of Cd, Pb, and Zn that was attached to three fractions—bioavailable, Fe-oxides, and organic/residual. The latter was calculated by subtracting the metal attached to the first two extractions from the pseudo-total metal content. The first extraction targeted the exchangeable and carbonate phases and includes the metal that would be released under alkaline to slightly acidic conditions and therefore potentially bioavailable [28].

The second extraction measured the metal attached to Fe–Mn oxides and hydroxides (referred from here on as Fe-oxides). After these two extractions, only the metal strongly attached to the mineral lattices is left in the solid state, which is considered inert for environmental purposes and which, according to sequential extraction terminology [11,28], includes the organic (mainly sulfides) and residual phases.

2.4. Analyses

Two commonly used methods that have been extensively tested for replicability and suitability for soil/sediment matrices include Tessier with five extractions [11] and the Community Bureau of Reference (BCR) with four extractions [28]. Many of the authors who follow these methods apply

slight modifications to fit specific objectives. For example, one study used the Tessier method but separated the metal into eight fractions instead of the customary five [8]. One common modification is to separate the Fe–Mn oxide phase into two separate phases, one for Mn oxides (easily reducible) and one for Fe oxides (moderately reducible). Another common modification is to use *aqua regia* instead of a hydrogen fluoride (HF) acid mixture to determine the total metal content. The latter method also is commonly referred to as pseudo-total metal content [13].

In the first extraction, 4.00 g of sediment was placed in 50 mL centrifuge tubes together with 40 mL of acetic acid (0.11 M). The samples were intermittently shaken for 24 h, after which they were centrifuged at 3000 revolutions per minute for 5 min in an IEC Model K Centrifuge (International Equipment Co. USA), and then the liquid and solid were carefully separated. The liquid portion (extract) was kept refrigerated and was analyzed within the following week for Cd, Pb, and Zn using an ICP-AES Varian Liberty AX-150 Turbo (Varian Analytical instruments, USA). The metal in this first extract corresponded to easily released metal stored in the exchangeable and carbonate phases and thus easily released.

To the solid part, 40 mL of hydroxylammonium chloride (hydroxylamine hydrochloride) (0.5 M) was added. The tubes were intermittently shaken for 24 h, after which they were centrifuged in the same manner as the first extraction. This second extractant contained the metal attached to the Fe-oxides that corresponds to the metal that would be released under reducing conditions [10,25].

Quality control included laboratory control checks, replicates, and blanks about every eight samples. Blank samples showed concentrations below detection limits and the replicate variation (including loss on ignition) was <5%, which was considered acceptable. Standard solutions were prepared, and the detection limits of the metal analyses were calculated after running blanks on the ICP five times.

A consensus-based SQG using a geometric mean of published toxicity studies provides a guideline to separate toxic and nontoxic sediments [14]. These SQGs were determined for 28 common freshwater contaminants, including Cd, Pb, and Zn that were used in this study. The PEC values for Cd, Pb, and Zn for North America [14] and for the TSMD area [15] are listed in Table 1. These SQGs work well for each of these metals or for mixtures of them, but there are some limitations in using these numbers, i.e., the effects of bioaccumulation are not included [14]. Table 1 lists the values reported in the literature for other contaminated sites within the TSMD. Note that the average of the metal concentrations exceeds the PEC guidelines for all these sites.

Table 1. Probable effect concentration (PEC), TSMD-specific PEC, and median of total (and pseudo-total*) metal concentrations in stream sediments reported in the literature for contaminated sites within the Tri-State Mining District (TSMD).

	Cd, mg/kg	Pb, mg/kg	Zn, mg/kg	Source
PEC	4.98	128	459	[14]
PEC-TSMD	11.1	150	2083	[15]
Empire Lake, Kansas N = 428	29	270	4900	[29]
Turkey Creek, Kansas N = 1	50	900	8000	[6]
*Turkey Creek, Missouri N = 27	14	238	2850	[23]
*Chat Creek, Missouri N = 33	35	190	5791	[12]
Tar Creek, Oklahoma N = 3	45	110	5800	[30]

Statistical analyses included the determination of trends after a regression analysis and its coefficient R^2 , a value that varies between -1 and 1 , where near 0 values indicate a lack of trend. A Pearson correlation was utilized to determine the association between metal concentrations; an association expressed by the correlation coefficient R , a value varying between -1 and 1 , where 0 denotes no correlation and 1 (or -1) a perfect correlation. Both of these calculations were performed using Microsoft Excel, and the significance of the correlation under a probability of $p < 0.05$, using the hypothesis test and a test statistic, was calculated using an online calculator.

3. Results

The pH values of the water in the sampling sites were all above 7.0. The total concentrations of Cd, Pb, and Zn and their fractionation are shown in Figure 4.

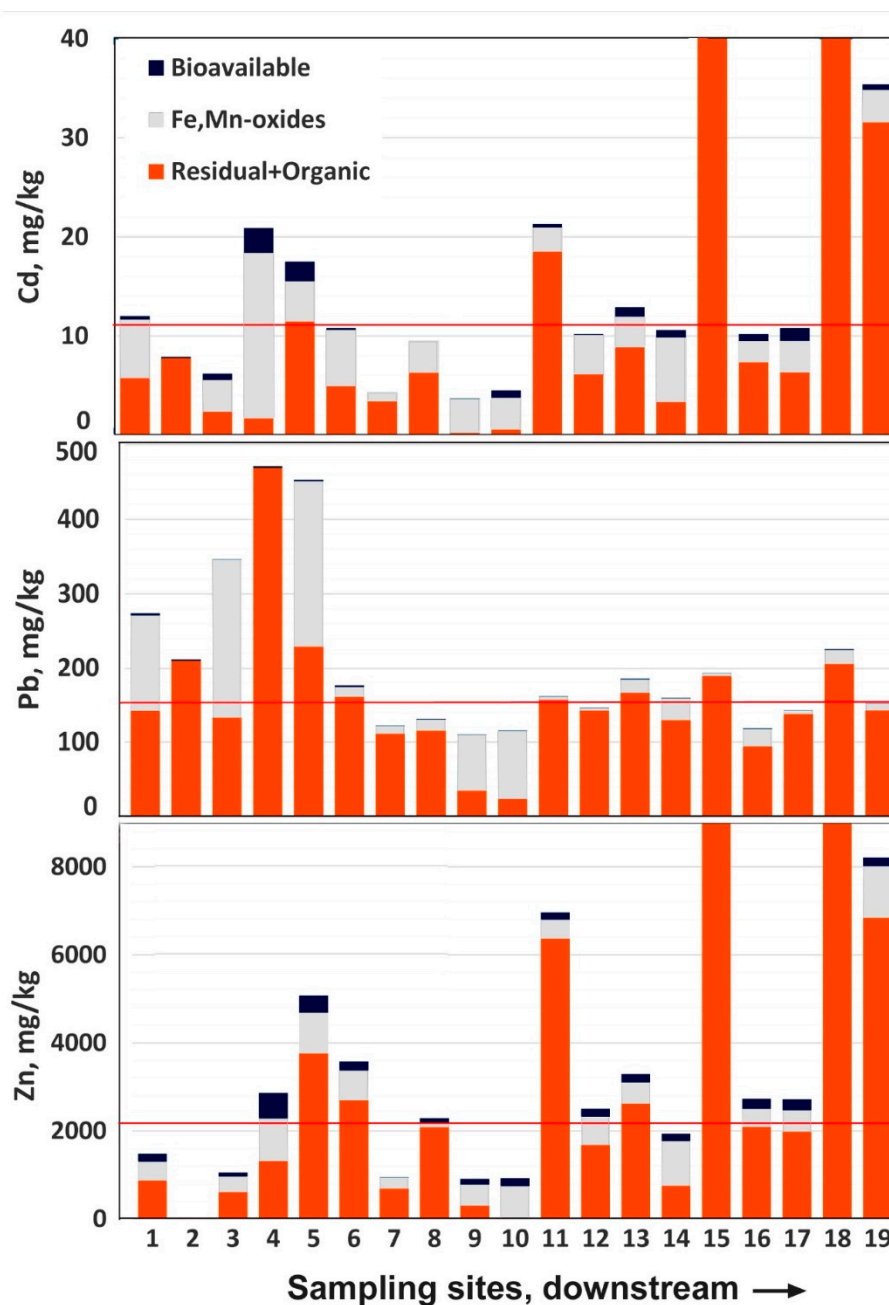


Figure 4. Total content of Cd, Pb, and Zn in Turkey Creek sediments and their fractionation into bioavailable, Fe-oxides, and organic/residual phases. The red line corresponds to the metal concentration identified by toxicology studies as probable effect concentration (PEC) [15].

As seen in Figure 4, the total concentrations in soil and sediments within the TSMD were highly variable (up to 10 times), in agreement with the concentration variation reported by other studies within the TSMD [4,12,25,30]. The lack of a downstream trend in metal concentration is also shown in Figure 4, substantiated by regression coefficients (R^2) of 0.22 for Zn, 0.30 for Pb, and 0.22 for Cd. The metal content increased in random spots along the stream channel, which could be explained as a result of the historic location of tailing piles and/or disturbances caused by recent remediation actions.

Furthermore, the concentration pattern of Cd mimics that of Zn, while Pb has a different concentration pattern, as indicated by the strong correlation coefficients (R) obtained for Zn and Cd (0.99), whereas no correlation was found between Pb and Zn (0.03) or Pb and Cd (0.08). Outliers (see Zn and Cd in samples 15 and 18 in Figure 4) are also common in the area [6,25] and are likely the result of an unweathered sphalerite (ZnS) fragment mixed with the sediment, based on the large concentration obtained and its enrichment in the organic/residual fraction.

The fractionation results show a large variation among the samples as well. The small amount of Pb bound to the bioavailable fraction is evident; however, 21% of Pb bound to the Fe-oxide fraction. To visualize the fractionation results and to compare Turkey Creek (Joplin) to another stream within the TSMD, the average values of metal fractionation (in %) are listed in Table 2. A correlation between pseudo-total metal and its bioavailable fraction showed no correlation for Zn ($R = 0.36$) nor Cd (0.02), but a correlation was obtained for Pb ($R = 0.53$, significant at $p < 0.05$), in agreement with the consistently low amount of Pb in the bioavailable fraction mentioned above.

Table 2. Average of percent metal in fractionation in sediment samples from Turkey Creek. Metal fractionation of Chat Creek is shown for comparison purposes. Standard deviation is in parentheses.

	%Bioavailable	%Fe-oxides	%Org/Residual
Turkey Creek, N = 19			
Cd	5.0 (5.2)	35.1 (26.6)	59.8 (29.1)
Pb	0.4 (0.4)	21.3 (25.7)	78.3 (25.7)
Zn	7.7 (5.8)	25.1 (20.0)	66.7 (24.1)
Chat Creek, N = 33			
Cd	9.9 (20.8)	32.4 (15.8)	58.9 (5.0)
Pb	13.4 (11.8)	26.9 (2.05)	59.8 (13.9)
Zn	17.1 (12.8)	35.0 (15.0)	48.0 (2.2)

Between the pseudo-total and Fe-oxide fractions, a correlation was found for Zn ($R = 0.69$, significant at $p < 0.05$) and for Pb (0.54, significant at $p < 0.05$). Interestingly, Cd did not attach to the Fe-oxide phase ($R = 0.19$) as strongly as Zn, in spite of their close association in the pseudo-total metal content. These results agree with the previously reported strong association between Zn and the Fe-oxide fraction [24,25].

With respect to sediment toxicity, Figure 4 shows that Zn exceeded the PEC-TSMD value (red line) in 13 samples (68%), Pb in 12 (63%), and Cd in 8 (42%). Interestingly, the median values for the total metal content are 10.8 mg/kg Cd, 161 mg/kg Pb, and 2700 mg/kg Zn, which are only slightly higher than the PEC-TSMD recommended values of 11.1, 150, and 2083 mg/kg.

Loss on ignition (LOI%) varied between 3.7 and 24.0, with an average of 7.6%. No correlation was found among the metals in any fraction to LOI%, indicating that the metals do not show a particular preference to attach to organic matter and that this part of the sediment does not affect the partitioning of the metals into the different chemical phases.

4. Discussion

The pH values of the water at the sample locations were all in the alkaline range, indicating that, unlike in the Oklahoma part of the TSMD [8,25], acid mine drainage (AMD) in this part of the TSMD has not developed. The alkaline pH values limit the mobility of all three metals, especially Pb, which is evident by the small amount of Pb (average 0.4%) released by the exchangeable-acid extractable (bioavailable) fraction. Pb shows a preference (78%) for binding to the inert fraction (organic/sulfidic and residual) and, secondly (26%), to the reducible fraction (Fe-oxides). Cd and Zn fractionate in a similar manner as Pb, with the sole difference being that a larger amount of metal binds to the bioavailable fraction (5–8%). These results agree with those reported for Aurora [12] in the TSMD, as well as with other sites outside the TSMD affected by historic Pb–Zn mining, e.g., soils in southern Poland [3] and sediments of the North River in South China [19].

However, our results differ to some extent from the results reported for sediments and chat piles from the Oklahoma part of the TSMD, in which most (50–80%) of the metal is reported to bind to the carbonate (acid extractable, and part of the bioavailable fraction) and Fe-oxide (reducible) fractions, and only a small part to the residual phase [8,25]. More studies that involve different regions within both parts of the TSMD are needed to explain if the source rock/ores can help explain these differences. A possible explanation, at least in part, is a higher content of iron in the ore in the western part of TSMD, causing acidic conditions that, in turn, affect the chemical weathering and adsorption/desorption reactions.

In spite of the studies within the TSMD being limited in areal coverage and in time, it is evident that remediation actions are being successful, based on the presence of wildlife [22] and by sediments containing intermingled large and small concentrations of metals within a stream segment [12]. However, the presence of large metal concentrations in certain sections of a stream segment indicates that the effects of the mining wastes continue simultaneously with the ongoing processes of weathering and stabilization. These sediments exceed the SQGs, and aquatic biota may find conditions that negatively affect their behavior and reproduction [15,18].

Fractionation results can be used to estimate the amount of metal that could potentially be released in case of a drop of the pH and after an onset of reducing (e.g., anoxic) conditions. A change to reducing conditions would have a larger impact to the amount of metal released, since about 30% of the total metal binds to the reducible fraction. Thus, the alkaline conditions of the streams are allowing a minute amount of Zn and Cd to be released, and, as long as the conditions remain oxic and alkaline, the metals will remain relatively immobile in the solid phase.

Furthermore, the Ozark aquifer, a drinking water source for the region, seems to be well protected by a thick (457 m; 1500 ft) sequence of mainly carbonate rocks that have the ability to remove soluble metals from the water and prevent them from reaching the deeper regions of the aquifer [20]. A study on the Ozark aquifer underlying the TSMD showed that, for the most part, the water in the Ozark aquifer contained no heavy metals, except for one well containing Pb on the Kansas–Missouri border, which was likely a result of water from the upper aquifer leaking into the deep aquifer via a fracture in the rocks [31]. Wells are continuing to be monitored for metal content as well as for other revealing signs (sulfate content or young age) of leakage from the surface aquifer into the Ozark aquifer [31].

5. Conclusions

The metal content of sediments within Turkey Creek, Missouri, was found to be highly variable and a downstream trend in concentration was lacking. The median values of the metal content were 10.8 mg/kg for Cd, 161 mg/kg for Pb, and 2700 mg/kg for Zn. A high variability of metal concentrations is a common occurrence in the sediments of areas affected with mining wastes within the TSMD, due to the tailing material being far from homogeneous in size and composition and the disturbance of sediments by the intermittent remediation actions in the past few decades. The amount of metal stored in the different chemical phases, or fractionation, showed a small amount (about 6%) of metal bound to the bioavailable fraction for Cd and Zn and an almost insignificant amount (0.4%) for Pb. In contrast, all of the three metals bound to the Fe-oxide fraction (about 30% each), while the rest of the metal remained stored in the inert (immobile) fraction.

About half of the sediments had metal concentrations above the PEC-TSMD guidelines that distinguish toxic from nontoxic levels. These toxicity guidelines are based on the effect of metals on sediment-dwelling organisms, in view of the fact that they are highly sensitive to contamination.

Remediation seems to have been successful from both a physical and chemical point of view. Some high metal concentrations are still present in parts of streams, in regions directly adjacent to former chat piles. The area surrounding Turkey Creek has been remediated in several stages, one of which was after an F5 tornado hit the area in 2011. Disturbances caused by remediation actions include the mechanical relocation of chat and contaminated soils in the Turkey Creek floodplain, and such disturbances are expected to have an effect on the metal content in the adjacent stream.

The fractionation results show the relative amounts of metals that are released from the sediments at the present time and also the amount that would be released if the environmental conditions within the stream channel (pH and oxidation) changed.

Author Contributions: Conceptualization, M.G. and K.M.; formal analysis, Z.J.C.; investigation, A.M.M.; methodology, M.G., Z.J.C., and A.M.M.; resources, Z.J.C. and A.M.M.; validation, M.G.; writing—original draft, M.G.; writing—review and editing, K.M.

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