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Metal Accumulation in American Sycamores in a Mining-Contaminated River in Southeastern Missouri

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Abstract The Big River, in the Old Lead Belt, southeast Missouri, experienced large-scale contamination of channel sediments and floodplain soils from over 200 years of lead mining pollution. Sediments of gravel bars downstream of mining in Big River are contaminated with Pb and Zn and have higher metal concentrations than upstream sites. Plants on these contaminated gravel bars are thus exposed to high metal concentrations and can accumulate metals. We measured multielement concentrations in leaves, branches, stems, and bark of American sycamores (*Platanus occidentalis*) from a contaminated and non-contaminated gravel bar in the Big River to determine the extent of metal accumulation in these trees. Element concentrations were 2–70 times higher in contaminated than non-contaminated tree parts. Contaminated sycamores were enriched with Cd, Co, Pb, and Tl in leaves; Cd, Na, Ni, Pb, Tl, and Zn in branches; Cd, Co, Pb, Tl, U, Zn, and Zr in stems; and Cd, Co, Ni, Pb, Tl, and Zn in bark (enrichment ratio >2). Contaminated bark accumulated higher concentrations of Ba, Cd, Co, Fe, Er, Ho, Li, Na, Ni, Pb, Tl, U, Zn, and Zr than other tree parts. Leaves had the highest P concentrations and the second highest concentrations of Ba, Fe, Li, Tl, U, Zn, and Zr after bark. Contaminated sycamores have the potential to disperse accumulated metals in the environment, particularly those in bark and leaves, as sycamores frequently shed these tree parts. After contaminated tree parts shed and become detritus, they can transfer accumulated metals from the sediment to food webs. The resulting detritus can change microbial and macroinvertebrate communities and subsequently inhibit decomposition in rivers.

Keywords Gravel bars · Lead · Mining-contamination · Metals · *Platanus* · Sycamore

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1 Introduction

Mining has led to widespread metal contamination of lands and waterways. Plants growing in

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mining-contaminated areas accumulated metals (Deng et al., 2004; Migeon et al., 2009) and can continue to accumulate metals when their aboveground tissues become detritus (Yue et al., 2019). Metal accumulation varies among plant species in terms of metal type and allocation and reflects bioavailable concentrations of the contaminated soils or sediments. Some plant species accumulate higher Cd, Pb, or Zn in leaves compared to other species growing in the same location highlighting differences in uptake among different species (Liu et al., 2007; Migeon et al., 2009). Concentrations of Cu and Zn in *Urtica dioica*, *Rubus fruticosus*, and *Acer pseudoplatanus* leaves and Pb in leaves and roots of *U. dioica* and *R. fruticosus* indicated varying levels of bioavailability of these metals in the soils of these trees (Murphy et al., 2000). Concentrations of Pb and Cd in aboveground parts of *Salix* sp. and *Populus* sp. increased as the concentrations of these metals increased in soils, indicating that these metals were present in forms that were available for uptake (Kacálková et al., 2014). The degree of metal accumulation in plants varies widely depending on the metal contamination source, bioavailability, and site and substrate characteristics (Pulford & Watson, 2003).

Plants differ in metal translocation and accumulation among plant parts (Pulford & Watson, 2003). Some plants accumulate high concentrations of metals in roots and restrict translocation to shoots. Studies reported higher Pb concentrations in roots than leaves of multiple tree species (Günthardt-Goerg et al., 2019; Kacálková et al., 2014; Lepp & Eardley 1978) while others reported higher Zn in leaves than other tree parts (Evangelou et al., 2013; Günthardt-Goerg et al., 2019; Meers et al., 2007). Like roots, bark is an important sink for metals and can restrict translocation of toxic metals to leaves (Pulford & Watson, 2003), yet few studies addressed the implications of higher bark metal concentrations. The bark of *Platanus* sp., *Betula* sp., *Salix* sp., and *Laurus nobilis* trees accumulated higher metal concentrations than aboveground tree parts (McGregor et al., 1996; Yaşar et al. 2012). In addition to leaves and bark, stem and branches can also accumulate metals (Kacálková et al., 2014; Nikolova, 2015). After plants accumulate metals, they can be a secondary source by releasing these accumulated metals to soil or nearby waters via deposition, senescence, and decomposition (Van Nevel et al., 2014). Higher metal concentrations in plants can inform us about the contamination risk of metal deposition from plant litter, which can increase bioavailable metal concentrations after decomposition in soils (Vandecasteele et al., 2009; Van Nevel et al., 2014). Consumption of metal-contaminated plant parts or detritus can result in the accumulation of metals and subsequent deleterious effects in consumers (Allert et al., 2013; Beyer et al., 2004; Liu et al., 2021).

Organisms in the Big River watershed are exposed to high metal concentrations due to widespread mining contamination. The Big River watershed drains the Old Lead Belt mining district in southeast Missouri, which was a global leader in lead (Pb) production from 1869–1972 (Buckley, 1909; Pavlowsky et al., 2017). Mine tailings sites and surrounding areas in the Big River watershed are a part of the Southeast Missouri Superfund National Priority List Pb sites (US EPA 2017). Large quantities of metalliferous tailings and other mineral wastes were released to Big River resulting in large-scale contamination of channel sediments and floodplain soils (Smith & Schumacher, 1991, 1993; Meneau, 1997; Pavlowsky et al., 2017). Gravel bars downstream of historical mining sites in Big River are contaminated with Pb and Zn (Wang et al., 2016; Pavlowsky et al., 2017) and often contain woody vegetation such as *Platanus* sp. and *Salix* sp. that can influence contaminated sediment deposition (Dietz, 1952; McKenney et al., 1995). Plants take up metals from soil and water; thus, gravel bar vegetation can play an important role in element cycling in rivers (Schade et al., 2001; Weis & Weis, 2004) and provide pathways for metal uptake from sediments to the food chain (Peralta-Videa et al., 2009).

Plants are often the source of metal contamination for organisms at higher trophic levels, such as birds and fish (Peralta-Videa et al., 2009; Besser et al., 2007; Beyer et al., 2004). Palmer and Kucera (1980) reported high Pb concentrations in sycamore leaves near mines and smelters in the Viburnum Trend and Old Lead Belt. Vascular plant detritus is the main energy source in streams (Whitledge & Rabeni, 1997) and was reported to have higher concentrations of Cd, Pb, and Zn downstream of mining contamination in Big River (Allert et al., 2013). Elevated Cd, Pb, and Zn concentrations were detected in fish, macroinvertebrates (Allert et al., 2013; Besser et al., 2007), and birds (Beyer et al., 2004; Beyer et al., 2013) in Missouri mining areas. Birds in the Tri-state Mining District in Missouri, Oklahoma, and Kansas had elevated levels of Pb in their blood, liver, kidneys, and pancreas after exposure to high metal concentrations from ingested soil, plants, or detritivores (Beyer et al., 2004). Fish and invertebrates in the Viburnum Trend of southeast Missouri had higher metal concentrations near mining sites, with Cd and Zn concentrations being higher at more sites than Pb (Besser et al., 2007). These studies indicate that water, soils, sediments, and plants in mining-contaminated areas could be possible routes of exposure to metal contamination.

There is evidence of metal accumulation in detritus and consumers in southeast Missouri (Allert et al., 2013), but the extent of metal accumulation in plants is not fully understood. Bar and floodplain plants play an important role in controlling flow and sediment deposition, but few studies addressed the role of these plants in the distribution of metals on bar surfaces. Palmer and Kucera (1980) reported Pb concentrations decreased in American sycamore (*Platanus occidentalis*) leaves and twigs, from uplands and floodplains, with increasing distance up to 8 km from mines in the Big River watershed. Other research in the Old Lead Belt reported negative relationships between metal concentrations in soil and floristic quality of plants with distance away from mining activities (Struckhoff et al., 2013). The current study assessed metal concentrations in vegetation growing on a Pb- and Zn-contaminated gravel bar in Big River to evaluate if plants accumulated metals to levels of environmental concern in different tree parts. Our study adds to previous work by focusing on trees within the channel and including analysis of leaves, branches, stems, and bark, which could be secondary sources of metals through shedding or senescence. In addition to Pb and Zn, we measured the concentration of 59 other elements in leaves, branches, stems, and bark of American sycamores on gravel bars in mining contaminated and non-contaminated reaches of Big River, southeast Missouri. We hypothesized that metals typically enriched in ores and tailings (e.g., Cd, Pb, and Zn) would be found in higher concentrations in trees growing in contaminated bar deposits compared to a similar bar located in a non-contaminated reach upstream of mining activities. Since sycamores frequently shed outer bark tissues (Gilman et al., 2018), we also hypothesized that metals would be higher in bark compared to stems, branches, and leaves.

2 Methods

2.1 Study Sites

We completed this study during the first week of August 2017 on two gravel bars in Big River, southeast Missouri. One gravel bar (contaminated gravel bar) was within the mining-contaminated segment of Big River in Saint Francois State Park below Bonne Terre, Missouri, at river-kilometer (R-km) 140.2 from the mouth (Fig. 1). Previous studies indicated metal concentrations in fine sediment fractions (<2 mm) of channel sediment at this site ranged from 1,200 to 1,600 mg/kg Pb and 600 to 900 mg/kg Zn with higher values associated with finer particles and organic-rich samples (Gale et al., 2002, 2004; Pavlowsky et al., 2017; Schmitt & Finger, 1982; Smith and Schumacher, 1993). This was a side or longitudinal bar (125 m long, 15 m wide) located along a straight reach between two valley bends. The bar surface had mostly woody species with >80% canopy cover except for the active tail area (20 m long) at the downstream end of the bar. Vegetation cover was primarily sycamore, black willow (*Salix nigra*), and buttonbush (*Cephalanthus occidentalis*).

The other gravel bar (non-contaminated gravel bar) was in Washington County near Irondale, Missouri at river-kilometer 191.7 km about 20 km above mining influence (Fig. 1). The fine sediment fraction (<2 mm) in non-contaminated bar deposits tend to contain metal concentrations at regional background levels at <34 mg/kg Pb and <71 mg/kg Zn (Pavlowsky et al., 2010, 2017). This sampling site is often used as a control site for biological and geochemical assessments in Big River by other researchers (e.g., Allert et al., 2013; Gale et al., 2004; Stroh et al., 2015). The center bar complex sampled at this site is 250 m long and 40 m wide and located at the downstream end of a long (500 m), straight channel reach. The bar head is located about 100 m below a high bridge and large pool. Vegetation canopy covered 60–80% of the bar with mainly sycamore, black willow, and areas of

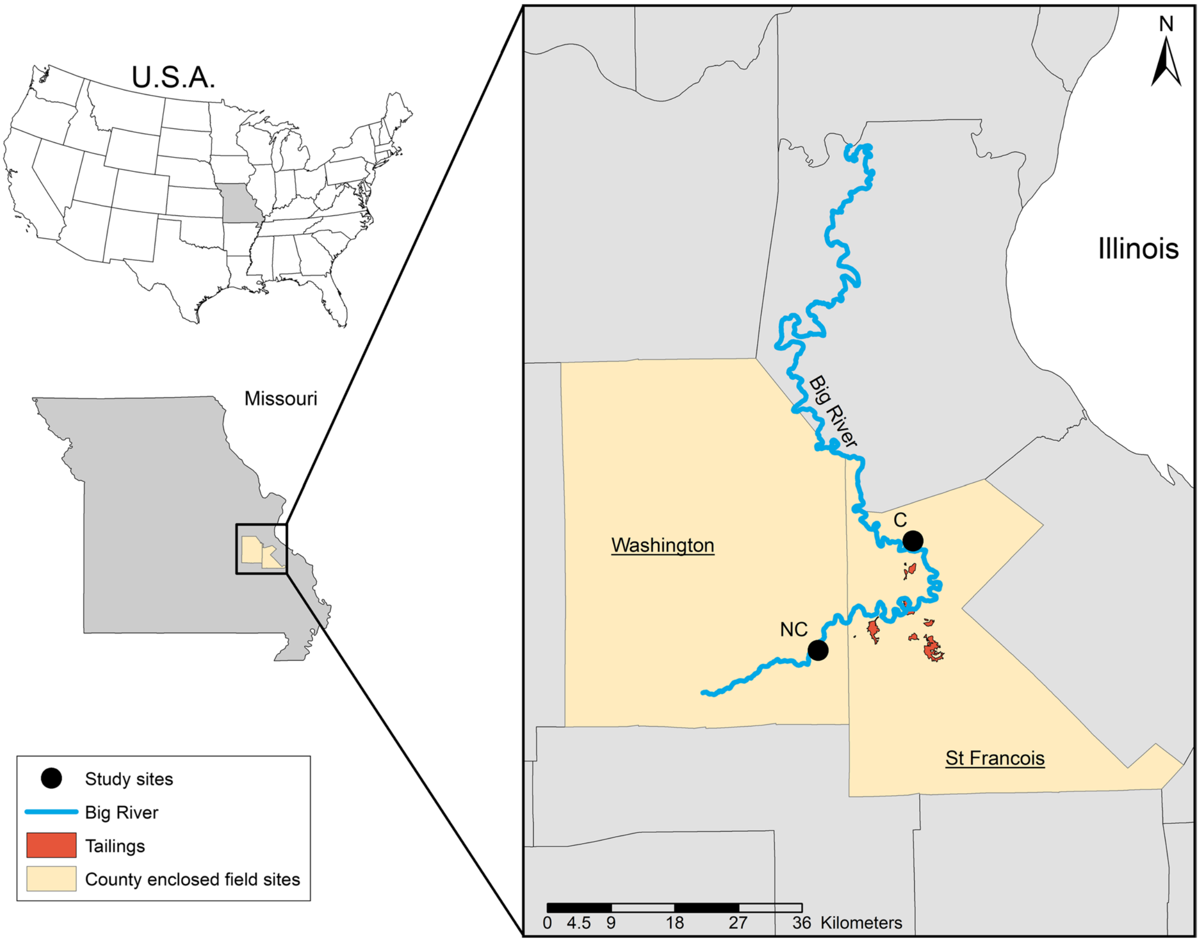

Fig. 1 Map showing the Big River study sites sampled in August 2017 in the Old Lead Belt, southeast Missouri (NC = non-contaminated; C = contaminated)

non-vegetated gravel substrates. Both gravel bars contained woody vegetation of varying sizes and were composed of sand and gravel substrates. Most of the tree root mass growing in the river bar deposits was above the saturated zone during low flow periods.

2.2 Sediment and Tree Sampling and Analyses

We sampled bar deposits to assess tree substrate characteristics and degree of contamination from mining and other sources. We collected sediments at 10–30-cm depth from shallow pits with a stainless-steel shovel to assess the spatial variability of fine sediment (<2 mm) and Pb and Zn concentrations in bar substrates. Since bar surfaces commonly form coarse pavements due to scour during falling flood stages or selective transport of finer sediment (Bunte & Abt, 2001), subsurface bar samples were more representative of the sediment stored in the bar overall. Previous depth probing and coring studies of bar deposits in Big River indicated that Pb and Zn concentrations in fine sediment fractions were relatively similar across bar depth and area at a site (Pavlowsky et al., 2010, 2017; Smith, 2013). Sediment <2 mm in diameter was targeted for metals analysis since the finest fractions (e.g., < 63 um, <250 um, and <2 mm) typically contain geochemical substrates that control metal availability in the aquatic environment (Horowitz, 1991; Schmitt & Finger, 1982; Smith & Schumacher, 1993). In addition, while major volumes of metalliferous Pb tailings up to 16 mm in diameter were released to Big River, the finer waste particles released during ore milling by shaking table and froth flotation methods contained high residual Pb concentrations and were most easily transported downstream by fluvial processes (Pavlowsky et al., 2017; Taggart, 1945).

We collected sediment samples in a grid pattern to evaluate the spatial variability of metal concentrations in bar sediments. At the contaminated bar site, we collected 62 sediment samples at 3–5-m intervals across the contaminated bar along transects spaced downstream at 10 m intervals. We also collected 13 duplicate samples (20% of total) from one pit on each transect from a location 1-m downstream of the first sample. At the non-contaminated bar site, we collected three samples and one duplicate from the bar head along one transect only with 15 m spacing since previous research indicated background metal concentrations were present at this site (Gale et al., 2002; Horowitz, 1991; Pavlowsky et al., 2010, 2017; Schmitt & Finger, 1982; Smith & Schumacher, 1993). To compare the substrate conditions between the two sites, we completed modified Wolman pebble counts within 10–20 m^2 areas with uniform bar substrate characteristics using a paced grid, blind finger-touch selection, and gravelometer measurement procedure (Bunte & Abt, 2001). We measured 30 pebbles at each of 15 sampled contaminated bar areas across the bar surface for a total of 450 individual pebble counts.

Sediment samples were dried at 60 °C, sieved (32 and 2 mm), and weighed for gravimetric size analysis. An Oxford Instruments Portable X-MET 3000 TXS+ X-ray Fluorescence (XRF) analyzer was used to measure Pb and Zn concentrations in the <2-mm sediment fraction (US EPA, 1998). We used laboratory duplicate and check standard analyses and calibration curves derived by comparison with paired-split sample results after aqua regia extraction and ICP-AES analysis to verify results (Pavlowsky et al., 2017).

We selected sycamores for sampling after a preliminary survey found it was the most abundant species on both gravel bars. *Platanus* spp. were sampled for similar purposes in the Missouri Lead Belt (Palmer & Kucera, 1980) and other areas (Kim et al., 2020; Rykowska & Wasiak, 2011). We set transects at 10-m intervals across the length (125 m) of the contaminated gravel bar, starting at the head. We identified nine sycamores for sampling within each bar form unit (BFU) along transects located at 10, 30, 50, 70, 90, 100, and 110 m. We selected sycamores from within 1-m^2 quadrats placed at 3–6 random locations along each transect. Due to time constraints and thunderstorms, we did not set transects to sample sycamores at random on the non-contaminated gravel bar. We were able to identify the locations of the bar head, middle, and tail and sample three sycamores of similar size (DBH and height) within each of these BFUs.

We sampled sycamores ranging from 2–31-cm diameter at breast height (DBH at 1.37 m, Jenkins et al., 2004). Trees were cut down to sample leaves, branches, stem, and bark above the DBH. We picked live leaves from different locations in the crown and cut branches with a stainless-steel bypass tree lopper from parts of the stem that branched out from the center. Stem samples contained the same tissues as branches but were collected from the main tree stem by cutting from above 1.37 m with a handsaw (within 1 m above DBH). We peeled outer bark from branch and stem samples by hand or with a chisel (cleaned with 75% ethanol between samples). We used only bark from stems for analysis. Bark samples included outer bark, i.e., the tissue outside the vascular cambium and inner bark (Raven et al., 1992). We used a different set of tools for collecting samples from each gravel bar and sampled each bar on different days to prevent cross contamination. Each sample was stored in clean and labeled polyethylene bags.

For each tree, we pooled samples for each tree part, triple rinsed samples with deionized water, dried until constant weight at 60 °C, crushed using mortar and pestle and liquid nitrogen, and then homogenized and sieved (1-mm) crushed samples. We used a different set of acid-washed mortar and pestles for samples from each gravel bar and tree part and cleaned these with 70% ethanol in between replicate samples. We also used different sieves for samples from each gravel bar and for each tree part to prevent cross contamination. Each sample was acid digested (aqua regia at 95 °C for 2 h) and analyzed for 61 elements using ICP-MS (Perkin Elmer Sciex ELAN) by Activation Laboratories (www.actlabs.com). See Appendix for a complete list of elements, method detection limits (MDL), and recovery rates (Table A1). Element analyses were validated with NIST 1575a and an internal laboratory standard. Quality control was verified by checking sample duplicates, method blanks, and standards every 12–15 samples. We calculated percent recovery rates for elements using measured and expected values for NIST 1575a (Table A1). Most elements had recovery rates >80% while Sb had a recovery rate of 60%. This suggests that our results may be conservative estimates of true values for Sb. Values at or below the

MDL were replaced with half the MDL, and elements where >50% of the data was below the MDL were not included in statistical analyses (Reimann et al., 2008).

2.3 Statistical Analysis

Prior to statistical analysis, we transformed the tree element concentration data (Box Cox or Johnson transformation) to obtain homogeneity of variance and normality. We determined significant differences using a General Linear Model with two-way ANOVA (P<0.05) and multiple comparison tests (Tukey Method, P<0.01). Some elements (Au, B, Ba, Ca, Cd, Cs, Dy, Er, Eu, Ga, Gd, Ho, La, Li, Mo, Nd, P, Pr, Se, Sm, Sr, Th, Ti, Tm, Y, Zr) could not be transformed, so we used Kruskal-Wallis test (P<0.05) to test for differences. Element concentration data were first analyzed to determine variability in sycamores within the gravel bars between BFUs for equivalent tree parts of (1) the contaminated and (2) the non-contaminated gravel bar. Element concentrations did not differ between equivalent tree parts from the head, middle, and tail of each gravel bar, so we pooled these data for both gravel bars. We then tested for differences: (1) between equivalent tree parts of the contaminated and non-contaminated gravel bar and (2) among tree parts of the contaminated gravel bar. We compared element concentrations between tree parts of the contaminated sycamores because concentrations in these trees were higher than the non-contaminated sycamores. Concentrations for elements that did not differ between gravel bars were included in the Appendix (Tables A2–A5). To test for relationships between elements in trees, we calculated Spearman's rank correlation coefficients and associated P values (using non-transformed data). We only reported significant correlations (P<0.05). All statistical analyses were carried out in Minitab (Minitab19 ©2020 Minitab Inc.).

We also calculated enrichment ratios to identify elements that were enriched in the different tree parts by dividing the element concentration of the contaminated tree part by the element concentration of the corresponding non-contaminated tree part (Mingorance et al., 2007). We selected enrichment ratios >2 to identify elements enriched in the different tree parts (Mingorance et al., 2007). We set our enrichment ratio threshold at 2 because most elements had enrichment ratios <2 in leaf, branch, stem, and bark except for Cd and Pb, which had enrichment ratios >2 for every tree part.

3 Results

3.1 Fine Sediment and Metal Concentrations in Gravel Bar Sediment

Bar deposits at the contaminated site were finer-grained compared to the non-contaminated site. The median diameters of surface materials from pebble-counts were 11–16 mm for the contaminated bar and 16–32 mm for the upstream non-contaminated bar. The relative mass of fine sediment (%<2 mm) in subsurface deposits including the root zone averaged 40% for the contaminated site and 20% for the non-contaminated site. The average metal concentrations in subsurface samples at the contaminated site were 1,390 mg/kg Pb (42% Cv%) and 734 mg/kg Zn (34% Cv%). Metal concentrations in the fine sediment fraction of the non-contaminated bar were below detection limit for XRF analysis at about 30 mg/kg for Pb and 70 mg/kg for Zn.

3.2 Element Concentrations in Sycamores and Enrichment Ratios

Contaminated sycamore bark had higher Au, B, Ba, Cd, Co, Na, Ni, P, Pb, Tl, and Zn concentrations than non-contaminated bark (P<0.05, Table 1). Bark had enrichment ratios >2 for Cd, Co, Ni, Pb, Tl, and Zn (Fig. 2). Concentrations of Ba, Cd, Co, Fe, Er, Ho, Li, Na, Pb, Tl, U, Zn, and Zr were highest in contaminated bark. Contaminated leaves and bark had similar B concentrations, which were higher than stems and branches.

Contaminated leaves had higher Cd, Co, Pb, Tl, Zn, and Zr than non-contaminated leaves (P<0.05, Table 1). Leaves had enrichment ratios >2 for Cd, Co, Pb, and Tl (Fig. 2). Contaminated leaves had higher P concentrations than other contaminated tree parts and along with bark and branch had the highest Ni concentrations. Contaminated leaves also had the second highest Ba, Fe, Li, Tl, U, Zn, and Zr concentrations after bark.

Contaminated branches had higher Cd, Co, Er, Fe, Ho, Na, Ni, Pb, Tl, U, and Zn concentrations than non-contaminated branches (P<0.05, Table 2). Branches had enrichment ratios >2 for Cd, Na, Ni, Pb, Tl, and Zn (Fig. 2). Contaminated branches had the second highest concentrations after bark for Co and Na and the second highest B concentrations after bark and leaf.

Table 1 Mean element concentrations ± standard deviation for American sycamore bark and leaves from a non-contaminated (n=9) and contaminated (n=18) gravel bar. Degree of significance indicated by stars, *=P<0.05, **=P<0.01, ***=P<0.001 indicate significant differences between non-contaminated and contaminated bark or leaves (determined by Two-Way ANOVA or †Kruskal-Wallis test). Elements that differed between contaminated and non-contaminated for at least one tree part shown.

		Bark		Leaves	
Element	Units	Non-contaminated	Contaminated	Non-contaminated	Contaminated
Au†	µg/kg	1.5 ± 1	0.81 ± 1 *	0.89 ± 0.5	0.84 ± 0.4
B†	mg/kg	15 ± 2	17 ± 2 *	14 ± 5	18 ± 5.8
Ba†	mg/kg	58 ± 11	47 ± 7 *	27 ± 9	21 ± 5.3
Cd†	mg/kg	0.01 ± 0.01	1 ± 0.52 ***	0.007 ± 0.01	0.14 ± 0.06 ***
Co	mg/kg	0.19 ± 0.15	0.91 ± 0.58 ***	0.04 ± 0.02	0.08 ± 0.04 ***
Er†	µg/kg	19 ± 15	20 ± 12	0.89 ± 0.5	1.03 ± 0.5
Fe	mg/kg	141 ± 141	155 ± 95	47 ± 13	59 ± 22
Ho†	µg/kg	6.9 ± 5	7.8 ± 5	0.27 ± 0.1	0.31 ± 0.3
Li†	µg/kg	62 ± 63	68 ± 40	11 ± 6	12 ± 6
Na	mg/kg	33 ± 16	64 ± 25 ***	13 ± 8	14 ± 9
Ni	µg/kg	0.35 ± 0.17	1.1 ± 0.7 ***	0.61 ± 0.34	0.93 ± 0.5
P†	g/kg	0.41 ± 0.11	0.54 ± 0.11 *	1.6 ± 0.43	1.5 ± 0.41
Pb	mg/kg	0.62 ± 0.4	36 ± 27 ***	0.13 ± 0.05	1.7 ± 1.7 ***
Tl	µg/kg	5.3 ± 4	21 ± 11 ***	3.3 ± 3	11 ± 7 ***
U	µg/kg	15 ± 10	23 ± 15	3.4 ± 2	4.5 ± 3
Zn	mg/kg	7.7 ± 3	63 ± 39 ***	13 ± 3	24 ± 7 ***
Zr†	µg/kg	107 ± 102	113 ± 73	61 ± 23	21 ± 13 ***

Contaminated branches and leaves had similar Li, Tl, U, Zn, and Zr concentrations, which were higher than stems.

Contaminated stems had higher B, Ba, Cd, Co, Ni, Pb, Tl, U, and Zn concentrations than non-contaminated stems (P<0.05, Table 2). Stems had enrichment ratios >2 for Cd, Co, Pb, Tl, U, Zn, and Zr (Fig. 2). Contaminated stems had the lowest Ba, B, Fe, Ni, Li, P, Tl, U, Zn, and Zr concentrations. Contaminated stems, leaves, and branches had similar Cd, Er, Ho, and Pb concentrations, which were all lower than bark.

There were positive correlations between elements that were enriched in tree parts including Cd, Co, Pb, Tl, and Zn (Table 3). Co also had positive correlations with Er, Ho, Li, Na, and U (r>0.70). Zn had positive correlations with B, Fe, and Ni. There were also positive correlations between other elements that differed between the contaminated and non-contaminated sycamores such as the rare earth elements Er and Ho, which correlated with each other and had positive correlations with Ba, Co, Li, and U.

4 Discussion

This study showed contaminated sycamores accumulated higher metal concentrations than non-contaminated sycamores. Cd, Co, Pb, and Tl were higher in contaminated sycamores and had enrichment ratios >2 for all tree parts. Similarly, Mingorance et al. (2007) reported enrichment ratios >2 for Cu and Pb in leaves and bark of *Nerium oleander* L. and for Cu in *Pinus pinea* L. from their most polluted sites. Contaminated sycamores in the current study were from a gravel bar downstream of mine tailings, and sediments of that gravel bar had elevated Pb and Zn concentrations, which might explain the higher metal concentrations in these trees. Concentrations of Pb and Zn in bar deposits of the current study closely followed the results of previous studies (Gale et al., 2002, 2004; Pavlowsky et al., 2017; Schmitt & Finger, 1982; Smith & Schumacher, 1993). The probable effect concentration (PEC) is 128 mg/kg for Pb and 459 mg/kg for Zn (MacDonald et al., 2000), which was 11 times lower for Pb and 1.6 times lower for Zn than the contaminated sediments of the current study. Average Pb probable effects quotient (PEQ) values were high (range of 10–12), and Zn PEQ values were marginal (<2) for the contaminated gravel bar. Metal concentrations in fine sediment of the non-contaminated gravel bar were below the detection limit and thus below the PEC. PEQs for Pb indicated toxic effects for sediment-dwelling organisms on the contaminated gravel bar.

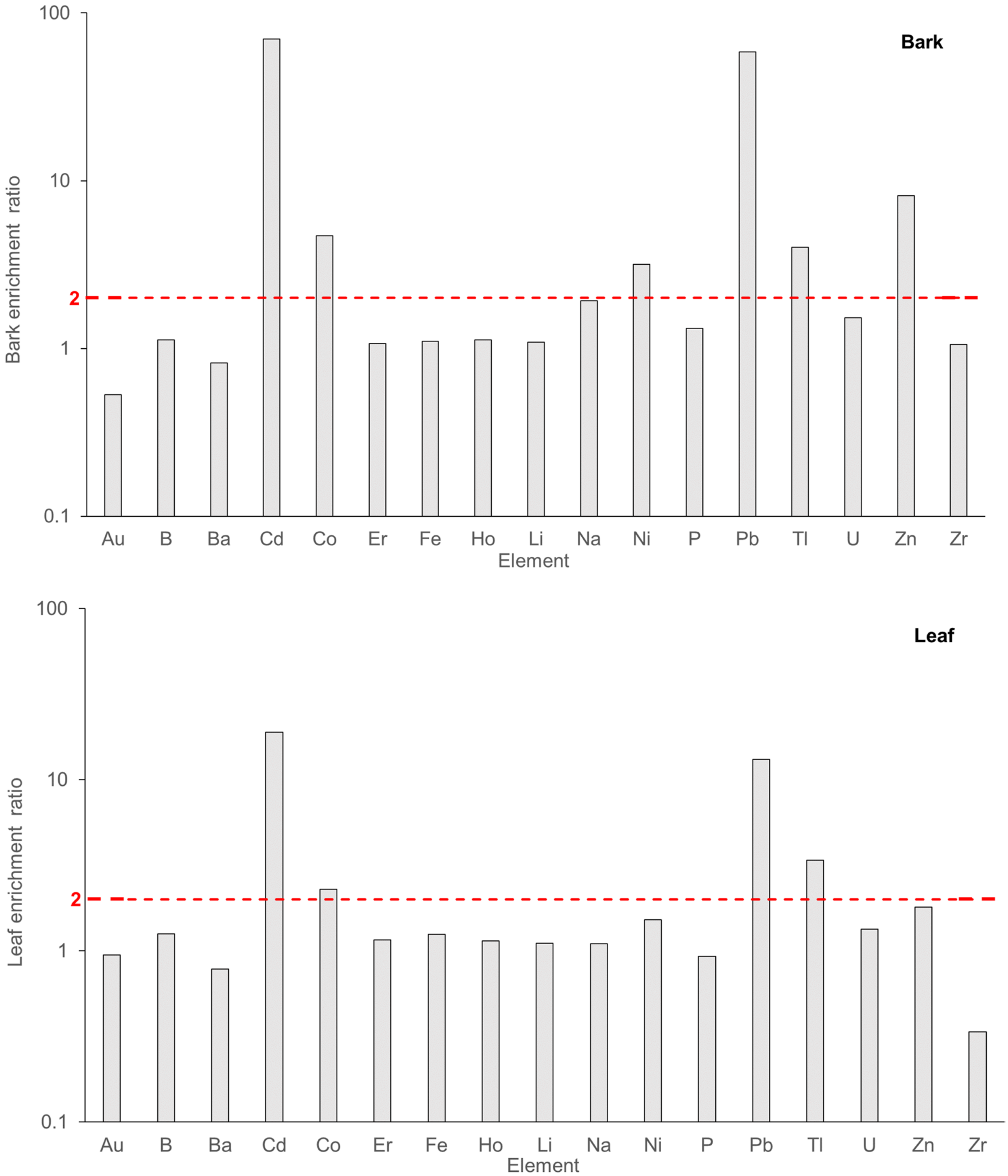

Fig. 2 Mean enrichment ratios of bark, leaf, branch, and stem for elements that differed between contaminated and non-contaminated American sycamore trees (*Platanus occidentalis*) (dashed horizontal line indicates enrichment ratio threshold = 2)

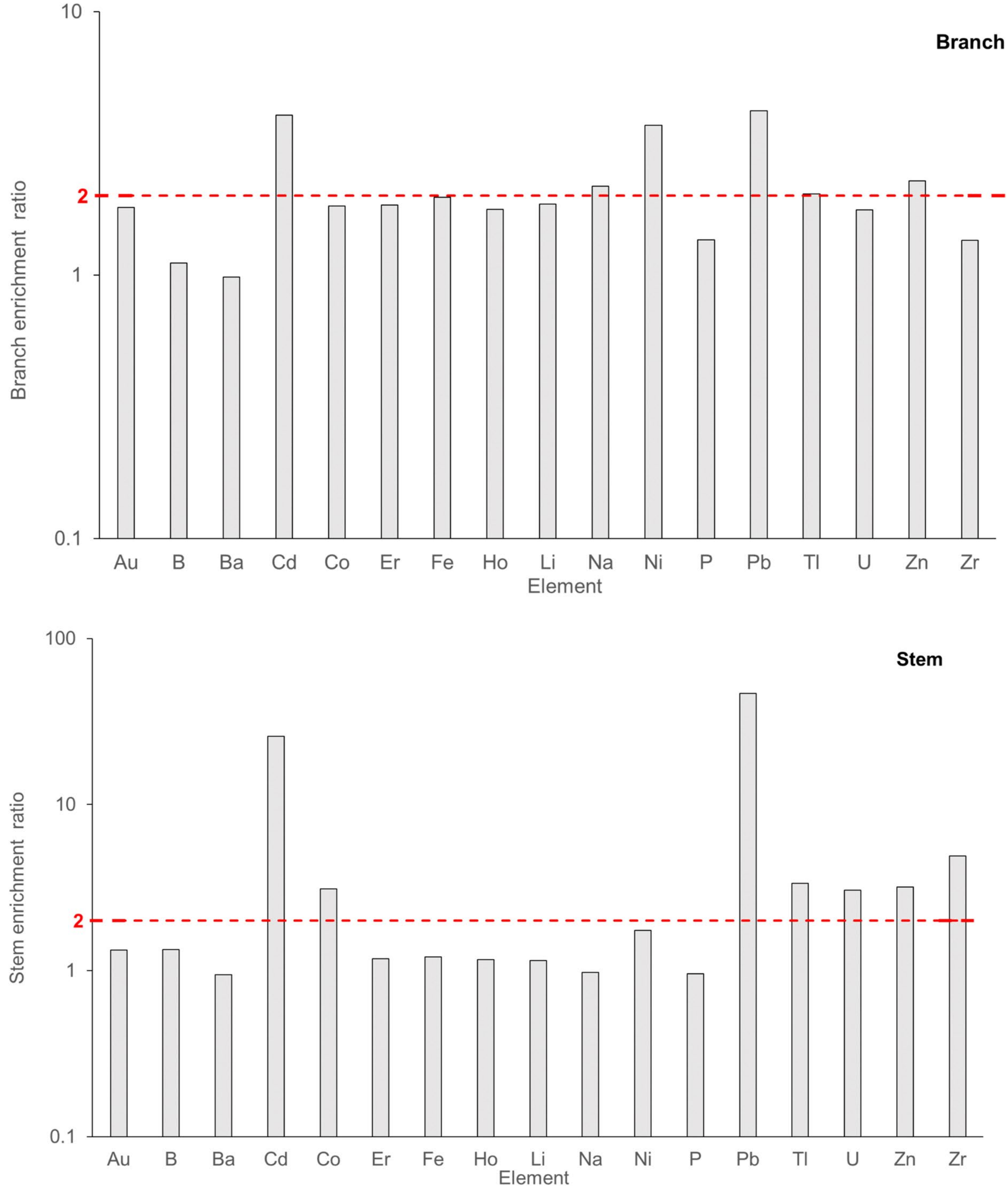

Fig. 2 (continued)

Table 2 Mean element concentrations ± standard deviation for American sycamore branches and stems from a non-contaminated (n=9) and contaminated (n=18) gravel bar. Degree of significance indicated by stars, *=P<0.05, **=P<0.01, ***=P<0.001 indicate significant differences between non-contaminated and contaminated branches or stems (determined by Two-Way ANOVA or †Kruskal-Wallis test). Elements that differed between contaminated and non-contaminated for at least one tree part shown.

		Branches		Stems	
Element	Units	Non-contaminated	Contaminated	Non-contaminated	Contaminated
Au†	µg/kg	0.4 ± 0.3	0.66 ± 0.6	0.42 ± 0.4	0.56 ± 0.6
B†	mg/kg	7.4 ± 3	7.3 ± 1	2.4 ± 0.5	3.3 ± 0.8 **
Ba†	mg/kg	17.4 ± 5	15 ± 2	6.7 ± 1	6.4 ± 3 *
Cd†	mg/kg	0.08 ± 0.13	0.29 ± 0.13 **	0.006 ± 0.002	0.14 ± 0.08 ***
Co	mg/kg	0.10 ± 0.09	0.16 ± 0.07 **	0.02 ± 0.01	0.08 ± 0.03 ***
Er†	µg/kg	2.1 ± 0.8	3.6 ± 2 *	0.61 ± 0.2	0.72 ± 0.5
Fe	mg/kg	17 ± 8	30 ± 15 **	8.9 ± 5	11 ± 8
Ho†	µg/kg	0.75 ± 0.4	1.2 ± 0.5 *	0.2 ± 0	0.23 ± 0.1
Li†	µg/kg	8.1 ± 5	14 ± 9 *	5.6 ± 2	6.4 ± 4
Na	mg/kg	15 ± 8	28 ± 12 **	18 ± 28	17 ± 7
Ni	µg/kg	0.32 ± 0.3	1.1 ± 1.86 **	0.12 ± 0.07	0.2 ± 0.11 **
P†	g/kg	0.43 ± 0.1	0.52 ± 0.26	0.32 ± 0.17	0.3 ± 0.13
Pb	mg/kg	1.4 ± 2.3	5.1 ± 3 **	0.06 ± 0.4	3 ± 2 **
Tl	µg/kg	5.7 ± 5	10 ± 5 **	1.2 ± 1	4 ± 4 **
U	µg/kg	2.7 ± 1	4.3 ± 2 *	0.58 ± 0.3	1.8 ± 2 **
Zn	mg/kg	7.9 ± 8	16 ± 7 **	2.4 ± 1	7.7 ± 4 ***
Zr†	µg/kg	20 ± 12	26 ± 12	11 ± 3	54 ± 104

Table 3 Spearman Rank correlation coefficients (r) for select elements that showed significant differences between contaminated and non-contaminated sycamores. Only significant correlations shown (P<0.05). Correlations where r≥0.70 (P<0.001) are in bold.

	Au	B	Ba	Cd	Co	Er	Fe	Ho	Li	Na	Ni	P	Pb	Tl	U	Zn
B	0.41															
Ba	0.39	**0.83**														
Cd		0.29														
Co		0.47	0.55	**0.77**												
Er	0.27	0.54	**0.77**	0.51	**0.78**											
Fe	0.43	**0.84**	**0.86**	0.43	0.65	**0.72**										
Ho		0.47	**0.72**	0.53	**0.79**	**0.94**	0.66									
Li		0.64	**0.73**	0.53	**0.77**	**0.79**	**0.8**	**0.80**								
Na		0.35	0.47	0.64	**0.73**	0.65	0.54	**0.70**	**0.71**							
Ni		**0.72**	0.56	0.57	0.61	0.48	**0.74**	0.42	0.64	0.42						
P	0.35	0.67	0.44				0.55				0.59					
Pb		0.28	0.28	**0.94**	**0.80**	0.58	0.46	0.60	0.54	0.69	0.51					
Tl		0.53	0.52	**0.73**	**0.78**	0.57	0.63	0.55	0.6	0.57	0.66	0.31	0.69			
U	0.32	**0.70**	**0.82**	0.57	**0.74**	**0.84**	**0.86**	**0.80**	**0.78**	0.62	0.61	0.29	0.6	0.63		
Zn	0.28	**0.72**	0.56	**0.76**	0.69	0.52	**0.75**	0.47	0.62	0.52	**0.82**	0.56	**0.72**	**0.78**	0.69	
Zr	0.31	0.49	0.61	0.33	0.49	0.59	0.66	0.63	0.65	0.50	0.43		0.41	0.33	0.62	0.44

Consistent with other studies, trees exposed to mining pollution were enriched with metals relative to trees from non-polluted areas. Domínguez et al. (2008) reported enrichment of As, Bi, Cu, and Zn in *Quercus ilex* and Cd and Zn in *Populus alba* from a mining-contaminated site. Hasnaoui et al. (2020) reported that plants from a Pb-Zn mining area accumulated As, Cd, Cu, Ni, Pb, and Zn. Elevated Fe, Mg, Mn, and Sb concentrations tend to be associated with mine wastes, in particular from Zn-Pb mines (Kucha et al., 1996), which might explain why some element concentrations were higher in the contaminated sycamores. Trees in mining areas accumulate metals, can be a secondary source of metal pollution, and create pathways for metals from contaminated environments to producers and consumers (Peralta-Videa et al., 2009; Torres & Johnson, 2001).

Other studies also reported higher metal concentrations in contaminated compared to non-contaminated sycamores. Hashemi et al. (2015) reported higher Pb concentrations in sycamore leaves where concentrations were highest in the air. Mean leaf Pb concentrations (29 mg/kg) from their most contaminated site were about 17 times higher than our contaminated sycamore leaves. Carlson and Bazzaz (1977) reported that Pb concentrations increased in sycamore leaves and stems combined (from 5 to 30 mg/kg) when exposed to treated soil with increasing concentrations of Pb (0–1000 mg/kg). Similarly, Cd concentrations in sycamore stems increased (from 1 to 10 mg/kg) with increasing Cd (0–100 mg/kg) in treated soils (Carlson & Bazzaz, 1977). These studies indicated sycamores from contaminated environments accumulated Cd and Pb. Several studies also reported metal accumulation in other plant species that reflected metal concentration patterns of their contaminated environments (Delapierre et al., 2021; Günthardt-Goerg et al., 2019; Meers et al., 2007).

4.1 Metal Accumulation in Bark

Several metals were higher in contaminated bark than leaves, stems, and branches, which indicated immobilization of these metals in this metabolically inactive tissue. Some of these metals are essential to plants (e.g., Co and Fe), but some are toxic at low concentrations and/or are not essential (e.g., Ba, Cd, Li, Pb, Tl, and U) (Kabata-Pendias, 2011; Pais & Jones, 1997). These findings are consistent with other studies that reported higher metal concentrations in bark than other tree parts. For example, studies reported higher Cd, Cu, and Zn in willow bark than wood (Mertens et al., 2006), higher Cd and Zn in *Picea abies* bark than other tree parts (Rothpfeffer & Karltun, 2007), and higher Fe, Ni, and Zn in bay tree bark than other tree parts (Yaşar et al., 2012). In contrast to our findings, Yaşar et al. (2012) found lower Cd and Pb concentrations in bay tree bark than other tree parts. In the current and previous studies, bark accumulated essential and nonessential metals and might serve as a sink for these metals (Pulford & Watson, 2003).

In the current study, contaminated sycamore bark had Ba, Cd, and U concentrations that were higher than normal and Pb, Tl, and Zr that occurred at toxic concentrations generalized for leaves of plants (Kabata-Pendias, 2011). Toxic effects were not apparent in the sycamores in the current study or in other tree species that were reported to have toxic concentrations in the bark (Mertens et al., 2006). When compared to bark concentrations of a similar species, *Platanus acerifolia*, the contaminated sycamore bark in the current study accumulated higher Fe (2–13 times higher) and Zn (3–29 times higher) concentrations (Rykowska & Wasiak, 2011). Contaminated bark in our study also had higher Cd (about 1.5–3 times higher), Pb (about 9–12 times higher), and Zn (about 3–12 times higher) compared to bark from *L. nobilis* in rural and urban areas (Yaşar et al., 2012). It is not surprising that the *L. nobilis* bark had lower metal concentrations than the contaminated sycamore bark since their associated soils had 140–230 times lower Pb and 22–29 times lower Zn than the contaminated sediments in the current study. The bark of other tree species from contaminated areas had higher concentrations than the sycamore bark in the current study. *Salix* spp. bark Cd concentrations (20–65 mg/kg) were about 19–23 times higher and Zn concentrations (700–900 mg/kg) were about 9 times higher than the contaminated sycamore bark in the present study (Mertens et al., 2006). Even though the *Salix* spp. bark had higher Zn concentrations than the contaminated sycamores, the associated sediments had 1.5–2 times lower Zn (361–475 mg/kg) than the contaminated gravel bar in the current study. Differences in metal accumulation in bark could be attributed to differences in metal availability, the extent of contamination, sediment physicochemical characteristics, and tree accumulation ability (Pulford & Watson 2003). In some tree species, bark accumulated metals for many years and thus could provide insights into the extent and source of historical pollution (Conkova & Kubiznakova, 2008; Satake et al., 1996).

The selectivity of plants for metals and the partitioning of metals in specific plant tissues tell us about the potential for those metals to reenter the surrounding environment from seasonal litter accumulations and decomposition. Metal tolerant plants immobilize metals by restricting translocation and accumulating metals in the roots (Deng et al., 2004). Trees can also immobilize metals by accumulation in metabolically inactive tissues, such as outer bark (Pulford & Watson, 2003). Frequent shedding or peeling of mature bark is a characteristic of species in the *Platanus* genera (International Dendrology Society, 2021). Shedding varies from year to year and might vary with environmental conditions, such as the amount of precipitation and winter temperatures (Jauron, 1996). Contaminated bark in this study had higher enrichment ratios for Cd and Pb (enrichment ratios >50) than other tree parts, indicating that bark was highly enriched with Cd and Pb and might be a sink for these metals. Bark metal accumulation and subsequent shedding by sycamores in this study might be a strategy to exclude toxic or excess metals from metabolic processes. Sycamore bark can enter the decomposition cycle sooner than other tree bark since it sheds frequently. Thus, sycamore bark can accelerate the return of these metals to the environment. Metal contamination and the metal content of shed bark can also inhibit decomposition. The results of a meta-analysis showed that chronic metal contamination from mining decreased litter decomposition rates in field and lab studies regardless of the litter type (Ferreira et al., 2016).

4.2 Metal Accumulation in Leaves

Contaminated leaves had the highest P concentrations and the second highest concentrations after bark of both essential (Fe and Zn) and nonessential metals (Ba, Li, Tl, U, and Zr) (Kabata-Pendias, 2011). Leaf metal concentrations were lower than bark and higher than stem for several metals (Ba, Fe, Li, Tl, U, Zn, and Zr) in contaminated sycamores in this study. In other studies, leaves often accumulated higher element concentrations than all other tree parts. Nikolova (2015) reported *Morus alba* leaves had higher Cd, Pb, and Zn concentrations than other tree parts. Meers et al. (2007) also reported higher Cd, Cr, Cu, Ni, Pb, and Zn concentrations in *Salix* spp. leaves than stems. Higher Zn was reported in leaves than stems of *Betula pendula*, *Populus* spp., and *Salix* spp. (Migeon et al., 2009; Günthardt-Goerg et al., 2019). Mertens et al. (2006) reported that leaves typically had higher Cd, Cu, and Zn concentrations than bark and stem. Evangelou et al. (2013) reported higher Cd and Zn but lower Pb in leaves than stem for multiple tree species. Safari et al. (2018) reported higher Pb concentrations in leaves than bark for tree species contaminated by industrial, urban, or rural contaminants. In contrast to these studies, leaf Cd and Pb concentrations were similar to concentrations measured in stem and branch but lower than bark of contaminated sycamores in the current study. The lower metal concentrations that we observed in leaves compared to other tree parts of contaminated sycamores could be due to restricted transport and compartmentalization to prevent metal accumulation in these metabolically active tissues, where high concentrations could cause significant harm to the trees (Baker & Walker, 1990).

Contaminated leaves in our study had above normal concentrations of Ba and Tl and excessive or toxic concentrations of Li and Zr generalized for leaves of various plants (Kabata-Pendias, 2011). Concentrations of B, Cd, Co, Fe, Ni, Pb, U, and Zn of contaminated leaves were within normal ranges generalized for plants (Kabata-Pendias, 2011; Pais & Jones, 1997). This contrasts with other studies that reported elevated metal concentrations in leaves of trees from contaminated areas. Palmer and Kucera (1980) reported 2.8–359 times higher Pb concentrations (4.7–611 mg/kg) in sycamore leaves from the Southeast Missouri Lead District than sycamore leaves in the current study. Their study area included sites near the Desloge mine, which is in the same county as our study sites. They reported sediment Pb concentrations (426–1817 mg/kg) near the Desloge mine that were similar to our contaminated sediments and Pb concentrations (6.5–40 mg/kg) in sycamore leaves that were 3.8–24 times higher than our contaminated sycamore leaves. These sites did not include gravel bars in the Big River, and some were within 1 km of mines, which might explain the differences in metal concentrations with the current study. In addition, Palmer and Kucera (1980) sampled sycamore leaves only about 10 years after mining operations in the Old Lead Belt ended (Schmitt et al., 2007). Metal accumulation in leaves was reported for other *Platanus* species in high-traffic, industrial areas. *P. acerifolia* leaves had 1.6 times higher Pb (2.65 mg/kg) and 3 times lower Cd (0.045 mg/kg) than contaminated sycamores in the current study (Liu et al., 2007). Even though the *P. acerifolia* leaves had higher Pb concentrations than our contaminated sycamore leaves, the associated soils had 29 times lower Pb (47 mg/kg) than our contaminated gravel bar sediments. These soils occurred along heavy traffic areas of Beijing, China (Liu et al., 2007), so the extent of contamination was lower than the mining contaminated sediments in the current study. Washed leaves of *Platanus orientalis* that experienced air and dust pollution accumulated 3–6 times higher Fe (191–380 mg/kg), 6 times higher Ni (5.7–6 mg/kg), 57–203 times higher Pb (97–345 mg/kg), and 1.2–1.4 times higher Zn (28–33 mg/kg) (Norouzi et al., 2015) compared to the contaminated sycamore leaves. In contrast, leaves of *P. orientalis* from high traffic areas in Nanjing, China, accumulated similar concentrations of Zn (20 mg/kg) and Pb (2 mg/kg) compared to the contaminated sycamores in the current study (Jia et al., 2021). In most cases, other sycamore or plane tree species accumulated higher metal concentrations than our contaminated sycamores. These differences could be attributed to differences in the contamination sources, extent of contamination, and the soil chemistry affecting metal mobility (Alloway, 1995; Pulford & Watson, 2003).

Leaves of other tree species also accumulated higher metal concentrations than the sycamore leaves in the present study. Guha and Mitchell (1966) reported 2–3 times higher B, Ba, Co, Fe, and Zn and similar Ni (0.78 mg/kg) and Pb (1.8 mg/kg) in *A. pseudoplatanus* leaves in late July compared to the contaminated sycamore leaves. Lepp and Eardley (1978) reported 5–35 times higher Cd (0.7–5 mg/kg), 2–5 times higher Pb (3.5–8.3 mg/kg), and 6-8 times lower Zn (145-185 mg/kg) in *A. pseudoplatanus* leaves than the contaminated sycamore leaves. Leaves of *Salix* spp. accumulated higher metal concentrations than other tree species (Evangelou et al., 2013; Kacálková et al., 2014; Migeon et al., 2009), as well as the contaminated sycamore leaves. Mertens et al. (2006) reported that leaves of different *Salix* spp. in August accumulated 143–464 times higher Cd (20–65 mg/kg), 3–7.5 times higher Ni (3–7 mg/kg), 2.4–7 times higher Pb (4–12 mg/kg), and 50–104 times higher Zn (1200–2500 mg/kg) compared to the contaminated sycamore leaves. Meers et al. (2007) reported that *Salix* spp. leaves accumulated 7–103 mg/kg Cd and 250–2882 mg/kg Zn, which were 50–728 times and 10–120 times higher than the Cd and Zn concentrations of the contaminated sycamore leaves in the current study. Even though the leaves of the different *Salix* spp. in these previous studies had higher concentrations of Pb than our contaminated sycamore leaves, the sediments had 7–19 times lower Pb (74–206 mg/kg) compared to our contaminated sediments (Meers et al., 2007; Mertens et al., 2006). Concentrations of Zn in the *Salix* spp. leaves in these studies were also higher than the contaminated sycamore leaves, but Mertens et al. (2006) reported 1.5–2 times lower sediment Zn (385–475 mg/kg) and Meers et al. (2007) reported 2.6 times lower to 1.6 times higher Zn (275–1160 mg/kg) compared to the contaminated sediments in the current study. Differences in the sediment metal concentrations might be due to extraction procedures and degree of contamination. Metal concentrations of contaminated sycamore leaves in the current study were typically lower than metal concentrations reported by other studies for leaves of other sycamores and other tree species. Differences in metal accumulation in the leaves could be due to a combination of factors such as differences in tree species, degree of contamination, type of contamination, site conditions, and substrate physicochemical characteristics (Pulford & Watson, 2003).

Metal accumulation in leaves is common and accumulation varies by tree species and metal (Evangelou et al., 2013; Kacálková et al., 2014; Mertens et al., 2004). Contaminated sycamore leaves in the current study had the second highest concentrations of several metals and were enriched with Cd, Co, Pb, and Tl. Metal accumulation in older leaves or leaves just prior to shedding could be a strategy to remove toxic and excess metals (Mertens et al., 2006). Higher metal concentrations in leaves could increase the chances of dispersal of bioavailable metals in the environment after leaves shed and decompose (Meers et al., 2007; Migeon et al., 2009). Shed leaves can release or accumulate metals. Van Nevel et al. (2014) reported that freshly fallen contaminated leaves from *B. pendula* and *Populus tremula* released metals to the surrounding soil. In contrast, Yue et al. (2019) reported that freshly fallen leaves from *Salix paraplesia*, *Rhododendron lapponicum*, *Sabina saltuaria*, and *Larix mastersiana* had lower metal concentrations than detritus and that detritus accumulated metals over time.

Detritus from mining sites in the Black River and Big River in southeast Missouri (Allert et al., 2009, 2013) had higher mean Pb (453 mg/kg; 2318 mg/kg), Zn (1170 mg/kg; 3084 mg/kg), and Cd (1.9 mg/

kg; 44.2 mg/kg) than the contaminated sycamore tree parts in the current study. Metal concentrations of detritus from sites downstream of mining in the Viburnum Trend of southeast Missouri also had higher concentrations of Pb (66–168 mg/kg) and Zn (65–989 mg/kg) and similar concentrations of Cd (0.7–1.1 mg/kg) compared to contaminated sycamore tree parts in the current study (Besser et al., 2007). Detritus from these mining-contaminated rivers in southeast Missouri (Allert et al., 2009, 2013; Besser et al., 2007) also had higher Pb concentrations than leaves sampled from several sites in the Southeast Missouri Lead District (Palmer & Kucera, 1980). The differences in concentrations between the detritus and tree parts in the current study could be due to detritus accumulating metals during the decomposition process. Detritus in these studies could consist of multiple plant species, different plant parts, and mostly autumnal shed leaves, which tend to have higher metal concentrations than leaves from earlier in the season (Guha & Mitchell, 1966; Mertens et al., 2006).

4.3 Metal Accumulation in Branches

Contaminated branches did not have the highest concentration of any element, but they had the second highest concentrations after bark of Co and Na and had similar concentrations as leaves of Li, Ni, U, Tl, Zn, and Zr. Few studies reported element concentrations in branches. Rykowska and Wasiak (2007) reported 3.5 times higher Fe and 1.6 times lower Zn (mg/kg) concentrations in *P. acerifolia* branches compared to the contaminated sycamore branches in the current study. Rothpfeffer and Karltun (2007) reported that branches had the second highest Cd and Zn concentrations after bark in *P. abies* from different locations in Sweden. Yaşar et al. (2012) reported lower Fe, Pb, and Zn concentrations in *L. nobilis* branches than leaves and bark. These *L. nobilis* branches had Cd and Cu concentrations that were lower than leaves but higher than bark. Compared to contaminated sycamore branches in the current study, *P. abies* branches had similar concentrations of Cd (0.39 mg/kg) and 8 times higher Zn (130 mg/kg) (Rothpfeffer & Karltun, 2007). Urban *L. nobilis* branches accumulated about 2 times higher Cd (0.5–0.7 mg/kg), 2–4 times lower Ni (0.25–0.5 mg/kg), 2 times lower Pb (3 mg/kg), 3 times lower Zn (5 mg/kg), and similar Fe (20–30 mg/kg) concentrations compared to our contaminated sycamore branches (Yaşar et al., 2012). Although contaminated branches did not have the highest metal concentrations than other tree parts, these could still be a source of bioavailable metals after falling on the gravel bar or into the river since it was enriched with metals including Cd, Pb, and Zn.

4.4 Metal Accumulation in Stems

When comparing our findings with other studies, we considered wood to be similar to what we referred to as stems. Contaminated sycamore stems had the lowest B, Ba, Fe, Ni, P, Tl, U, Zn, and Zr concentrations and similar concentrations as leaves of Co, Cd, Er, Ho, Na, and Pb and as branches of Cd, Er, Ho, and Pb. In contrast to the current study, concentrations of Cu, Fe, Mn, and Zn were higher in stems than branches of *P. acerifolia* (Rykowska & Wasiak, 2011), and Pb was higher in stems than leaves of *Populus* spp., *Salix* spp., and *B. pendula* (Evangelou et al., 2013; Migeon et al., 2009). Tree stems can be important sinks for metals since these grow much slower than other tree parts (Pulford & Watson, 2003). However, stems contain metabolically active tissues (Raven et al., 1992), which might explain why concentrations of most metals such as Tl, U, and Zn in our contaminated sycamore stems were lower than other tree parts.

Contaminated sycamore stems often had lower metal concentrations than other tree parts in the present study, and metal concentrations were sometimes higher than stems of different species in other studies. Kim et al. (2020) reported 3–70 times lower Cd (0.002–0.049 mg/kg) in tree rings of sycamores from industrial areas than stems of contaminated sycamores in the present study. *A. pseudoplatanus* stems accumulated 4 times lower Pb (0.8 mg/kg) concentrations than the contaminated sycamore stems in the current study (Superville et al., 2017). Soils of the *A. pseudoplatanus* contained 995–1000 mg/kg Pb, which was 1.4 times lower than the Pb concentrations of the contaminated gravel bar sediments of the present study. *P. abies* wood had 1.5 times lower Cd (0.096 mg/kg) and 1.7 times lower Zn (15 mg/kg) than the contaminated sycamore stems (Rothpfeffer & Karltun, 2007). In contrast, metal concentrations in stems of other tree species from contaminated areas were sometimes higher than contaminated sycamore stems in the current study. *P. acerifolia* stems had 5 times higher Cu (10 mg/kg), 20 times higher Fe (223 mg/kg), 4 times higher Mn (19 mg/kg), and 3 times higher Zn (24 mg/kg) than the contaminated sycamore branches (Rykowska & Wasiak, 2007). *A. pseudoplatanus* stems had 2–38 times higher Cd (0.3–5.4 mg/kg), 1.2–2.8 times higher Pb (3.7–8.5 mg/kg), and 20–25 times higher Zn (159–193 mg/kg) than the contaminated sycamores (Lepp & Eardley, 1978). Despite having higher Pb and Zn in the *A. pseudoplatanus* stems, the associated sediments had 254–348 times lower Pb (5.5–7.5 mg/kg) and 1.5–3 times lower Zn (226–501 mg/kg) than the contaminated sediments in this study. Nikolova (2015) reported 2 times higher Cu (3.62 mg/kg), 8.6 times higher Cd (1.21 mg/kg), 7.6 times higher Pb (22.9 mg/kg), and 12 times higher Zn (95 mg/kg) in *M. alba* stems compared to the contaminated sycamore stems. In some cases, the metal concentrations in the contaminated sycamore stems were similar or within the range of concentrations reported for other species. Sheppard and Funk (1975) reported 19 times lower to 14 times higher Zn (0.4–109 mg/kg) concentrations in tree rings of *Pinus ponderosa* from mining sites in Idaho than the contaminated sycamore stems. Meers et al. (2007) reported similar Ni (0.32–1.9 mg/kg) and 6.5 times lower to 1.3 times higher Pb in *Salix* spp. stems compared to the contaminated sycamore stems in the current study. Metal concentrations were quite variable in tree stems, which could be due to differences in tree species, element translocation, and tissues sampled (wood, tree rings or stem) (Kabata-Pendias, 2011; Pulford & Watson, 2003).

4.5 Implications of Metal Accumulation in Trees

Environmental factors, physiological processes, and element interactions could explain metal accumulation in the sycamores and patterns of element distribution in the different sycamore tree parts (Baker, 1987; Mingorance et al., 2007; Turner, 1994). Some metals accumulated in the sycamores probably because of their association with mining contamination and correlated with each other in the trees, possibly due to synergistic interactions resulting from the stress of the high metal concentrations in the trees (Kabata-Pendias, 2011). Cd, Pb, and Zn were positively correlated (r>0.75) and had the highest enrichment ratios for most tree parts. Cd, Pb, and Zn contamination is typically associated with Pb-Zn mining (Kucha et al., 1996), and Cd contamination is usually associated with Zn contamination (Migeon et al., 2009). Plant uptake of Cd mimics that of Zn and typically increases when Zn concentrations in soils are low (Kirkham, 2006). However, contaminated sycamore bark and leaves had Zn concentrations within normal ranges while Cd concentrations were normal or slightly above normal in the current study. Contaminated sycamores were also enriched with other metals associated with mining including Co and Tl. High Cd and Tl concentrations tend to occur near Pb and Zn mines, and these metals are readily taken up by plants from contaminated soils (Kabata-Pendias, 2011). Co is also enriched in soils near mining activities, but soil factors control plant uptake of this metal, which behaves similarly to Fe and Mn and has synergistic interactions with Zn (Kabata-Pendias, 2011).

Previous studies reported that metal uptake by plants increases under acidic and anoxic conditions (Evangelou et al., 2013; Guyette et al., 1991; Kissoon et al., 2010, 2011). However, Big River water was slightly alkaline near the contaminated bar site with an average pH of 7.9 and average dissolved oxygen concentration of 10.9 mg/L (Besser et al., 2009). Similarly, the pH of the water at the non-contaminated site averaged 7.5 (Meneau, 1997; Smith & Schumacher, 1993). The carbonate-buffered and balanced pH conditions in Big River were reflected in the moderate concentrations of dissolved metals observed at our contaminated study site in pore water (Pb 1.9 µg/L; Zn 3.8 µg/L) despite high metal concentrations in sediments (Pb 850 mg/kg; Zn 470 mg/kg) (Besser et al., 2009). Therefore, the results of this study show that uptake rates of metals by tree roots can be significant even while growing in well-buffered, slightly alkaline, and oxic substrates.

Metal accumulation in sycamores growing on gravel bars has important implications for decomposition processes in Big River. After tree parts (e.g., leaves and bark) enter the river, they undergo a series of changes as they are colonized and conditioned by microbes and invertebrates (Allan et al., 2020). Metal leaching to surroundings and uptake by organisms can occur during the decomposition process (Weis & Weis, 2004). Plants provide a pathway for metals to enter stream food webs and thus are the link between the abiotic and biotic environment. Liu et al. (2021) reported increased metal concentrations in detritivores that fed on metal-enriched litter and increased metal concentrations in the water following the consumption of this litter, indicating metal leaching. Van Nevel et al. (2014) also reported release of Cd and Zn from *B. pendula* and *P. tremula* leaf litter on a contaminated forest floor. Studies have shown that conditioned detritus in different ecosystems can also accumulate metals over time depending on the plant species and initial metal content (Van Nevel et al., 2014; Weis & Weis, 2004; Yue et al., 2019). These accumulated metals can then enter river food webs as crayfish break down detritus and the resulting particulates are consumed by other invertebrates. In situ exposure experiments showed that macroinvertebrates and crayfish near mining sites accumulated higher Cd, Zn, and Pb compared to reference sites (Allert et al., 2009, 2013). Detritus and minced fish provided as crayfish food also had higher metal concentrations downstream from mining than reference sites (Allert et al., 2009, 2013). Crayfish can also transfer accumulated metals to higher trophic levels, as they are an important food source for fish (Whitlege & Rabeni, 1997). Allert et al. (2009) reported that metal concentrations (Pb, Zn, Ni) of detritus were positively correlated with metal concentrations in crayfish and negatively correlated with crayfish survival. In the Missouri lead mining districts, elevated metal concentrations have been reported in organisms at higher trophic levels such as fish (Gale et al., 2004) and birds (Beyer et al., 2004, 2013), which suggests the transfer of metals through food webs in these contaminated areas.

Litter metal content could alter the structure of microbial and detritivore communities and thus inhibit and slow down decomposition in river ecosystems (Ferreira et al., 2016). Future studies are needed to assess the influence of contaminated tree litter on microbial and detritivore abundance and subsequent effects on decomposition in mining-contaminated areas of heterogeneous habitats. These studies should use freshly fallen leaves in leaf pack experiments to measure changes in leaf mass, metal content, and macroinvertebrate abundance and diversity over time. Future studies should also include comparisons of the metal content of freshly fallen leaves with detritus from multiple tree species and sites along a contamination gradient to better understand the contributions from different contaminated sites and trees.

5 Conclusions

Contaminated sycamores tree parts had higher (2–70 times) metal concentrations (e.g., Ba, Cd, Co, Fe, Ni, Pb, Tl, and Zn) than non-contaminated tree parts. Accumulation occurred in the order bark>leaves>branch>stem for most metals. Cd, Co, Pb, Tl, and Zn were enriched in most contaminated sycamore tree parts. The contaminated gravel bar sediments averaged 40 times higher Pb and 10 times higher Zn than the non-contaminated gravel bar. Similarly, the contaminated sycamores were more enriched with Pb than Zn. Contaminated sycamores had 4–58 times higher Pb and 2–8 times higher Zn than non-contaminated tree parts. Contaminated gravel bar sediments had 10–12 higher Pb concentrations than probable effect concentrations for sediment dwelling organisms and bark Pb concentrations were about 100 times higher than normal ranges generalized for plants. Contaminated bark and leaves can release bioavailable metals during decomposition since sycamores frequently shed these tree parts. Contaminated tree parts that become tree litter can accumulate metals as they become conditioned detritus. After contaminated tree parts shed and become detritus, they can transfer accumulated metals from the sediment to food webs. Metal-contaminated tree litter can also inhibit decomposition and alter the structure of microbial and detritivore communities. This can have far-reaching effects throughout food webs in metal-contaminated ecosystems.

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Data Availability The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Competing Interests The authors declare no competing interests.

References

Allan, J. D., Castillo, M. M., & Capps, K. A. (2020). *Stream ecology: structure and function of running waters*. Springer Nature.

Allert, A. L., Fairchild, J. F., Schmitt, C. J., & Brumbaugh, W. G. (2009). Effects of mining-derived metals on riffle-dwelling benthic fishes in Southeast Missouri, USA. *Ecotoxicology and Environmental Safety, 72*, 1642–1651.

Allert, A. L., DiStefano, R. J., Fairchild, J. F., Schmitt, C. J., McKee, M. J., Girondo, J. A., Brumbaugh, W., & G., & May T., W. (2013). Effects of historical lead–zinc mining on riffle-dwelling benthic fish and crayfish in the Big River of southeastern Missouri, USA. *Ecotoxicology, 22*(3), 506–521.

Alloway, B.J. (1995). Soil processes and the behavior of metals. In: B.J. Alloway (Ed.), *Heavy Metals in Soils* (2nd ed., pp. 11-37). Blackie Academic and Professional.

Baker, A. J. (1987). Metal tolerance. *New Phytologist, 106*, 93–111.

Baker, A. J. M., & Walker, P. L. (1990). Ecophysiology of metal uptake by tolerant plants. In A. J. Shaw (Ed.), *Heavy Metal Tolerance in Plants: Evolutionary Aspects* (pp. 155–177). CRC Press.

Besser, J. M., Brumbaugh, W. G., May, T. W., & Schmitt, C. J. (2007). Biomonitoring of lead, zinc, and cadmium in streams draining lead-mining and non-mining areas, Southeast Missouri, USA. *Environmental Monitoring and Assessment, 129*(1), 227–241.

Besser, J.M., Brumbaugh, W.G., Hardesty, D.K., Hughes, J.P., & Ingersoll, C.G. (2009). Assessment of metal-contaminated sediments from the Southeast Missouri (SEMO) mining district using sediment toxicity tests with amphipods and freshwater mussels. Administrative Report 09-NRDAR-02, Natural Resource Damage Assessment and Restoration Program, Columbia Environmental Research Center, U.S. Geological Survey, Columbia, Missouri.

Beyer, W. N., Dalgarn, J., Dudding, S., French, J. B., 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). *Archives of Environmental Contamination and Toxicology, 48*(1), 108–117.

Beyer, W. N., Franson, J. C., French, J. B., May, T., Rattner, B. A., Shearn-Bochsler, V. I., Warner, S. E., Weber, J., & Mosby, D. (2013). Toxic exposure of songbirds to lead in the Southeast Missouri Lead Mining District. *Archives of environmental contamination and toxicology, 65*(3), 598–610.

Buckley, E.R. (1909). *Geology of the Disseminated Lead Deposits of St. Francois and Washington Counties,* Volume IX. Part I. Missouri Bureau of Geology and Mines, The Hugh Stephens Printing Complany, Jefferson City, Missouri.

Bunte, K., & Abt, S.R. (2001). *Sampling surface and subsurface particle-size distributions in wadable gravel- and cobble-bed streams for analyses in sediment transport, hydraulics, and streambed monitoring*. (pp. 428). US Department of Agriculture, Forest Service, Rocky Mountain Research Station.

Carlson, R. W., & Bazzaz, F. A. (1977). Growth reduction in American sycamore (*Plantanus occidentalis* L.) caused by Pb Cd interaction. *Environmental Pollution, 12*(4), 243–253.

Conkova, M., & Kubiznakova, J. (2008). Lead isotope ratios in tree bark pockets: An indicator of past air pollution in the Czech Republic. *Science of the Total Environment, 404*(2–3), 440–445.

Delapierre, A., Ballesteros Canovas, J. A., Buzzi Marcos, J., Slaveykova, V., & Stoffel, M. (2021). Trees as sentinels of metallic pollution induced by mining along the Odiel River (Southern Iberian Peninsula). *Cuadernos de Investigación Geográfica, 47*(2), 371–390.

Deng, H., Ye, Z. H., & Wong, M. H. (2004). Accumulation of lead, zinc, copper and cadmium by 12 wetland plant species thriving in metal-contaminated sites in China. *Environmental pollution, 132*(1), 29–40.

Dietz, R. A. (1952). The evolution of a gravel bar. *Annals of the Missouri Botanical Garden, 39*(3), 249–254.

Domínguez, M. T., Maranón, T., Murillo, J. M., Schulin, R., & Robinson, B. H. (2008). Trace element accumulation in woody plants of the Guadiamar Valley, SW Spain: a large-scale phytomanagement case study. *Environmental Pollution, 152*(1), 50–59.

Evangelou, M. W., Robinson, B. H., Günthardt-Goerg, M. S., & Schulin, R. (2013). Metal uptake and allocation in trees grown on contaminated land: implications for biomass production. *International journal of phytoremediation, 15*(1), 77–90.

Ferreira, V., Koricheva, J., Duarte, S., Niyogi, D. K., & Guérold, F. (2016). Effects of anthropogenic heavy metal contamination on litter decomposition in streams–a meta-analysis. *Environmental Pollution, 210*, 261–270.

Gale, N. L., Adams, C. D., Wixson, B. G., Loftin, K. A., & Huang, Y. (2002). Lead concentrations in fish and river sediments in the Old Lead Belt of Missouri. *Environmental Science and Technology, 36*, 4262–4268.

Gale, N. L., Adams, C. D., Wixson, B. G., Loftin, K. A., & Huang, Y. (2004). Lead, zinc, copper, and cadmium in fish and sediments from the Big River and Flat River Creek of Missouri's Old Lead Belt. *Environmental Geochemistry and Health, 26*(1), 37–49.

Gilman, E.F., Watson, D.G., Klein, R.W., Koeser, A.K., Hilber, D.R., & McLean, D.C. (2018). *Platanus occidentalis*: *Sycamore*. EDIS 1993 (6) Retrieved on July 20, 2021 from https://edis.ifas.ufl.edu/st484

Guha, M. M., & Mitchell, R. L. (1966). The trace and major element composition of the leaves of some deciduous trees. *Plant and Soil, 24*(1), 90–112.

Günthardt-Goerg, M. S., Vollenweider, P., Hermle, S., & Schulin, R. (2019). Growth and metal accumulation of young forest trees and understorey plants on contaminated topsoil: influence of subsoil and time. *Plant and Soil, 437*(1), 375–395.

Guyette, R. P., Cutter, B. E., & Henderson, G. S. (1991). Long-term correlations between mining activity and levels of lead and cadmium in tree-rings of eastern Red-Cedar. *Journal of Environmental Quality, 20*(1), 146–150.

Hashemi, S. A., Alinejad, F., & FallahChay, M. (2015). Analyzing lead concentration in the sycamore tree species in high-and low-traffic areas of Rasht, Iran. *Toxicology and Industrial Health, 31*(6), 542–545.

Hasnaoui, S. E., Fahr, M., Keller, C., Levard, C., Angeletti, B., Chaurand, P., Triqui, Z. E. A., Guedira, A., Rhazi, C., & F., & Smouni, A. (2020). Screening of native plants growing on a Pb/Zn mining area in eastern Morocco: Perspectives for phytoremediation. *Plants, 9*(11), 1458.

Horowitz, A. J. (1991). *A primer on sediment-trace element chemistry* (Vol. 2). Lewis Publishers Chelsea.

International Dendrology Society. (2021). *Platanus L. Trees and Shrubs Online*. Retrieved July 20, 2021, from treesandshrubsonline.org/articles/platanus/

Jauron, R. (1996). *Shedding Bark. Horticulture and Home Pest News*. Iowa State University Extension and Outreach. Retrieved July 20, 2021, from https://hortnews.extension.iastate.edu/1996/8-9-1996/shedbark.html

Jenkins, J.C., Chojnacky, D.C., Heath, L.S., & Birdsey, R. (2004). *Comprehensive database of diameter-based biomass regressions for North American tree species*. General Technical Report NE-319 (pp 1–45). United States Department of Agriculture, Forest Service.

Jia, M., Zhou, D., Lu, S., & Yu, J. (2021). Assessment of foliar dust particle retention and toxic metal accumulation ability of fifteen roadside tree species: Relationship and mechanism. *Atmospheric Pollution Research, 12*(1), 36–45.

Kabata-Pendias, A. (2011). *Trace Elements in Soils and Plants, fourth edition.* CRC press, Taylor & Francis Group.

Kacálková, L., Tlustoš, P., & Száková, J. (2014). Chromium, nickel, cadmium, and lead accumulation in maize, sunflower, willow, and poplar. *Polish Journal of Environmental Studies*, *23*(3).

Kim, J. Y., Park, J., Choi, J., & Kim, J. (2020). Determination of metal concentration in road-side trees from an industrial area using laser ablation inductively coupled plasma mass spectrometry. *Minerals, 10*(2), 175.

Kirkham, M. B. (2006). Cadmium in plants on polluted soils: Effects of soil factors, hyperaccumulation, and amendments. *Geoderma, 137*, 19–32.

Kissoon, L. T., Jacob, D. L., & Otte, M. L. (2010). Multi-Element accumulation near *Rumex crispus* roots under wetland and dryland conditions. *Environmental Pollution, 158*, 1834–1841.

Kissoon, L. T., Jacob, D. L., & Otte, M. L. (2011). Multiple elements in *Typha angustifolia* rhizosphere and plants: Wetland versus dryland. *Environmental and Experimental Botany, 72*, 232–241.

Kucha, H., Martens, A., Ottenburgs, R., De Vos, W., & Viaene, W. (1996). Primary minerals of Zn-Pb mining and metallurgical dumps and their environmental behavior at Plombières, Belgium. *Environmental Geology, 27*, 1–15.

Lepp, N. W., & Eardley, G. T. (1978). Growth and trace metal content of European sycamore seedlings grown in soil amended with sewage sludge. *Journal of Environmental Quality, 7*(3), 413–416.

Liu, R., Pan, Y., Fang, Y., Pang, L., Shen, J., & Tian, X. (2021). Effects of heavy metal-mediated intraspecific variation in leaf litter on the feeding preferences of stream detritivores. *Science of The Total Environment, 763*, 144591. https://doi.org/10.1016/j.scitotenv.2020.144591

Liu, Y.-J., Zhu, Y.-G., & Ding, H. (2007). Lead and cadmium in leaves of deciduous trees in Beijing, China: development of a metal accumulation index (MAI). *Environmental Pollution, 145*(2), 387–390.

MacDonald, D. D., Ingersoll, C. G., & Berger, T. A. (2000). Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology, 39*, 20–31.

McGregor, S.D., Duncan, H.J., Pulford, I.D., & Wheeler, C.T. (1996). Uptake of heavy metals from contaminated soil by trees. In: I. Glimmerveen (Ed.), *Heavy Metals and Tees. Proceedings of a Discussion Meeting, Glasgow*. (pp. 171–6) Edinburgh: Institute of Chartered Foresters.

McKenney, R., Jacobson, R. B., & Werheimer, R. C. (1995). Woody vegetation and channel morphogenesis in low-gradient, gravel-bed streams in the Ozarks Plateaus, Missouri and Arkansas. *Geomorphology, 13*, 175–198.

Meers, E., Vandecasteele, B., Ruttens, A., Vangronsveld, J., & Tack, F. M. G. (2007). Potential of five willow species (*Salix* spp.) for phytoextraction of heavy metals. *Environmental and Experimental Botany, 60*(1), 57–68. https://doi.org/10.1016/j.envexpbot.2006.06.008

Meneau, K.J. (1997). *Big River Watershed Inventory and Assessment*. Missouri Department of Conservation. Retrieved on January 17, 2021 from http://mdc.mo.gov/fish/watershed/big/contents/

Mertens, J., Vervaeke, P., De Schrijver, A., & Luyssaert, S. (2004). Metal uptake by young trees from dredged brackish sediment: limitations and possibilities for phytoextraction and phytostabilisation. *Science of the Total Environment, 326*(1–3), 209–215.

Mertens, J., Vervaeke, P., Meers, E., & Tack, F. M. (2006). Seasonal changes of metals in willow (*Salix* sp.) stands for phytoremediation on dredged sediment. *Environmental Science & Technology, 40*(6), 1962–1968.

Migeon, A., Richaud, P., Guinet, F., Chalot, M., & Blaudez, D. (2009). Metal accumulation by woody species on contaminated sites in the north of France. *Water, Air, and Soil Pollution, 204*(1), 89. https://doi.org/10.1007/s11270-009-0029-5

Mingorance, M. D., Valdes, B., & Oliva, S. R. (2007). Strategies of heavy metal uptake by plants growing under industrial emissions. *Environment International, 33*(4), 514–520.

Murphy, A. P., Coudert, M., & Barker, J. (2000). Plants as biomarkers for monitoring heavy metal contaminants on landfill sites using sequential extraction and inductively coupled plasma atomic emission spectrophotometry

(ICP-AES). *Journal of Environmental Monitoring, 2*(6), 621–627. https://doi.org/10.1039/B005594H

Nikolova, T. S. (2015). Absorption of Pb, Cu, Zn and Cd type *Morus alba* L. cultivated on soils contaminated with heavy metals. *Bulgarian Journal of Agricultural Science, 21*(4), 747–750.

Norouzi, S., Khademi, H., Cano, A. F., & Acosta, J. A. (2015). Using plane tree leaves for biomonitoring of dust borne heavy metals: a case study from Isfahan, Central Iran. *Ecological Indicators, 57*, 64–73.

Pais, I., & Jones, J. B. (1997). *The Handbook of Trace Elements*. CRC Press LLC.

Palmer, K. T., & Kucera, C. L. (1980). Lead contamination of sycamore and soil from lead mining and smelting operations in eastern Missouri. *Journal of Environmental Quality, 9*(101), 106–111.

Pavlowsky, R. T., Lecce, S. A., Owen, M. R., & Martin, D. J. (2017). Legacy sediment, lead, and zinc storage in channel and floodplain deposits of the Big River, Old Lead Belt Mining District, Missouri, USA. *Geomorphology, 299*, 54–75.

Pavlowsky, R.T., Owen, M.R., & Martin, D.J. (2010). Distribution, Geochemistry, and Storage of Mining Sediment in Channel and Floodplain Deposits of the Big River System in St. Francois, Washington, and Jefferson Counties, Missouri. In: *OEWRI EDR-10-002 Report Prepared for US Fish and Wildlife Service, Columbia, MO. Ozarks Environmental and Water Resources Institute*. https://bearworks.missouristate.edu/oewri-tech/1

Peralta-Videa, J. R., Lopez, M. L., Narayan, M., Saupe, G., & Gardea-Torresdey, J. (2009). The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain. *The International Journal of Biochemistry & Cell Biology, 41*(8–9), 1665–1677. https://doi.org/10.1016/j.biocel.2009.03.005

Pulford, I. D., & Watson, C. (2003). Phytoremediation of heavy metal-contaminated land by trees—a review. *Environment International, 29*(4), 529–540. https://doi.org/10.1016/S0160-4120(02)00152-6

Raven, P.H., Evert, R.F., & Eichorn, S.E. (1992). *Biology of Plants.* (5th ed., pp 527-532). Worth Publishers.

Reimann, C., Filtzmoser, P., Garrett, R., & Dutter, R. (2008). *Statistical data analysis explained. Applied environmental statistics with R*. John Wiley & Sons.

Rothpfeffer, C., & Karltun, E. (2007). Inorganic elements in tree compartments of *Picea abies*—concentrations versus stem diameter in wood and bark and concentrations in needles and branches. *Biomass and Bioenergy, 31*(10), 717–725.

Rykowska, I., & Wasiak, W. (2011). Bioconcentration of mercury and heavy metals by the bark of maple-leaf plane tree. *Proceedings of ECOpole*, *5*.

Safari, M., Ramavandi, B., Sanati, A. M., Sorial, G. A., Hashemi, S., & Tahmasebi, S. (2018). Potential of trees leaf/bark to control atmospheric metals in a gas and petrochemical zone. *Journal of Environmental Management, 222*, 12–20.

Satake, K., Tanaka, A., & Kimura, K. (1996). Accumulation of lead in tree trunk bark pockets as pollution time capsules. *Science of the Total Environment, 181*, 25–30.

Schade, J. D., Fisher, S. G., Grimm, N. B., & Seddon, J. A. (2001). The influence of a riparian shrub on nitrogen cycling in a Sonoran desert stream. *Ecology, 82*(12), 3363–3376. https://doi.org/10.1890/0012-9658(2001)082[3363:TIOARS]2.0.CO;2

Schmitt, C. J., & Finger, S. E. (1982). The dynamics of metals from past and present mining activities in the Big and Black River watersheds, southeastern Missouri. Final Report for USCOE, St. Louis District, Project DACW43-80-A-0109.

Schmitt, C. J., Brumbaugh, W. G., & May, T. W. (2007). Accumulation of metals in fish from lead–zinc mining areas of southeastern Missouri, USA. *Ecotoxicology and Environmental Safety, 67*, 14–30.

Sheppard, J. C., & Funk, W. H. (1975). Trees as environmental sensors monitoring long-term heavy metal contamination of Spokane River, Idaho. *Environmental Science & Technology, 9*(7), 638–642.

Smith, D.C. (2013). Subsurface investigation of five gravel bars located on the Big River in Southeast Missouri. Prepared for David Mosby, U.S., Fish and Wildlife Service, Columbia MO by the USGS Missouri Water Science Center, Rolla, MO.

Smith, B.J., & Schumacher, J.G. (1991). *Hydrochemical and Sediment Data for the Old Lead Belt, Southeastern Missouri* – 1988-89. USGS Open-File Report 91-211.

Smith, B.J., & Schumacher, J.G. (1993). *Surface-water and Sediment Quality in the Old Lead Belt, Southeastern Missouri* – 1988-89. USGS Water Investigations Report # 93-4012.

Stroh, E.D., Struckhoff, M.A., & Grabner, K.W. (2015). *Soil lead and zinc effects on growth and survival of native plant species*. U.S. Geological Survey Administrative Report to the Missouri Trustee Council.

Struckhoff, M. A., Stroh, E. D., & Grabner, K. W. (2013). Effects of mining-associated lead and zinc soil contamination on native floristic quality. *Journal of Environmental Management, 119*, 20–28.

Superville, P.-J., de Winter, N., Phung, A. T., Proix, N., Baeyens, W., & Gao, Y. (2017). Radial metal concentration profiles in trees growing on highly contaminated soils. *Chemosphere, 172*, 80–88. https://doi.org/10.1016/j.chemosphere.2016.12.142

Taggart, A. F. (1945). *Handbook of Mineral Dressing: Ores and Industrial Minerals*. John Wiley & Sons.

Torres, K. C., & Johnson, M. L. (2001). Bioaccumulation of metals in plants, arthropods, and mice at a seasonal wetland. *Environmental Toxicology and Chemistry, 20*(11), 2617–2626. https://doi.org/10.1002/etc.5620201130

Turner, A.P. (1994). The responses of plants to heavy metals. In: S. Ross (Ed.), *Toxic Metals in Soil-Plant Systems*. pp 153-187. John Wiley and Sons, Inc.

United States Environmental Protection Agency (US EPA). (1998). *Field portable X-Ray fluorescence spectrometry for the determination of elemental concentrations in soils and sediments*. EPA-AW-846-6200. US EPA, Washington DC.

United States Environmental Protection Agency (US EPA). (2017). *Big River Mine Tailings National Priorities List (NPL) Superfund Site, St. Francois County, Missouri - Fact Sheet*. US EPA, Washington DC. Retrieved on January 13, 2022 from https://www.epa.gov/mo/

big-river-mine-tailings-national-priorities-list-npl-superfund-site-st-francois-county-missouri

Van Nevel, L., Mertens, J., Demey, A., De Schrijver, A., De Neve, S., Tack, F. M. G., & Verheyen, K. (2014). Metal and nutrient dynamics in decomposing tree litter on a metal contaminated site. *Environmental Pollution, 189*, 54–62. https://doi.org/10.1016/j.envpol.2014.02.009

Vandecasteele, B., Quataert, P., Genouw, G., Lettens, S., & Tack, F. M. G. (2009). Effects of willow stands on heavy metal concentrations and top soil properties of infrastructure spoil landfills and dredged sediment-derived sites. *Science of The Total Environment, 407*(20), 5289–5297. https://doi.org/10.1016/j.scitotenv.2009.06.022

Wang, C., Pavlowsky, R. T., Huang, Q., & Chang, C. (2016). Chanel bar feature extraction for a mining-contaminated river using high-spatial multispectral remote-sensing imagery. *GIScience & Remote Sensing, 53*, 283–302.

Weis, J. S., & Weis, P. (2004). Metal uptake, transport and release by wetland plants: implications for phytoremediation and restoration. *Environment International, 30*, 685–700.

Whitledge, G. W., & Rabeni, C. F. (1997). Energy sources and ecological role of crayfishes in an Ozark stream: insights from stable isotopes and gut analysis. *Canadian Journal of Fisheries and Aquatic Sciences, 54*, 2555–2563.

Yaşar, Ü., Özyiğit, İ. İ., Yalçın, İ. E., Doğan, İ., & Demir, G. (2012). Determination of some heavy metals and mineral nutrients of bay tree (*Laurus nobilis* L.) in Bartin city, Turkey. *Pakistan Journal of Botany*, 44, 81-89. https://gcris.iyte.edu.tr/handle/11147/4882.

Yue, K., Yang, W., Tan, B., Peng, Y., Huang, C., Xu, Z., Ni, X., Yang, Y., Zhou, W., Zhang, L., & Wu, F. (2019). Immobilization of heavy metals during aquatic and terrestrial litter decomposition in an alpine forest. *Chemosphere, 216*, 419–427.