

Screening Level Assessment of Metal Concentrations in Streambed Sediments and Floodplain Soils within the Grand Lake Watershed in Northeastern Oklahoma, USA

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Received: 21 September 2016 / Accepted: 3 February 2017 / Published online: 22 February 2017
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Abstract Metal releases have been received by the Grand Lake watershed from the Tri-State Mining District (TSMD) since the mid 1800s. To address data gaps in metal distributions in the Oklahoma portion of the watershed, streambed sediment and floodplain soil was sampled on various streams. The <63- μm fraction was analyzed for Cd, Pb, and Zn concentrations by portable X-ray fluorescence spectroscopy and inductively coupled plasma-mass spectrometry. Mean metal concentration results at reference transects indicated that background sediment/soil concentrations for Cd, Pb, and Zn within the watershed were 0.5, 19, and 68 mg/kg, respectively. A significant difference in the distributions of metal concentrations was found between reference and impacted transects (Cd, Pb, Zn: $p = 0.00$; Cd: $n = 29$; Pb, Zn: $n = 283$). These results demonstrated that concentrations of metals in streambed sediments and floodplain soils were significantly higher in areas downstream of major mining influences relative to upstream reference sites, and the source of metal contamination within these media was the result of mining releases from the TSMD. Toxicity risks to benthic macroinvertebrates were evaluated using a TSMD-specific sediment mixture model ($\sum\text{PEC-Q}_{\text{Cd,Pb,Zn}}$) for metals (MacDonald et al. in Development and evaluation of sediment and pore-water toxicity thresholds to support sediment quality assessments in the Tri-State Mining District (TSMD), Missouri, Oklahoma, and Kansas. Draft Final Technical

Report. Volume I: Text. Prepared for the U.S. Environmental Protection Agency and the U.S. Fish and Wildlife Service. Prepared by MacDonald Environmental Sciences Ltd., U.S. Geological Survey, and CH2M Hill, Nanaimo, 2009). Toxicity risks to plant populations were also assessed by comparing soil metal concentrations to Ecological Soil Screening Levels (Eco-SSLs). It was found that the survival and/or biomass of benthic invertebrates was highly impacted at Tar Creek, highly to moderately impacted at Spring River and Elm Creek, and unimpacted at Lost Creek and Grand Lake as a result of sediment metal concentrations. It also was found that soil metal concentrations were likely sufficient to impact plant populations at all streams. Within the Oklahoma portion of the watershed, the majority of environmental studies, remediation, and restoration efforts by local, state, and federal agencies have been primarily focused within the Tar Creek Superfund Site (TCSS) boundary. Importantly, the findings of this study highlighted the downstream extent of metals contamination as well as the resulting potential toxicities to benthic invertebrates and plants that is present outside of the TCSS boundary. Because the Oklahoma portion of the watershed comprises the jurisdictional lands of ten tribes, these results emphasized the potential tribal loss of use of benthic invertebrates and plants due to their decline in population as a result of metal toxicity. These overall findings provide an important basis for future data needs in assessing metal concentrations in aquatic and terrestrial biota that are consumed by tribal communities within the watershed to determine if certain organisms are unsafe to consume or warrant consumption advisories. This will allow risk assessors and risk managers to better understand the potential loss of use of tribal biological resources as well as improving risk-based decision making to be protective of these resources and tribal human health.

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The Grand Lake o' the Cherokees (Grand Lake) watershed is located in southeastern Kansas, southwestern Missouri, and northeastern Oklahoma. Since the mid 1800 s, it has received metals contamination from historic Pb and Zn mining, ore processing, and smelting operations within a 6500-km² area known as the Tri-State Mining District (TSMD) (Stewart 1986). Mining activities created an extensive interconnected network of underground mine workings, as well as a vast accumulation of surface mine wastes in the form of mill tailings, primarily composed of pebble-size chert fragments (known as chat) and fine-grained waste sediments in flotation ponds (U.S. EPA 2008). The weathering and leaching of abandoned mine areas serve as sources for metal releases via groundwater or surface water runoff within the Neosho and Spring River watersheds of the watershed (Bailey 1911; Barks 1977; Spruill 1987). Due to large-scale metals contamination within the TSMD, the U.S. Environmental Protection Agency (USEPA) has established four Superfund National Priority List (NPL) sites, which include the Cherokee County Site in Cherokee County, KS, the Oronogo-Duenweg Mining Belt Site in Jasper County, MO, the Newton County Mine Tailings Site in Newton County, MO, and the Tar Creek Superfund Site (TCSS) in Ottawa County, OK.

Previous studies have demonstrated that the upper Spring River and its tributaries in Missouri and Kansas have elevated Cd, Pb, and Zn concentrations in streambed sediments (Allert et al. 1997, 2012; Angelo et al. 2007; Barks 1977; Dames & Moore 1995; Ferrington et al. 1989; Juracek 2006; Pope 2005; Schmitt et al. 1997). However, even though the Oklahoma portion of the Neosho and Spring River watersheds of the watershed lie immediately downstream of the TSMD, there have been limited studies in assessing metal concentrations within potentially impacted environmental media that are present outside of the TCSS boundary. Elevated Cd, Pb, and Zn concentrations have been found in streambed sediments on segments of the Neosho River, Spring River, Elm Creek, Lost Creek, Tar Creek, and Grand Lake (Andrews et al. 2009; Angelo et al. 2007; Juracek and Becker 2009; MacDonald et al. 2010; McCormick and Burks 1987) and in floodplain soils of Tar Creek (Andrews et al. 2009).

The focus of this study was to address data gaps in the distributions of Cd, Pb, and Zn concentrations in streambed sediments and floodplain soils within the Oklahoma portion of the Grand Lake watershed. These environmental media are an exposure pathway of metal contamination to benthic invertebrates and terrestrial plants. Benthic invertebrates and terrestrial plants represent key elements of stream food webs, because they are important food sources to fish, amphibians, reptiles, birds, and mammals. Their reduction in survival or biomass, as well as accumulation of metals due to contamination within a stream habitat, can have

profound ecological (e.g., impacts to populations) and physiological (e.g., tissue metal accumulation) effects on higher trophic organisms. Ultimately, these effects impact the availability and consumption of biological resources by local tribal communities,¹ whose jurisdictional lands comprise the study area. As part of their traditional culture, these tribal communities regularly consume crayfish, fish, freshwater mussels, and plants from potentially contaminated stream or riparian environments in the watershed. To understand the potential loss of use of resources by tribal communities, it is important to understand what ecological impairments may be present within the watershed as a result of metal contamination. Determining metal concentrations of streambed sediments and floodplain soils will serve to identify areas within the watershed that are potentially toxic to aquatic and terrestrial organisms. Comparing sediment metal concentrations to sediment quality guidelines established by MacDonald et al. (2009) for metal-mixtures and soil metal concentrations to Ecological Soil Screening Levels (Eco-SSLs) will aid in quantifying the potential toxicity risk to benthic invertebrates and plants. These findings can provide an important basis for future studies assessing potential loss of use of tribal biological resources as well as improving risk-based decision making to be protective of these resources and human health.

Materials and Methods

Study Area

The study location was the Neosho and Spring River watersheds within the Oklahoma portion of the Grand Lake watershed that receive mining impacts from the TSMD (Fig. 1). The tributaries of the Neosho River that drain upstream mined areas are Elm Creek, which drains mined areas in Cherokee County, KS, and Tar Creek, which also drains mined areas in Cherokee County, KS, as well as the TCSS in Ottawa County, OK. Spring River drains several portions of the TSMD in areas of Cherokee County, KS and Jasper and Newton counties, MO. It is joined by several tributaries in Oklahoma, including Beaver Creek and Quapaw Creek, both of which drain the TCSS. Immediately south of where the two rivers join, waters impacted by mining are received via Lost Creek from areas in Newton County, MO. The upper portion of Grand Lake begins just south of the mouth of Lost Creek.

¹ These are the Cherokee Nation, Eastern Shawnee Tribe of Oklahoma, Miami Tribe of Oklahoma, Modoc Tribe of Oklahoma, Ottawa Tribe of Oklahoma, Peoria Tribe of Indians of Oklahoma, Quapaw Tribe of Oklahoma, Seneca-Cayuga Tribe of Oklahoma, Shawnee Tribe, and Wyandotte Nation.

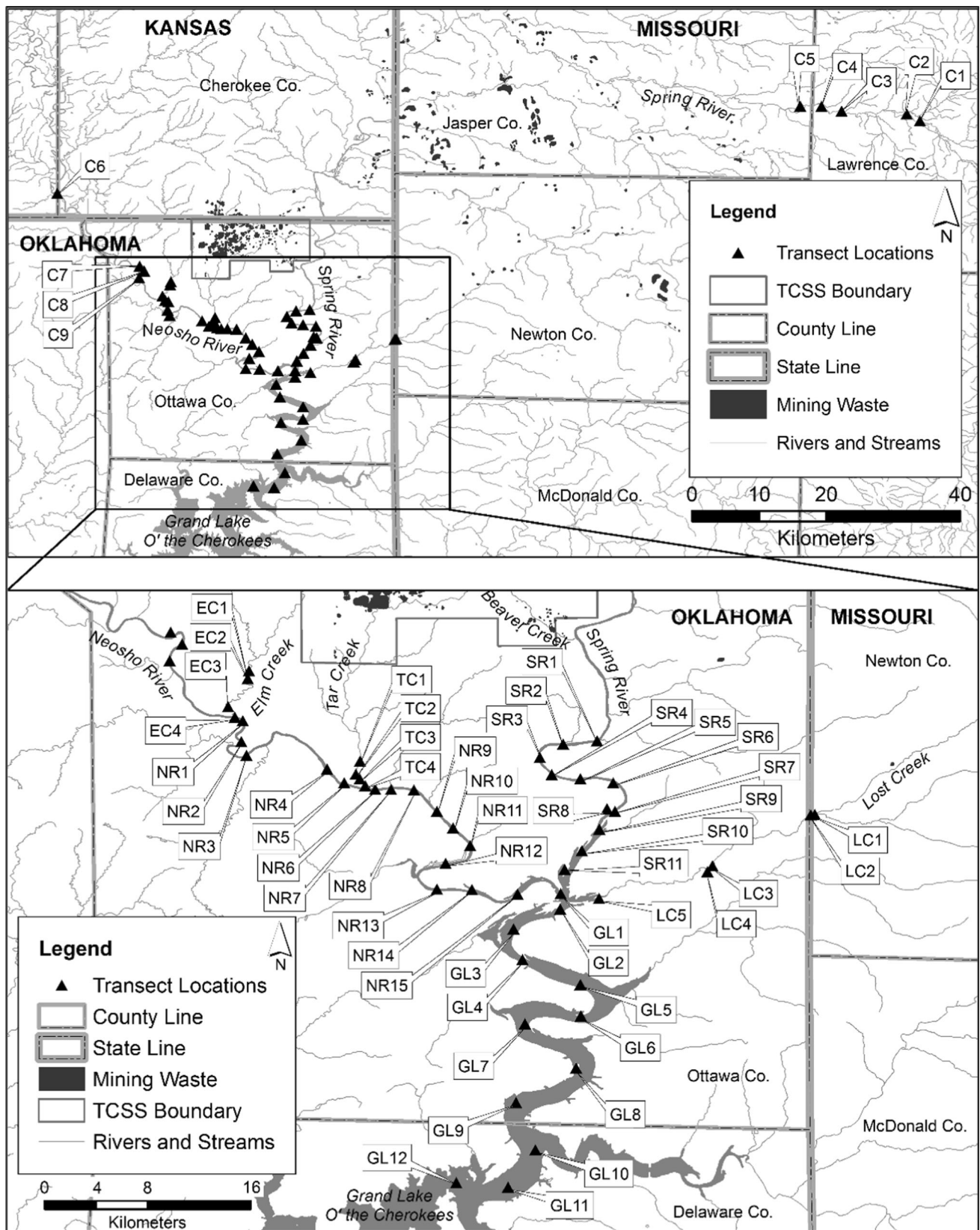


Fig. 1 Locations of sampled transects within the study area in relation to previously mined areas. Transect locations are named according to stream name and transect number. *C* Control, *EC* Elm Creek, *GL* Grand Lake, *LC* Lost Creek, *NR* Neosho River, *SR* Spring River, *TC* Tar Creek

Sampling Field Procedures

Sampled streams within the watershed included those that had substantial historically mined areas in their basins: Neosho and Spring Rivers, Elm Creek, Lost Creek, Tar Creek, and Grand Lake (Fig. 1). In 2009 and 2010, streambed sediment and floodplain soil samples were collected from designated transects downstream of mining impacts. Reference samples were collected from transects located on portions of the Neosho and Spring Rivers that were upstream from major mining influences. The number and spacing of sample collections along each transect were dependent upon channel complexity within the study reach and width of channel/floodplain. Streambed samples were collected using a hand operated auger or Van DornTM sampler. Floodplain samples were collected using a stainless steel hand trowel. At each sample location, a 400-g composite sample was collected no more than 5 cm below the surface over an area of approximately 0.5 m² and placed in a quart-sized ZiplocTM bag. After each sample collection, equipment was washed using a brush with a detergent solution and rinsed with deionized water.

Drying and Sieving Samples

Samples were oven dried at 110 °C for 8 h, ground with a mortar and pestle, and passed through a 5-, 10-, 35-, 60-, 120-, and 230-mesh sieve to achieve a homogenized sample that consisted of the <63- μ m fraction. A portion of the sieved sample was placed in a 31.0-mm polyethylene sample cup so that one-half to two-thirds of the sample cup was full. The sample cup was then covered with a 2.5- μ m MylarTM film for analysis by X-ray fluorescence. The mortar and pestle were thoroughly cleaned with a detergent solution, rinsed with deionized water, and dried between sample preparations to prevent cross contamination. The sieves and pan were cleaned between sample preparations by blowing compressed air through the mesh at 100 psi for 60 s per sieve.

XRF Analysis and Quality Control

Using a portable X-ray fluorescence (XRF) instrument (Olympus model DELTA Premium, Olympus Scientific Solutions Americas Inc., Waltham, MA), a 60-s measurement for each sample was recorded. Detection limits (mg/kg) varied depending on sample but were approximately as follows: Cd, 11; Pb, 8; and Zn, 10. Following EPA Method 6200, an instrument and method blank (SiO₂) was measured every 20 samples (U.S. EPA 2007d). For confirmatory analysis, 10 % (29 samples) of the total number of samples collected were split and sent to Trace Element Research Laboratory, Texas A&M University, College

Station, TX for total metal analysis by inductively coupled plasma-mass spectrometry (ICP-MS) using EPA Methods 3050B and 6020A (U.S. EPA 1996, 2007c). ICP-MS detection limits (in mg/kg) were reported as follows: Cd, 0.03; Pb, 3; and Zn, 3.

Evaluating Metal Toxicity Risk to Benthic Invertebrates and Terrestrial Plants

The incidence for toxicity to benthic invertebrates for each sediment sample was evaluated using a TSMD-specific metals mixture model (\sum PEC-Q_{Cd,Pb,Zn}) developed by MacDonald et al. (2009). The sum of the probable effect concentration-quotient, or PEC-Q, for each metal was determined by dividing its concentration (mg/kg dry weight) within a sediment sample by its corresponding probable-effect concentration (PEC). The PEC for each metal (Cd: 4.98, Pb: 128, Zn: 459) represents the concentration in mg/kg dry weight of sediment above which adverse effects are highly probable with exposures for benthic invertebrates (MacDonald et al. 2000). TSMD-specific sediment toxicity thresholds have been derived by MacDonald et al. (2009) using 28-d survival endpoint tests with the amphipod *Hyaella azteca*. These thresholds are considered to be the most reliable tools for predicting the nature and magnitude of toxicity to *H. azteca*, as well as to the freshwater mussel, *Lampsilis siliquoidea*. Using the model \sum PEC-Q_{Cd,Pb,Zn}, a sediment sample is considered to pose a low risk to benthic invertebrates if

$$\frac{[\text{Cd}]}{4.98} + \frac{[\text{Pb}]}{128} + \frac{[\text{Zn}]}{459} < 6.47.$$

A sample poses a moderate risk if \sum PEC-Q_{Cd,Pb,Zn} is between 6.47 and 10.04 and a high risk if \sum PEC-Q_{Cd,Pb,Zn} is above 10.04. The low risk and high risk thresholds correspond to the amphipod survival rate at the lower limit and 10% below the lower limit of the reference envelope within the TSMD (MacDonald et al. 2009).

The potential toxicity of soil metal concentrations to terrestrial plants was evaluated using Ecological Soil Screening Levels (Eco-SSLs). Eco-SSLs are the concentration limits of specific contaminants within soil that have been derived to be protective of certain ecological receptors, including plants. They are intended to be protective of the receptors at the conservative end of the exposure and associated effects on species distribution. Eco-SSLs are applied at the screening stage of an ecological risk assessment in order to identify the contaminations of potential concern that require further evaluation in a site-specific ecological risk assessment. The Eco-SSLs for plants are as follows (in dry wt): 32 mg/kg Cd, 120 mg/kg Pb, and 160 mg/kg Zn. Eco-SSLs for each metal were calculated as the geometric mean of the maximum

acceptable toxicant concentration (MATC) values for a specific number of test plant species under varying test conditions of pH and % organic matter (U.S. EPA 2005a, b, 2007a).

Statistical Analysis

All statistical tests were performed using Statistica 10.2 software (Statsoft®, Tulsa, OK). Normality was tested using two methods: (1) by using histograms to visually inspect the data, and (2) by performing a Shapiro–Wilks (Royston 1992; Shapiro et al. 1968) statistical test for normality. All parameters tested were found to have a nonnormal distribution; therefore, nonparametric statistical analyses were used. Statistical differences between two groups of data were determined using a two-sample Kolmogorov–Smirnov test (Massey 1951). Statistical comparisons between groups of data were made using a Spearman rank correlation (Gibbons and Chakraborti 1992; Hotelling and Pabst 1936; Spearman 1904). All statistical analyses were performed at a 95% confidence interval.

Results and Discussion

XRF Versus ICP-MS

Concentrations of metals in samples analyzed by ICP-MS were compared to corresponding concentrations in samples analyzed by XRF. Results of a Spearman rank correlation showed a significant, positive correlation for Cd, Pb, and Zn (Cd: $R = 0.92$, $p = 0.00$, $n = 13$; Pb and Zn: $R = 0.99$, $p = 0.00$, $n = 29$). These results indicated that metal concentrations analyzed via XRF met definitive level criteria per the requirements set forth by EPA Method 6200 (U.S. EPA 2007d).

Estimating Nondetectable Cd Concentrations

Approximately 252 of the 283 total samples collected (89%) had Cd concentrations that were below the detection limit of the handheld XRF instrument (<11 mg/kg). Results of a Spearman rank correlation showed a significant, positive correlation between Cd and Zn ($R = 0.94$, $p = 0.00$, $n = 13$). A linear regression model was generated based on known Cd and Zn concentration data obtained using ICP-MS. The model was then used to predict Cd concentrations relative to Zn concentrations within each sample analyzed by XRF where Cd was nondetectable. Only the paired data points where Cd concentrations were <14 mg/kg were used to generate the model ($R = 0.97$; $R^2 = 0.95$; $SE = 0.94$; $y = 0.0061x + 0.0655$; F significance = 2.73×10^{-11} ; $p = 0.00$; $n = 17$).

Importantly, all Cd concentrations reported within this study were estimated using the values predicted within the model.

Background Concentrations

Pope (2005) previously estimated Cd, Pb, and Zn background concentrations within the Kansas portion of the watershed as 0.6, 20, and 100 mg/kg, respectively. Nationally, Horowitz (1991) estimated Pb and Zn background concentrations as 23 and 88 mg/kg. Within this study, mean Cd, Pb, and Zn concentrations at reference transects were 0.5, 19, and 68 mg/kg, respectively. It should be noted that Pb and Zn concentrations reported within this study are the result of XRF analysis, and Cd concentrations are estimated as described in Sect. 3.2.

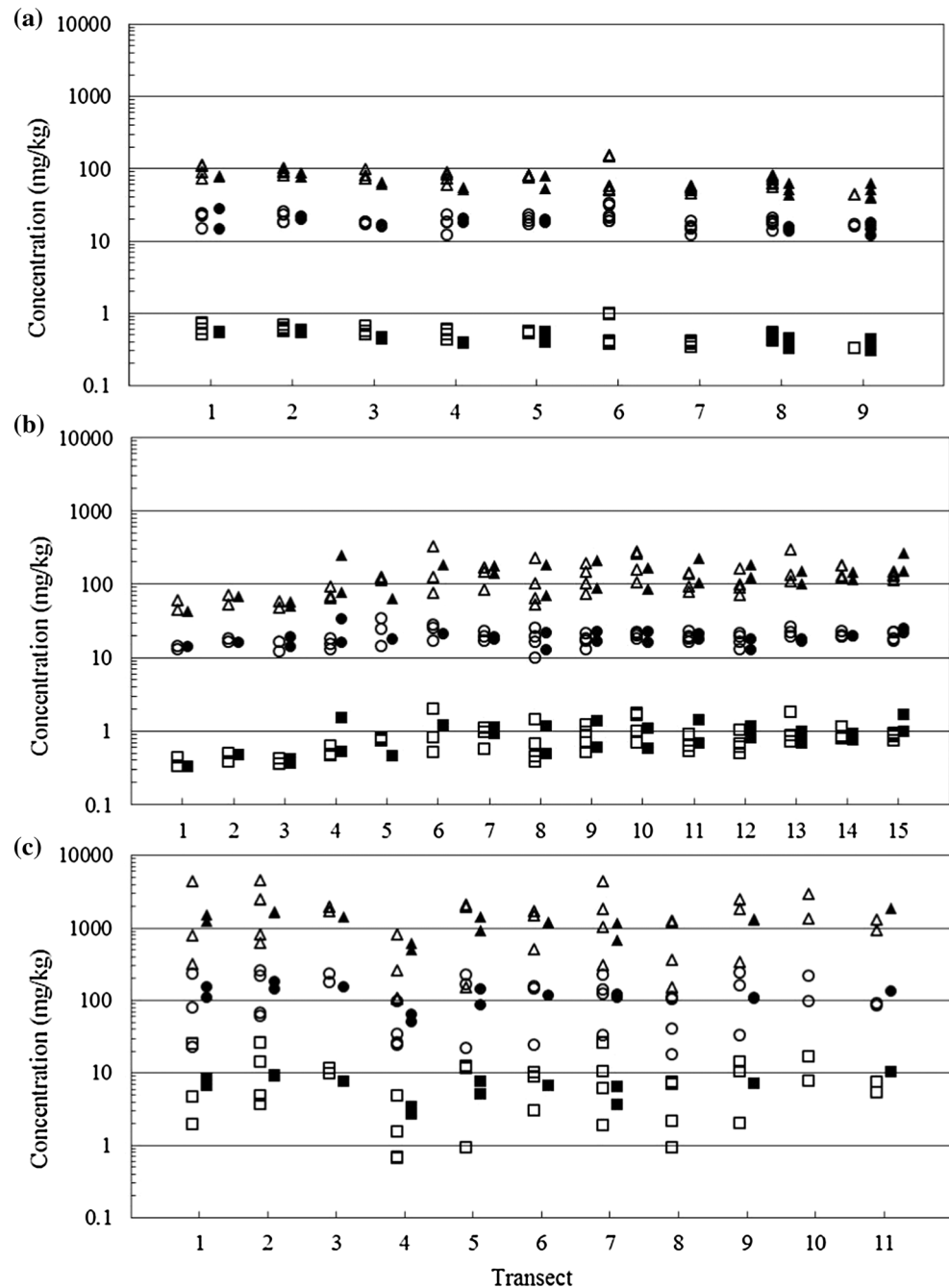
Reference Versus Impacted Streams

Cd, Pb, and Zn concentrations (in mg/kg) in streambed sediment and floodplain soil samples at each stream transect are shown in Figs. 2a–c and 3a–d. Results of a two-sample Kolmogorov–Smirnov test showed a significant difference in the distributions of Cd, Pb, and Zn concentrations between reference and impacted transects (Cd, Pb, Zn: $p = 0.00$; Cd: $n = 29$; Pb, Zn: $n = 283$). These results demonstrated that concentrations of metals in streambed sediments and floodplain soils were significantly lower in areas upstream of major mining influences than in downstream areas within the watershed. Thus, the source of metal contamination within streambed sediments and floodplain soils is the result of mining releases from the TSMD. These findings are in general agreement within previous studies on metal contamination trends in the Grand Lake watershed (Allert et al. 1997, 2012, Andrews et al. 2009; Angelo et al. 2007; Barks 1977; Dames & Moore 1995; Ferrington et al. 1989; Juracek 2006, 2013; Juracek and Becker 2009; Pope 2005; Schmitt et al. 1997).

Streambed Sediments Versus Floodplain Soils

In Table 1, the mean and range of metal concentrations are calculated separately for streambed and floodplain samples at transects. Results of a two-sample Kolmogorov–Smirnov test showed no significant difference in the distributions of Cd, Pb, and Zn concentrations between streambed sediments and floodplain soils. However, the majority of streams (Neosho River, Lost Creek, Tar Creek, and Grand Lake) had higher mean Cd, Pb, and Zn concentrations in the floodplain. Spring River had higher mean Cd concentrations in the streambed and higher mean Pb and Zn concentrations in the floodplain. Elm Creek and reference

Fig. 2 Concentrations of Cd, Pb, and Zn (mg/kg) within streambed and floodplain samples at reference (a), Neosho River (b), and Spring River (c) transects. Cd = square, Pb = circle, Zn = triangle; streambed = open symbol, floodplain = solid symbol. Pb and Zn concentrations were obtained using XRF analysis; Cd concentrations were estimated as described in Sect. 3.2



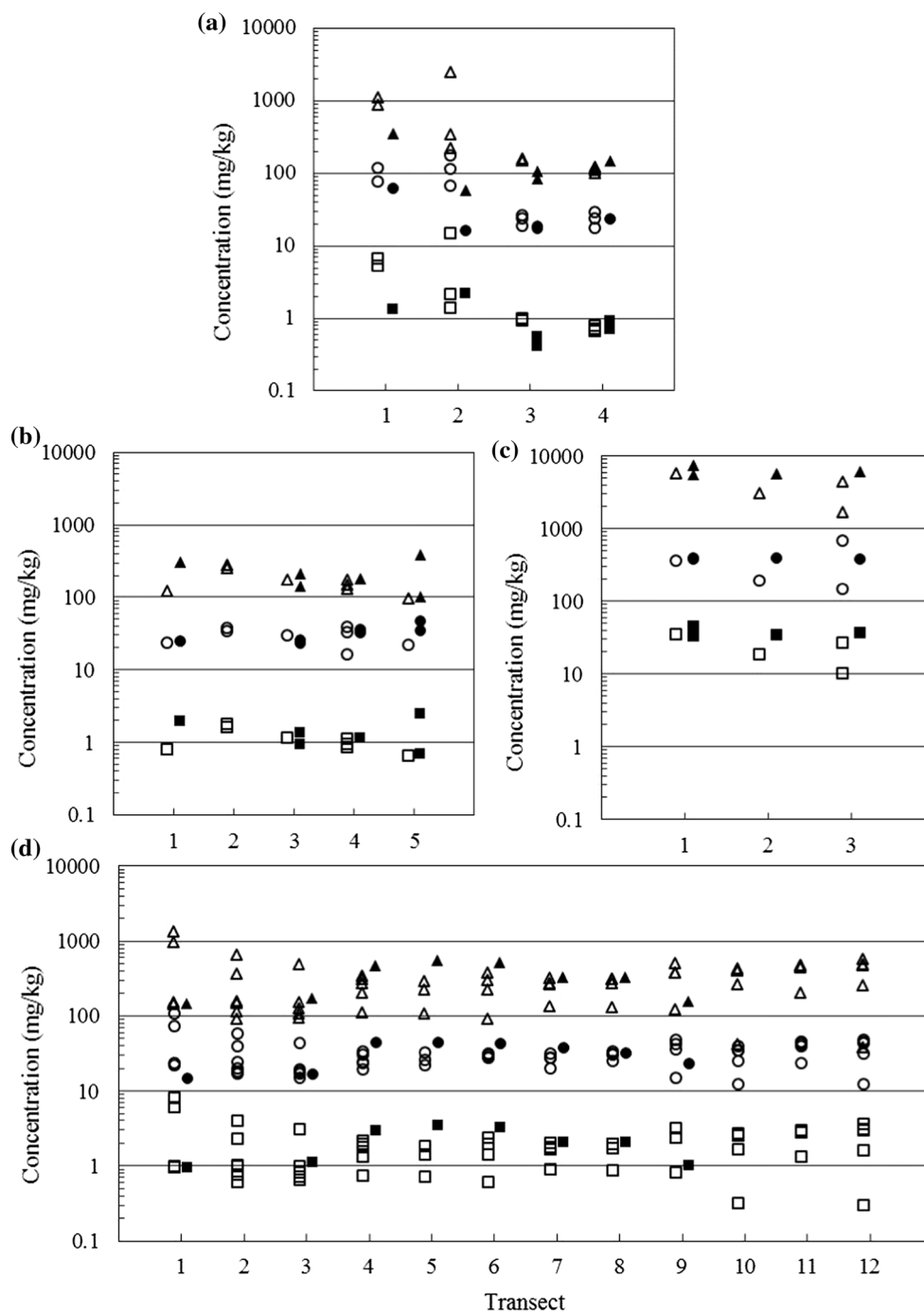
transects had higher mean Cd, Pb, and Zn concentrations in the streambed.

Trends of Metals Contamination

As shown in Table 1, streams that had the highest mean concentrations for Cd, Pb, and Zn were as follows in descending order: Tar Creek, Spring River, Elm Creek, Grand Lake, Lost Creek, and Neosho River. Tar Creek mean Cd, Pb, and Zn concentrations were 30.2, 365, and

4946 mg/kg, which were approximately 62, 19, and 71 times greater than mean reference concentrations. In Fig. 3c, metal concentrations in the streambed decreased with respect to downstream distance from the TSMD. In the floodplains, however, metal concentrations remained generally at the same levels. The highest concentrations of Cd, Pb, and Zn were found in floodplain soils at TC1 and were 45.6, 402, and 7477 mg/kg. Streambed sediments at TC1 were 35.2, 360, and 5758 mg/kg. TC3, located near Tar Creek's confluence with the Neosho River, had Cd, Pb,

Fig. 3 Concentrations of Cd, Pb, and Zn (mg/kg) within streambed and floodplain samples at Elm Creek (a), Lost Creek (b), Tar Creek (c), and Grand Lake (d) transects. Cd = square, Pb = circle, Zn = triangle; streambed = open symbol, floodplain = solid symbol. Pb and Zn concentrations were obtained using XRF analysis; Cd concentrations were estimated as described in Sect. 3.2



and Zn concentrations as high as 37.0, 381, and 6058 mg/kg in floodplain soils and 26.6, 669, and 4361 mg/kg in streambed sediments.

Spring River mean Cd, Pb, and Zn concentrations were 7.9, 96.5, and 984 mg/kg (Table 1), which were approximately 16, 5, and 14 times greater than mean reference concentrations. As shown in Fig. 3c, Cd, Pb, and Zn concentrations did not display a specific trend with respect to distance downstream from the TSMD but consistently remained at relatively similar elevated levels as far

downstream as SR10. SR1 had Cd, Pb, and Zn concentrations as high as 9.1, 153, and 1489 mg/kg in the floodplain and 25.9, 235, and 4239 mg/kg in the streambed. Near the Neosho River confluence, SR11 had concentrations of Cd, Pb, and Zn as high as 11.2, 134, and 1828 mg/kg in the floodplain and 7.7, 90, and 1246 mg/kg in the streambed.

Mean concentrations of Cd, Pb, and Zn at Elm Creek were 1.9, 49.4, and 324 mg/kg, which were approximately 4, 2.5, and 4.5 times greater than mean reference

Table 1 Mean and range of Cd, Pb, and Zn concentrations (mg/kg) in streambed sediments and floodplains soils at each stream

Stream	Sample ^a	<i>n</i>	Cd ^b	Pb ^b	Zn ^b
Reference	<i>F</i>	17	0.4 (0.3–0.6)	17(12–28)	61 (39–89)
	<i>S</i>	39	0.5 (0.3–0.7)	19 (12–24)	75 (43–115)
	Total	57	0.5	19	68
Tar Creek	<i>F</i>	4	37.8 (34.0–45.6)	389 (378–402)	6197 (5566–7477)
	<i>S</i>	4	22.6 (10.1–35.2)	341 (146–669)	3694 (1656–5758)
	Total	8	30.2	365	4946
Spring River	<i>F</i>	15	7.4 (3.0–11.2)	119 (51–184)	1198 (481–1828)
	<i>S</i>	34	8.4 (0.7–26.2)	73 (18–257)	847 (99–4283)
	Total	49	7.9	96	984
Elm Creek	<i>F</i>	6	1.0 (0.4–2.1)	38 (16–94)	152 (54–339)
	<i>S</i>	11	3.1 (0.6–14.3)	60 (17–172)	497 (95–2338)
	Total	17	1.85	49	324
Grand Lake	<i>F</i>	8	2.1 (1–3.4)	32 (15–45)	334 (147–551)
	<i>S</i>	54	1.9 (0.3–8.0)	31 (12–108)	308 (38–1306)
	Total	62	2.0	32	321
Lost Creek	<i>F</i>	7	1.3 (0.7–2.5)	32 (23–47)	215 (102–392)
	<i>S</i>	8	1.1 (0.6–1.8)	29 (16–38)	169 (94–277)
	Total	15	1.2	30	192
Neosho River	<i>F</i>	26	0.9 (0.3–1.5)	19 (13–34)	133 (43–263)
	<i>S</i>	49	0.8 (0.3–2.0)	18 (12–34)	123 (42–322)
	Total	75	0.8	19	128

Pb and Zn concentrations were obtained using XRF analysis. Cd concentrations were estimated as described in Sect. 3.2

^a *F* = total floodplain samples from transects, *S* = total streambed samples from transects, Total = floodplain and streambed values averaged

^b Displayed is “mean (range)”

concentrations (Table 1). In Fig. 3a, metal concentrations at transects decreased with respect to downstream distance from the TSMD. Concentrations of Cd, Pb, and Zn were highest in the streambed at EC2 (as high as 14.3, 172, and 2338 mg/kg). In the floodplain, the highest Cd and Zn concentration was at EC1 (2.1 and 339 mg/kg), and the highest Pb concentration was at EC2 (94 mg/kg). Cd, Pb, and Zn concentrations at EC3 and EC4 were slightly elevated relative to mean reference concentrations—as high as 0.9, 23, and 138 mg/kg in the floodplain and 0.9, 28, and 147 mg/kg in the streambed.

Grand Lake mean Cd, Pb, and Zn concentrations were 2.0, 32, and 321 mg/kg, which were approximately 4, 1.5, and 4.5 times greater than mean reference concentrations (Table 1). As shown in Fig. 3d, metals at transects did not display a specific trend with respect to downstream distance from the TSMD, but remained at similar elevated levels as far downstream as GL12. GL1 had the highest Cd, Pb, and Zn concentrations within streambeds (as high as 8.0, 108, and 1306 mg/kg), and GL5 had the highest concentrations in floodplains (3.4, 44, and 551 mg/kg). Due to limited shoreline access, GL9 was the furthest downstream site in which the floodplain was sampled. Cd, Pb, and Zn

concentrations in the floodplain at GL9 were 1.0, 23, and 157 mg/kg. GL12 had Cd, Pb, and Zn concentrations as high as 3.5, 47, and 571 mg/kg in the streambed.

As shown in Table 1, Lost Creek mean Cd, Pb, and Zn concentrations were 1.2, 30, and 192 mg/kg, which were approximately 2.5, 1.5, and 3 times greater than mean reference concentrations. In Fig. 3b, metal concentrations in the floodplain decreased downstream as far as LC4 and then increased at LC5 where Lost Creek joins with Grand Lake. Streambed metal concentrations steadily decreased downstream. The highest Cd, Pb, and Zn concentrations in the floodplains were at LC1 (1.9, 25, and 308 mg/kg) and in the streambed at LC2 (as high as 1.8, 37, and 277 mg/kg). Cd, Pb, and Zn concentrations at LC5 were as high as 2.5, 47, 392 mg/kg in the floodplain and 0.6, 22, and 94 mg/kg in the streambed.

Neosho River mean Cd, Pb, and Zn concentrations were 0.8, 19, and 128 mg/kg (Table 1). Mean Cd and Zn concentrations were approximately 1.5 and 2 times greater than mean reference concentrations. Mean Pb concentrations were equal to reference concentrations. As shown in Fig. 2b, Cd, Pb, and Zn concentrations were similar to reference concentrations as far downstream as NR6, near

the mouth of Tar Creek, where they increased to levels as high as 1.2, 21, and 186 mg/kg in the floodplain and 2.0, 28, and 322 mg/kg in the streambed. Metal concentrations generally remained at these concentrations as far downstream as NR15.

Exceedances of Toxicity Thresholds and Soil Screening Levels

Risk to Benthic Invertebrates

Table 2 shows the number of streambed sediment samples in each transect that exceeded TSMD-specific toxicity thresholds established by MacDonald et al. (2009) for the benthic community. The sediment thresholds are based on 28-d survival endpoint tests with the amphipod *H. azteca* that are exposed to sediments from the TSMD. A streambed sediment sample is considered to pose a low risk to the benthic community if $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}} < 6.47$, a moderate risk if 6.47–10.04, or a high risk if > 10.04 . The low and high risk thresholds of 6.47 and 10.04 correspond to the minimum survival of amphipods and 10% below the minimum value of the reference envelope. Also shown in Table 2 is the overall risk to the benthic community. Risk at a transect was characterized as “low” if all sediment samples within the transect were below the low-risk threshold, “moderate” if at least one sample exceeded the low-risk threshold, or “high” if at least one sample exceeded the high-risk threshold. In the following discussion, data collected within this study (Table 2) was compared to the findings reported by MacDonald et al. (2010) on the evaluation of risks to the benthic community within portions of the study area (Table 3). MacDonald et al. (2010) characterized potential toxicity to sediment-dwelling organisms via the sediment exposure pathway, as well as from pore water, invertebrate tissue, and surface water pathways, by comparing metal concentrations within these media to established TSMD-specific thresholds (sediment, $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}}$; pore water, $\sum \text{PW-TU}_{\text{Zinc}}$; invertebrate tissue, $\sum \text{TU}_{\text{metals}}$; surface water, $\sum \text{SW-TU}_{\text{Divalent Metals}}$). Additionally, MacDonald et al. conducted laboratory toxicity testing on the effect of TSMD sediments within portions of the study area on the survival and biomass of amphipods, midges, and mussels (Table 3). These data provide a basis for assessing the effects that have occurred (observed toxicity) or are likely to occur (predicted toxicity) to sediment-dwelling organisms within the TSMD. Based on a predictive ability evaluation for all established TSMD-specific thresholds, sediment thresholds were found by MacDonald et al. (2010) to have the highest predictive ability and provided the most reliable method for predicting toxicity to *H. azteca* and *L. siligoidea*. Pore water and surface water

thresholds, as well as laboratory sediment toxicity testing, were also considered by MacDonald et al. (2010) to provide primary lines of evidence for assessing risk to sediment-dwelling organisms. Invertebrate tissue was considered to provide secondary lines of evidence as a result of the higher level of uncertainty associated with the dataset from which thresholds were derived (MacDonald et al. 2010).

As shown in Table 2, all sediment samples collected within the nine reference transects were below the low risk threshold. These results indicate that sediment metal concentrations within reference locations pose low risks to sediment-dwelling organisms and are likely not sufficient to reduce their survival and/or biomass. There were no reference transect locations that coincided with data collected by MacDonald et al. (2010).

Sediment samples were below the low risk threshold within all 15 transects on the Neosho River (Table 2). Transect locations that coincided with data collected by MacDonald et al. (2010) were NR5, NR6, NR10, NR12, NR13, and NR15 (Table 3). NR6 exceeded the sediment low risk threshold; whereas, all other transects were below the threshold. NR6 also exceeded the high-risk threshold for invertebrate tissue and surface water. All pore water samples at transects were below the low risk threshold. The combined results from this study and MacDonald et al. (2010) indicated that metal concentrations in sediments, invertebrate tissue, and surface water are sufficient to moderately reduce the survival and biomass of sediment-dwelling organisms at NR6, near the confluence of Tar Creek. Metal concentrations at all other transects on the Neosho River are likely not sufficient to reduce survival and/or biomass.

Sediment samples exceeded the high risk threshold at SR1, SR2, SR7, and SR10, and the low risk threshold was exceeded at SR3, SR5, SR6, and SR9 (Table 2). As shown in Table 3, data collected by MacDonald et al. (2010) on the Spring River coincided with transects SR1, SR3, SR6, SR9, and SR11. Sediment samples exceeded the low risk threshold at SR1, SR6, SR9, and SR11. Even though sediments at SR3 did not exceed the low-risk threshold, toxicity in midges was observed (survival or biomass). Pore water also exceeded the high-risk threshold at SR3. Invertebrate tissue and surface water were below low-risk thresholds at all transects. Results from this study, in addition to the findings from MacDonald et al. (2010), highlighted the occurrence of contaminated hotspots on the Spring River. Metal concentrations in sediment and pore water are sufficient to highly reduce the survival and/or biomass of sediment-dwelling organisms at SR1, SR2, SR7, and SR10 and moderately reduce survival/biomass at SR3, SR5, SR6, SR9, and SR11.

Table 2 Streambed sediment sample exceedances of TSMD-specific toxicity thresholds and overall classification of risk to benthic community at each transect

Transect	n	Geometric mean of $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}}^{\text{a}}$	Samples in risk category ^b			Overall risk ^c
			Low	Moderate	High	
C1	4	0.50	4	0	0	Low
C2	4	0.48	4	0	0	Low
C3	4	0.42	4	0	0	Low
C4	4	0.41	4	0	0	Low
C5	4	0.44	4	0	0	Low
C6	6	0.45	6	0	0	Low
C7	5	0.31	5	0	0	Low
C8	6	0.38	6	0	0	Low
C9	2	0.29	2	0	0	Low
NR1	2	0.29	2	0	0	Low
NR2	2	0.35	2	0	0	Low
NR3	2	0.30	2	0	0	Low
NR4	3	0.38	3	0	0	Low
NR5	3	0.60	3	0	0	Low
NR6	3	0.69	3	0	0	Low
NR7	3	0.60	3	0	0	Low
NR8	4	0.47	4	0	0	Low
NR9	4	0.56	4	0	0	Low
NR10	4	0.81	4	0	0	Low
NR11	4	0.53	4	0	0	Low
NR12	4	0.49	4	0	0	Low
NR13	3	0.74	3	0	0	Low
NR14	4	0.68	4	0	0	Low
NR15	4	0.60	4	0	0	Low
SR1	3	4.02	2	0	1	High
SR2	4	6.02	2	1	1	High
SR3	2	7.55	0	2	0	Moderate
SR4	4	1.04	4	0	0	Low
SR5	3	3.57	1	2	0	Moderate
SR6	3	4.26	2	1	0	Moderate
SR7	4	5.03	2	1	1	High
SR8	4	2.19	4	0	0	Low
SR9	3	4.66	1	2	0	Moderate
SR10	2	7.56	1	0	1	High
SR11	2	4.27	2	0	0	Low
EC1	2	3.91	2	0	0	Low
EC2	3	2.82	2	1	0	Moderate
EC3	3	0.67	3	0	0	Low
EC4	3	0.54	3	0	0	Low
LC1	1	0.60	1	0	0	Low
LC2	2	1.18	2	0	0	Low
LC3	1	0.83	1	0	0	Low
LC4	3	0.74	3	0	0	Low
LC5	1	0.50	1	0	0	Low
TC1	1	22.42	0	0	1	High
TC2	1	11.71	0	0	1	High
TC3	2	11.68	0	0	2	High
GL1	4	1.76	4	0	0	Low

Table 2 continued

Transect	<i>n</i>	Geometric mean of $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}}^{\text{a}}$	Samples in risk category ^b			Overall risk ^c
			Low	Moderate	High	
GL2	6	0.89	6	0	0	Low
GL3	5	0.66	5	0	0	Low
GL4	5	1.00	5	0	0	Low
GL5	3	0.87	3	0	0	Low
GL6	4	1.01	4	0	0	Low
GL7	4	1.02	4	0	0	Low
GL8	4	1.08	4	0	0	Low
GL9	4	1.30	4	0	0	Low
GL10	5	1.05	5	0	0	Low
GL11	5	1.64	5	0	0	Low
GL12	5	1.19	5	0	0	Low

Pb and Zn concentrations used within the TSMD-specific metals mixture model were obtained using XRF analysis. Cd concentrations used within the model were estimated as described in Sect. 3.2

^a $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}}$ = sum of probable effect concentration quotient for Cd, Pb, and Zn in sediments; geometric mean was calculated for each transect as the *n*th root of the product of *n* values

^b Risk to benthic community thresholds are based on 28-d survival endpoint tests with the amphipod *H. Azteca*; Risk Category: “Low” if $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}} < 6.47$, “Moderate” if $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}} = 6.47\text{--}10.04$, and “High” if $\sum \text{PEC-Q}_{\text{Cd,Pb,Zn}} > 10.04$; 6.47 and 10.04 correspond to the minimum survival of amphipods and 10% below the minimum value of the reference envelope

^c “Low” if all samples in transect fell within the low-risk category; “Moderate” if at least one sample in transect fell within the moderate-risk category; and “High” if at least one sample in transect fell in the high-risk category

As shown in Table 2, sediments at EC2 exceeded the low-risk threshold. EC1 was the only transect that coincided with a location sampled by MacDonald et al. (2010) (Table 3). Sediments at EC1 were shown to exceed the high-risk threshold. Additionally, pore water and surface water at EC1 also exceeded high-risk thresholds. Combined, these results indicated that sediments, pore water, and surface water metal concentrations at EC1 are sufficient to reduce the survival and/or biomass highly of sediment-dwelling organisms. Sediment metal concentrations at EC2 are sufficient to reduce survival/biomass moderately.

Concentrations of metals in sediment samples collected from all transect locations on Lost Creek were below the low-risk threshold (Table 2). All transects sampled coincided with data locations in MacDonald et al. (2010). As shown in Table 3, sediment samples from all transects did not exceed the low-risk threshold. Pore water and surface water samples at all transect locations were below low-risk thresholds. These findings indicated that sediment, pore water, and surface water metal concentrations in Lost Creek are likely not sufficient to reduce the survival and/or biomass of sediment-dwelling organisms.

Sediment metal concentrations exceeded the high-risk threshold at all transect locations on Tar Creek (Table 2). Transects that coincided with data collected by MacDonald et al. (2010) were TC1 and TC3. Similar to the findings

within this study, sediment metal concentrations exceeded the high-risk threshold for TC1 and TC3 (Table 3). Surface water metal concentrations also exceeded the high-risk threshold for TC1 and TC3. Metal concentrations in invertebrate tissue at TC3 exceeded the high-risk threshold. Toxicity to mussels was observed in sediments from TC1, and to both amphipods and mussels at TC3. Pore water samples were below the low-risk threshold at TC1 and TC3. The combined results from Tables 2 and 3 indicated that metal concentrations in sediments, invertebrate tissue, and surface water at TC1 and TC3 of Tar Creek are likely sufficient to highly reduce the survival and/or biomass of sediment-dwelling organisms.

As shown in Table 2, sediment metal concentrations in Grand Lake did not exceed the low-risk threshold at any transect locations. These results indicated that sediment metal concentrations in Grand Lake, as far downstream as Sailboat Bridge, are likely not sufficient to reduce the survival and/or biomass of sediment-dwelling organisms. There were no Grand Lake transect locations within this study that coincided with data collected by MacDonald et al. (2010).

Risk to Terrestrial Plants

Floodplain soil samples that exceeded the plant-specific Eco-SSLs for Cd, Pb, and Zn at each stream transect are

Table 3 Summary of MacDonald et al. (2010) findings on the evaluation of risks to benthic invertebrates exposed to metals contamination in the study area

Transect ^a	Risk to Benthic community ^b				Observed sediment toxicity ^g
	Sediment ^c \sum PEC- Q _{Cd,Pb,Zn}	Pore-water ^d \sum PW-TU _{Zn}	Invertebrate tissue ^e \sum TU _{METALS}	Surface water ^f \sum SW-TU _{DIVALENT METALS}	
NR5	Low	Low	Low	Low	NA
NR6	Moderate	Low	High	High	NA
NR10	Low	NA	NA	Low	NA
NR12	Low	NA	NA	Low	NA
NR13	Low	NA	Low	Low	NA
NR15	Low	NA	NA	Low	NA
SR1	Moderate	NA	NA	Low	NA
SR3	Low	High	Low	Low	T-Mi; NT-A; NA-Mu
SR6	Moderate	NA	NA	Low	NA
SR9	Moderate	Low	NA	Low	NT-A,Mi; NA-Mu
SR11	Moderate	NA	Low	Low	NA
EC1	High	High	NA	High	NA
LC1	Low	NA	NA	Low	NA
LC2	Low	NA	NA	Low	NA
LC3	Low	NA	NA	Low	NA
LC4	Low	Low	NA	Low	NT-A, Mu, Mi
LC5	Low	Low	NA	Low	NT-A, Mi; NA-Mu
TC1	High	Low	NA	High	T-Mu; NT-A, Mi
TC3	High	Low	High	High	T-A,Mu; NT-Mi

NA = no data; \sum PEC-Q_{Cd,Pb,Zn} = probable effect concentration quotient for Cd, Pb, and Zn in sediment; \sum PW-TU_{Zinc} = sum pore water toxic units of Zn (calculated as the measured concentration of Zn in pore water divided by the hardness-adjusted CCC for Zn); \sum TU_{METALS} = sum of hazard quotients for Cd, Cu, Pb, Hg, and Zn; \sum SW-TU_{DIVALENT METALS} = sum surface water toxic units for divalent metals (calculated as measured concentrations of Cd, Cu, Pb, Ni, Ag, and Zn in surface water divided by their respective hardness-adjusted CCCs)

^a Matching transect that corresponds to data within MacDonald et al. (2010)

^b “Risk to Benthic Community” thresholds for sediment, pore water, and surface water are based on control-adjusted 28-d survival endpoint tests with the amphipod *Hyalella azteca*; thresholds for invertebrate tissue are based on control-adjusted 28-d survival endpoint tests with *H. azteca* and 28-d bioaccumulation tests with the oligochaete, *Lumbriculus variegatus*

^c Risk category for sediment = “Low” if \sum PEC-Q_{Cd,Pb,Zn} < 6.47, “Moderate” if 6.47–10.04, and “High” if > 10.04; 6.47 and 10.04 correspond to the minimum survival of amphipods and 10% below the minimum value of the reference envelope

^d Risk category for pore water = “Low” if \sum PW-TU_{Zinc} < 0.581, “Moderate” if 0.581–0.867, and “High” if > 0.867; 0.581 and 0.867 correspond to 10 and 20% below the mean survival for reference samples

^e Risk category for invertebrate tissue = “Low” if \sum TU_{metals} < 6.01, “Moderate” if 6.01–7.45, and “High” if > 7.45; 6.01 and 7.45 correspond to 10 and 20% below the mean survival for reference samples

^f Risk category for surface water = “Low” if \sum SW-TU_{DIVALENT METALS} < 1.03, “Moderate” if 1.03–1.41, and “High” if > 1.41; 1.03 and 1.41 correspond to 10 and 20% below the mean survival for reference samples

^g T = toxic; NT = not toxic; A = amphipod (*H. azteca*); Mi = midge (*Chironomus dilutus*); Mu = freshwater mussel (*Lampsilis siliquoidea*); Sediment samples were designated toxic if survival or biomass of amphipods (28-day), midges (10-day), and freshwater mussels (28-day) exposed to TSMD sediments was lower than the lower limit of the normal range for reference sediments

shown in Table 4. Plant-specific Eco-SSLs are as follows (in dry wt): Cd = 32 mg/kg, Pb = 120 mg/kg, and Zn = 160 mg/kg. Eco-SSLs for each metal were derived as the geometric mean of the maximum acceptable toxicant concentration (MATC) values for a specific number of test plant species under varying test conditions of pH and %

organic matter (U.S. EPA 2005a, b, 2007a). Eco-SSLs should not be treated as cleanup levels but rather should be applied at the screening stage of an ecological risk assessment to identify the contaminations of potential concern that require further evaluation in a site-specific ecological risk assessment (U.S. EPA 2005a, b, 2007a). To

Table 4 Floodplain soil sample exceedances of Ecological Soil Screening Levels (Eco-SSLs) for Cd, Pb, and Zn that have been derived for plants (U.S. EPA 2005a, b, 2007a)

Transect	<i>n</i>	Number of samples in exceedance of Eco-SSL			Transect	<i>n</i>	Number of samples in exceedance of Eco-SSL		
		Cd	Pb	Zn			Cd	Pb	Zn
C1	2	0	0	0	EC1	1	0	0	1
C2	2	0	0	0	EC2	1	0	0	1
C3	2	0	0	0	EC3	2	0	0	0
C4	2	0	0	0	EC4	2	0	0	0
C5	2	0	0	0	LC1	1	0	0	1
C8	3	0	0	0	LC3	2	0	0	1
C9	4	0	0	0	LC4	2	0	0	2
NR1	1	0	0	0	LC5	2	0	0	1
NR2	1	0	0	0	TC1	2	2	2	2
NR3	2	0	0	0	TC2	1	1	1	1
NR4	2	0	0	1	TC3	1	1	1	1
NR5	1	0	0	0	GL1	1	0	0	0
NR6	1	0	0	1	GL3	1	0	0	1
NR7	2	0	0	1	GL4	1	0	0	1
NR8	2	0	0	1	GL5	1	0	0	1
NR9	2	0	0	1	GL6	1	0	0	1
NR10	2	0	0	1	GL7	1	0	0	1
NR11	2	0	0	1	GL8	1	0	0	1
NR12	2	0	0	1	GL9	1	0	0	0
NR13	2	0	0	0					
NR14	2	0	0	0					
NR15	2	0	0	1					
SR1	2	0	0	2					
SR2	2	0	1	2					
SR3	1	0	0	1					
SR4	2	0	0	2					
SR5	2	0	0	2					
SR6	1	0	0	1					
SR7	2	0	1	2					
SR9	2	0	0	2					
SR11	1	0	1	1					

Pb and Zn concentrations used for the comparison of plant Eco-SSLs were obtained using XRF analysis. Cd concentrations were estimated as described in Sect. 3.2

date, no other studies have been conducted within the study area on the assessment of metal concentrations in floodplain soils.

As shown in Table 4, metal concentrations in soil samples at reference transects did not exceed the Eco-SSLs for Cd, Pb, or Zn. These results indicated that soil metal concentrations at all reference transects are likely not sufficient to impact plant populations.

Soil samples collected on the Neosho River did not exceed the Eco-SSL for Cd or Pb at transect locations (Table 4). However, many transects had one soil sample

that exceeded the Eco-SSL for Zn at NR4, NR6-12, and NR15. These findings suggested that soil Zn concentrations at NR4, NR6-12, and NR15 may likely be sufficient to impact plant populations.

Spring River soil samples did not exceed the Eco-SSL for Cd at transect locations (Table 4). Transects SR2, SR7, and SR11 had one sample each that exceeded the Eco-SSL for Pb. All soil samples collected from every transect exceeded the Eco-SSL for Zn. These results indicated that Pb soil concentrations are likely sufficient to impact plant populations at SR2, SR7, and SR11, and Zn soil

concentrations are likely sufficient to impact plant populations at all transect locations.

In Table 4, Elm Creek soil samples did not exceed the Eco-SSL for Cd or Pb at transects. Two transects (EC1 and EC2) had soil samples that exceeded the Eco-SSL for Zn. Therefore, Zn soil concentrations at EC1 and EC2 may be sufficient to impact plant populations.

On Lost Creek, soil samples did not exceed the Eco-SSLs for Cd or Pb at transects (Table 4). However, at least one soil sample from each transect exceeded the Eco-SSL for Zn. These results indicated that Zn soil concentrations may be sufficient to impact plant populations at all transects.

All soil samples from every transect on Tar Creek exceeded the Eco-SSLs for Cd, Pb, and Zn (Table 4). These data suggested that soil Cd, Pb, and Zn concentrations on Tar Creek are likely sufficient to impact plant populations.

As shown in Table 4, soil samples did not exceed the Eco-SSLs for Cd or Pb at Grand Lake transects. However, all soil samples from transects GL3-8 exceeded the Eco-SSL for Zn. These findings indicated that soil Zn concentrations may likely be sufficient to impact plant populations at transects GL3-8.

Conclusions

To date, the majority of TSMD risk-related studies, remediation, and restoration efforts within the Oklahoma portion of the Grand Lake watershed by local, state, and federal agencies have been focused primarily within the EPA-designated TCSS boundary. The results of this study have established that the downstream extent of streambed and floodplain contamination in Oklahoma (that is present outside the TCSS boundary) is far more expansive than previously thought. Elm Creek, Spring River, and Tar Creek especially had sufficient metal concentrations to warrant ecological risk concerns for benthic invertebrates and plants, in addition to higher trophic organisms that depend on them for food. Because the subsistence practices and thus health of local tribal communities are reliant on the health and abundance of the biological resources within the watershed, the results of this study suggested that metal contamination present within tribal jurisdictions has greatly impacted these communities in terms of their capacity to use their resources so as to preserve and continue their cultural practices. These overall findings provided an important basis for future data needs in assessing metal concentrations in aquatic and terrestrial biota that are consumed by tribal communities within the watershed to determine if certain organisms/species are unsafe to consume or warrant consumption advisories. Ultimately, these

findings aid in more appropriately evaluating the potential loss of use of tribal biological resources, as well as improving risk-based decision making to be protective of these resources and human health.

Acknowledgements The authors would like to thank the Cherokee Nation, Eastern Shawnee Tribe of Oklahoma, Miami Tribe of Oklahoma, Ottawa Tribe of Oklahoma, Seneca-Cayuga Tribe of Oklahoma, and Wyandotte Nation for funding this study. The authors also extend their sincere appreciation to Janice Wilson and Kathy Welch (Wyandotte Nation Environmental Department) for their sampling assistance, Jason White (Cherokee Nation Environmental Department) for his aid in XRF metal analysis, and Kit Garvin (Tribal Environmental Management Services) for driving the boat and sampling assistance.

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