

Southeastern Missouri Heavy Metal Soil Concentrations within Mississippi River Floodplain Environments

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Abstract

The Mississippi River watershed encompasses a substantial portion of the central United States, receiving effluent from soil runoff, urban and industrial centers. In Missouri, two soil series, with two pedons per series, located on the Mississippi River annual floodplain were morphologically described, classified, and chemically characterized. Aqua regia digestion and sodium acetate extractions were performed to assess the concentrations of 20 elements. A special emphasis was devoted to lead, cadmium, and zinc as these elements are commonly associated with heavy metal pollution. Cadmium was the only element showing an elevated concentration on one of the soil series. The pollution index and enrichment factor values suggested “cadmium impacted soils”. The elements used for geochemical background concentrations were determined using adjacent floodplain soils not experiencing annual Mississippi River flooding. However, geochemical background concentrations for cadmium were smaller than the sampled Mississippi River floodplain soils. Thus, the pollution index and the enrichment factor may have indicated “cadmium impacted soils”; however, the main difference is the soils used for the geochemical background soils and the Mississippi River floodplain soils simply exhibited slightly different cadmium concentrations. We conclude that cadmium may be accumulating in these annual flood prone soils; however, the intensity of the current cadmium accumulations is not appreciably above values that would warrant immediate remediation.

Keywords

Heavy Metals, Adsorption, Alluvium, Pollution Index, Lead

1. Introduction

The Mississippi River flows from the State of Minnesota to the Gulf of Mexico. Major tributaries include the Missouri and Ohio Rivers. Substantial heavy and light industry in metropolitan and rural areas exist along the river's course way. Cities such as Minneapolis, St. Louis, Memphis, and New Orleans lie adjacent to the river.

The floodplains along the Mississippi River provide both direct and indirect ecosystem services, including: (i) regulating (flood control, water quality maintenance, nutrient cycling, etc.), (ii) provisioning (forestry products, food production), (iii) environmental stewardship (air quality, water runoff, erosion abatement, biodiversity), and (iv) cultural (sacred lands, recreation, ecotourism, existence values) (Aide et al., 2021; Aide, 2021; Petsch et al., 2022). Existence values are economic values, which benefit people because knowing that a particular environmental resource exists, and provides comfort and peace-of-mind.

Numerous studies estimated heavy metal soil impacts along the Mississippi River floodplain. Concentrating on floodplain soils, Kelly et al. (2020) noted that contaminant sources include (i) geogenic sources (erosion and rock weathering) and (i) anthropogenic sources (transported emission/deposition, industrial waste, mining, sewage treatment facilities, fertilizer and pesticide runoff, and other sources). Garbarino et al. (1995) municipal wastewater treatment facilities, manufacturing, mining, and phosphate fertilizers as major heavy metal contributors to Mississippi River floodplain soils.

Presley et al. (1980) documented that zinc, cadmium, and lead were elevated heavy metals in Mississippi River sediment. Garbarino et al. (1995) noted that the upper Mississippi River exhibited a distinctive water chemistry seasonality, which they attributed to the diversity of sediment sources and navigation channels. The lower Mississippi River exhibits a comparatively mild seasonality of 10 to 20%, which was attributed to progressive episodes of deposition and resuspension.

This manuscript aims to assess selected transition, post-transition and metalloid concentrations in soil profiles that experience annual Mississippi River flooding in east-central Missouri. Furthermore, these elements were Na-acetate extracted to estimate their exchangeable concentrations to estimate their potential biological availability.

2. Floodplain Soils Having Accumulations of Lead and Zinc

In a major review, Sharifi et al. (2023) discussed lead and zinc as soil and water contaminants and their influence on aquatic ecosystems, plant uptake, crop contamination, health hazards, human exposure risks, biodiversity, and other topics. In selected regions, soil zinc and lead impacts are associated with extensive mining, especially in the Upper Mississippi Valley Lead Belt (Wisconsin), the Missouri Old Lead Belt and the currently active Viburnum Trend, near St. Louis, Missouri (Garbarino et al., 1995). In the eastern Ozarks, Mississippi Valley Type lead ores occur in Paleozoic carbonate rocks as galena (PbS), with the auxiliary minerals

sphalerite (ZnS) and pyrite (FeS₂). On a worldwide basis, lead concentrations range from 10 to 40 mg·Pb·kg⁻¹ in felsic and argillaceous sediments, whereas ultramafic and carbonate sediments range from 0.1 to 10 mg·Pb·kg⁻¹ (Kabata-Pendias, 2020). Naturally occurring zinc-bearing minerals include: (i) sphalerite (α ZnS), (ii) wurzite (β ZnS), (iii) zincite (ZnO), (iv) smithsonite (ZnCO₃), (v) willemite (Zn₂SiO₄) and (vi) hemimorphite (Zn₄Si₂O₇(OH)₂·H₂O). Argillaceous sediments generally have zinc concentrations averaging 120 mg·Zn·kg⁻¹. Typical surface horizon zinc concentrations range from 60 to 89 mg·Zn·kg⁻¹ (Kabata-Pendias, 2020).

3. Floodplain Soils and Cadmium

Typical United States soils have cadmium concentrations ranging from 0.01 to 2 mg·Cd·kg⁻¹ (Kabata-Pendias, 2020). Cadmium typically exists in the soil environment, ranging from 0.01 to 0.3 mg Cd·kg⁻¹ in coarse-textured soils and ranging from 0.2 to 0.8 mg·Cd·kg⁻¹ in loamy soils (Kabata-Pendias, 2020). Soil Cd ranges from 0.01 to 1 mg·kg⁻¹ with a worldwide mean of 0.36 mg·kg⁻¹ (Kubier et al., 2019). Cadmium-bearing minerals include: greenockite (CdS), octavite (CdSe), and monteponite (CdO), with many minerals having measurable cadmium concentrations because of isomorphic substitution (Kabata-Pendias, 2020).

Important anthropogenic Cd sources include mining, sewage, landfill leachates, atmospheric deposition because of combustion emissions, and the use of Cd-containing fertilizers (Kubier et al., 2019).

4. Floodplain Soils and Other Metals

In this manuscript, we concentrated on Fe, Mn, Zn, Cd, and Pb. Iron (Fe) and Manganese (Mn) are ubiquitous soil metals and form a variety of oxyhydroxides. Other metals were assessed and present in concentrations appropriate for pristine soils (Co, Ni, Cu, V, Cr, Mo, Ag, Sn, Sb, Nb, Sc, Au, Zr, Ti and Hg); however, some of these metals may pose environmental risks in other soils along the Mississippi River.

5. Materials and Methods

5.1. Climate, Physiography, and Soils of the Mississippi River Floodplain in East Central Missouri

Forest species within the Mississippi River floodplain include northern red oak (*Quercus rubra*), eastern cottonwood (*Populus deltoides*), American elm (*Ulmus americana*) white oak (*Quercus alba*), black walnut (*Juglans nigra*), silver maple (*Acer saccharinum*), yellow poplar (*Liriodendron tulipifera*), pin oak (*Quercus palustris*), American sycamore (*Platanus occidentalis*), green ash (*Fraxinus pennsylvanica*), sweetgum (*Liquidambar styraciflua*), black willow (*Salix nigra*), red maple (*Acer rubrum*), nuttall oak (*Quercus texana*), water oak (*Quercus nigra*), common hackberry (*Celtis occidentalis*), river birch (*Betula nigra*), boxelder (*Acer negundo*), and bald cypress (*Taxodium distichum*) (*Aide et al., 2021). In

many locations, the forest vegetation has been cleared for urbanization and agriculture.

Two pedons of the Commerce series (Fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquepts) and two pedons of the Caruthersville series (Coarse-silty, mixed, superactive, calcareous, thermic Typic Udifluvents) were morphologically described and sampled. The Commerce pedons presented A-Bw-Bg-Bssg horizon sequences and displayed ochric and cambic horizons, whereas the Caruthersville pedons presented A-C-Cg horizon sequences and displayed ochric epipedons.

Nine surface horizons of the Wilbur series (Coarse-silty, mixed, superactive, mesic Fluvaquentic Eutrudepts) were sampled using aqua regia digestion to specify the Geochemical Background concentrations. The Wilbur pedons have no history of environmental impact and these soils drain into the Mississippi River floodplain study area. The Wilbur pedons have A – Bw – Cg silt loam horizon sequences and reside on silty floodplains. The ochric and cambic soil horizons do not have sediment deposition from the modern Mississippi River, rather they receive silty sediment arising from erosion of the surrounding loess uplands. Additionally, one pedon of the Commerce soil series, which is not currently experiencing annual flooding, was also sampled to provide alternative lead, zinc, and cadmium geochemical background concentrations.

The climate is humid continental. The historical weather data base for Cape Girardeau County provides that the annual rainfall is 1.07 m (49.3 inch), the average daily maximum annual air temperature of 20°C (68°F), average daily minimum annual air temperature of 8.6°C (48°F), average daily annual air temperature of 14°C (57°F), and the average annual total solar radiation of 14 MJ·m⁻² (Festervand, 1981). Annual flooding durations are generally 1 to 7 days; however, long flood intervals may occur during spring snowmelt in the upper Mississippi River watershed. The local floodplain geomorphology features broad to narrow flood prone areas with incised variably sized stream channels that supply sediment from the overlying hinterland. Mississippi River floodplain soils are Holocene age, which include the soil orders Entisol, Inceptisol, Mollisol, and Vertisol (Festervand, 1981).

5.2. Laboratory Protocols

Soil pH in water, exchangeable cations, total neutralizable acidity, soil organic matter content by loss on ignition, Bray 1 phosphorus, and 2M potassium chloride extractable SO₄-S were determined by the University Missouri-Columbia Soil Testing Laboratory.

An aqua-regia digestion was performed to estimate elemental concentrations associated with whole soil soluble, exchangeable, organically-complexed, adsorbed/co-precipitated with oxyhydroxide environments and the lattice degradation of phyllosilicates (Aide & Fasnacht, 2010). In this procedure, 0.25 g of finely ground fine earth fraction was digested in 0.01 liter of aqua regia (1 HCl:3HNO₃)

for one hour, followed by 0.45 μm filtering with an aliquot analyzed using inductively coupled plasma—atomic emission spectrometry. Quality assurance and analytical accuracy involved four certified reference materials for mining and exploration and duplicate samples.

For the Na-acetate leach, a 0.75 g sample of passing a 60-mesh soil horizon material is leached with a sodium acetate matrix at 30°C for 1 hour. Two controls and duplicate samples were also Na-acetate leached. The solutions are analyzed using inductively coupled plasma-mass spectrometry. Soil analysis for the aqua regia digestion and Na-acetate extraction were performed by Activation Laboratories (Ancaster, Ontario).

6. Results and Discussion

The Caruthersville pedons (Universal Transverse Mercator latitude, 283178, 4115480, 16S) exhibit silt loam to sandy loam horizons, slightly alkaline pH levels and limited soil organic matter contents (**Table 1(a)**). The soil organic matter content is 1.1% in the A horizons, whereas the soil organic matter contents in the deeper horizons irregularly alternate from 0.4 to 1.3%. The Bray-1 phosphorus concentrations are greater than the 22.5 ppm threshold for a 100% soil fertility index. Calcium is the dominant exchangeable cation, with the exchange capacity varying from 10.0 to 23.3 $\text{cmol}\cdot\text{kg}^{-1}$. The exchange capacity values roughly correspond with the clay content. The unit $\text{cmol}\cdot\text{kg}^{-1}$ is a centimole of protonic charge per kilogram.

The Commerce pedons (Universal Transverse Mercator latitude, 277755, 4133200, 16S) exhibit silty clay to clayey-textured horizons, having slightly alkaline pH levels and moderate soil organic matter contents (**Table 1(b)**). The soil organic matter content is 3.4% in A horizons and the deeper horizons have somewhat smaller values, ranging from 2.2 to 3.1%. The Bray-1 phosphorus concentrations are greater than the 22.5 ppm threshold for a 100% soil fertility index. Calcium is the dominant exchangeable cation, with the exchange capacity varying from 23.6 to 40.4 $\text{cmol}\cdot\text{kg}^{-1}$.

Table 1. (a) Chemical composition of the Caruthersville soils; (b) Chemical composition of the Commerce soil series.

(a)						
Horizon	Depth	pH	SOM	P	Ca	CEC
	cm	water	%	ppm	cmol/kg	cmol/kg
A	15	7.7	1.1	50	14.4	16.9
C1	30	7.9	0.6	51	16.8	19.8
C2	46	8.0	0.6	59	15.2	17.8
C3	61	7.9	1.6	23	19.6	23.3
C4	91	8.0	0.8	39	12.1	14.4
C5	122	8.1	1.0	34	14.2	16.5

Continued

A	15	8.1	1.1	45	14.5	16.6
C1	30	8.1	0.8	52	13.4	15.5
C2	46	8.1	0.6	59	12.3	14.0
C3	61	8.1	0.6	61	12.0	13.5
C4	91	7.9	1.3	62	12.6	14.2
C5	122	8.1	0.4	64	8.7	10.0

(b)

Horizon	Depth	pH	SOM	P	Ca	CEC
	cm	water	%	ppm	cmol/kg	cmol/kg
A	15	7.8	3.4	37	30.1	34.8
Bw1	30	7.8	2.6	46	21.7	26.3
Bw2	46	7.9	2.3	38	23.0	27.5
Bw3	61	7.9	2.5	44	19.2	23.6
Bw4	91	7.6	2.9	48	23.6	29.0
A	15	7.9	3.4	33	20.0	24.2
Bw1	30	7.9	3.1	44	23.2	28.0
Bw2	46	7.9	2.3	33	33.1	38.6
Bw3	61	7.8	2.2	37	34.0	40.4
Bw4	91	7.7	2.2	43	23.9	29.4

SOM is soil organic matter; CEC is cation exchange capacity.

6.1. The Aqua Regia Digestion Values

The aqua regia digestion concentrations in the Caruthersville pedons are typical and are within the ranges for soils without evidence of heavy metal impact (Kabata-Pendias, 2020). The iron concentrations range from 8,300 to 11,800 mg·kg⁻¹, whereas the manganese concentrations range from 194 to 456 mg·kg⁻¹ (Table 2(a)). We selected zinc, cadmium, and lead for additional scrutiny because the literature suggests that some Mississippi River floodplain soils are impacted by these elements. The elemental aqua regia digestion concentration ranges are: (i) 24.2 < zinc < 37.4 mg·kg⁻¹, (ii) 0.08 < cadmium < 0.26 mg·kg⁻¹, and (iii) 5.9 < lead < 8.8 mg·kg⁻¹.

For the Caruthersville pedons, the mean and standard deviation values for other selected aqua regia digestion elemental concentrations (mg·kg⁻¹, except Au which is µg·kg⁻¹) are: Metal (mean, standard deviation), Co (4.6, 0.5), Ni (13.3, 3.7), Cu (5.0, 1.6), V (20.0, 2.6), Cr (10.7, 1.4), Mo (0.22, 0.07), Ag (0.032, 0.006), Sn (0.38, 0.11), Sb (0.18, 0.03), Ti (0.04, 0.005), Nb (0.36, 0.05), Sc (1.38, 0.27), Au (1.44 ppb, 0.72 ppb), Zr (2.56, 0.28), Y (6.64, 0.55), Hg (0.03, 0.01) and Tl (0.09, 0.03). For both soil series, the concentrations for some elements were below detection: (i) tungsten and hafnium are less than 0.1 mg·kg⁻¹, (ii) Tantalum is less than 0.05 mg·kg⁻¹, and (iii) rhenium is less than 0.001 mg·kg⁻¹.

Table 2. (a) Aqua regia digestion metal concentration for the Caruthersville soils; (b) Aqua regia digestion metal concentration for the Commerce soils.

(a)					
Horizon	Fe	Mn	Zn	Cd	Pb
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
A	10,600	340	33.5	0.19	7.3
C1	11,300	380	36.7	0.22	8.8
C2	8,300	235	23.5	0.08	5.9
C3	10,100	358	32.9	0.16	7.3
C4	8,400	257	24.2	0.12	6.5
C5	10,000	289	31.2	0.12	7.9
A	11,800	456	37.4	0.26	8.3
C1	9,700	404	28.8	0.18	7.2
C2	9,400	282	25.9	0.16	6.7
C3	9,000	205	26.6	0.13	6.4
C4	9,900	266	33.4	0.12	8.8
C5	9,000	194	26.5	0.10	7.1
Mean	9,790	306	30.1	0.2	7.4
STD	1,070	82	4.8	0.1	0.9
CV%	11	27	16	34	13
(b)					
Horizon	Fe	Mn	Zn	Cd	Pb
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
A	22,800	890	76.3	0.47	17.8
Bw1	24,500	1,130	82.2	0.55	21.5
Bw2	21,200	820	74.4	0.46	20.7
Bw3	21,800	800	71.5	0.52	22.2
Bw4	22,600	890	82.5	0.64	27.8
A	24,200	1,020	80.6	0.54	20.0
Bw1	25,200	1,120	93.9	0.57	22.7
Bw2	24,200	930	85.7	0.50	22.6
Bw3	24,100	1,030	84.0	0.81	24.8
Bw4	18,300	650	56.4	0.45	17.4
Mean	22,890	928	78.8	0.60	21.5
STD	1,950	143	9.5	0.01	2.4
CV%	9	15	12	19	11

The aqua regia digestion concentrations in the Commerce pedons are typical and are within the ranges for soils without evidence of environmental impact (Kabata-Pendias, 2020). The selected elemental values for the Commerce pedons are significantly greater than those of the Caruthersville pedons, features attributed to the greater clay contents. The iron concentrations range from 18,300 to 25,200 $\text{mg}\cdot\text{kg}^{-1}$, whereas the manganese concentrations range from 650 to 1,120 $\text{mg}\cdot\text{kg}^{-1}$ (Table 2(b)). The measured elemental concentrations range from (i) $56.4 < \text{zinc} < 85.7 \text{ mg}\cdot\text{kg}^{-1}$, (ii) $0.45 < \text{cadmium} < 0.81 \text{ mg}\cdot\text{kg}^{-1}$, and (iii) $17.4 < \text{lead} < 27.8 \text{ mg}\cdot\text{kg}^{-1}$. Normal soil metal concentrations range for selected elements are: (i) $60 < \text{Zinc} < 89 \text{ mg}\cdot\text{kg}^{-1}$, (ii) $0.2 < \text{cadmium} < 1.1 \text{ mg}\cdot\text{kg}^{-1}$, and (iii) $3 < \text{lead} < 90 \text{ mg}\cdot\text{kg}^{-1}$.

For the Commerce pedons, the aqua regia digestion mean and standard deviation concentrations ($\text{mg}\cdot\text{kg}^{-1}$, except Au which is $\mu\text{g}\cdot\text{kg}^{-1}$) for other selected elements include: Co (9.8, 1.1), Ni (25.3, 3.2), Cu (18.7, 2.3), V (47, 5), Cr (25, 3), Mo (0.76, 0.52), Ag (0.11, 0.01), Sn (0.93, 0.07), Sb (0.39, 0.09), Ti (0.03, 0.01), Nb (0.49, 0.08), Y (12.3, 1.0), Zr (2.44, 0.30), Sc (3.58, 0.40), In (0.028, 0.006), Te (0.05, 0.01), Hg (0.06, 0.01) and Au (2.28 ppb, 1.15 ppb). The concentration values are within the geogenic concentrations documented in Kabata-Pendias (2020).

6.2. The Sodium Acetate Extraction Values

Sodium acetate extractions estimate metal concentrations that readily participate in cation exchange with ion-bearing solutions. As an example, $[\text{clay} =] \text{Cd}^{2+} + 2\text{Na}^+ = [\text{clay} =] 2\text{Na}^+ + \text{Cd}^{2+}$. For the two pedons of the Caruthersville series the mean and standard deviation values ($\mu\text{g}\cdot\text{kg}^{-1}$) for iron, manganese, cadmium, and lead concentrations are: iron (19,000, 12,000), manganese (100,000, 50,000), cadmium (81, 31), and lead (463, 274). Iron, manganese and cadmium show little soil depth variation, whereas lead shows somewhat greater concentrations in the deeper soil horizons and zinc is generally less concentrations than the detection limit. For the Caruthersville pedons the mean and standard deviation values for other selected Na-acetate extraction concentrations ($\mu\text{g}\cdot\text{kg}^{-1}$) include: Co (156, 76), Ni (1,411, 865), Cu (417, 119), V (90, 32), Mo (43, 14), Nd (Sb (17, 7), Nd (754, 147), Ti (2350, 261), Tl (4.4, 0.6), and Y (879, 165). For the Na-acetate extraction, undetected concentration values are: (i) Cr is less than $100 \mu\text{g}\cdot\text{kg}^{-1}$, (ii) Ag is less than $5 \mu\text{g}\cdot\text{kg}^{-1}$, (iii) Sn is less than $10 \mu\text{g}\cdot\text{kg}^{-1}$ and (iv) Zn is less than $2,000 \mu\text{g}\cdot\text{kg}^{-1}$. The zinc concentration was less than the detection limit ($2,000 \mu\text{g}\cdot\text{kg}^{-1}$).

The mean and standard deviation values ($\mu\text{g}\cdot\text{kg}^{-1}$) for iron, manganese, cadmium, and lead concentrations for the two pedons of the Commerce series are: iron (8,000, 3,000), manganese (52,000, 20,000), cadmium (242, 36), lead (386, 39), and Zinc (3,700, 675). The mean lead value of the Commerce series is smaller than that of the Caruthersville; however, the t-test value ($P = 0.18$) is not significant. The mean cadmium value of the Commerce series is significantly greater than that of the Caruthersville series.

For the Commerce pedons, the mean and standard deviation values ($\mu\text{g}\cdot\text{kg}^{-1}$) for other elemental Na-acetate extractions include: Co (37, 19), Ni (785, 159), Cu

(440, 52), V (121, 28), Mo (23, 5), Sb (24, 3), Nd (865, 64), Ti (2550, 673), Tl (6, 0.5), Y (1017, 97). Soil depth variations for Mn are slightly greater for the near surface horizons; however, the soil depth variations for zinc, cadmium and lead are rather uniform. Undetected Na-acetate extraction concentration values include (i) Cr less than $100 \mu\text{g}\cdot\text{kg}^{-1}$, (ii) Ag less than $5 \mu\text{g}\cdot\text{kg}^{-1}$, and (iii) Sn less than $10 \mu\text{g}\cdot\text{kg}^{-1}$.

For the Caruthersville pedons, the comparison of the Na-acetate manganese extraction concentration ($100 \text{ mg}\cdot\text{kg}^{-1}$) with the manganese aqua regia digestion concentration ($306 \text{ mg}\cdot\text{kg}^{-1}$) presents a ratio percentage of 33%. The corresponding values for cadmium (41%) and lead (6.3%) vary greatly, testifying to their intrinsically different soil chemistries, including adsorption intensities. The cadmium value of 41% suggests that a near majority of the cadmium cations are biologically available, whereas the lead is only incidentally biologically available at 6.3%. For the Commerce pedons, the comparison of the Na-acetate manganese extraction ($52 \text{ mg}\cdot\text{kg}^{-1}$) with the manganese aqua regia digestion ($928 \text{ mg}\cdot\text{kg}^{-1}$) is a ratio percent of 5.6%. The corresponding values for cadmium (40%), zinc (4.7%) and lead (2%) also vary with their respective elemental chemistries. Interestingly, the cadmium and lead values are similar between the soil series.

6.3. Metal Pollution Index Values

The PI pollution index for aqua regia digestion concentrations (PI) is described as:

$$\text{PI} = [\text{Metal Concentration}]/[\text{Geochemical Background Concentration}]$$
. The calculated PI values may be interpreted as: (i) $\text{PI} < 1$ is absent, (ii) $1 < \text{PI} < 2$ is low, (iii) $2 < \text{PI} < 3$ is moderate, (iv) $3 < \text{PI} < 5$ is strong, (v) $\text{PI} > 5$ is very strong (Kowalska et al., 2018; Gong et al., 2008).

The EF Enrichment factor pollution index for aqua regia digestion concentrations is described as: $\text{EF} = [\text{Metal Concentration}/\text{Ti Concentration}]/[\text{Background Metal Concentration}/\text{Ti background Concentration}]$. The calculated EF values may be interpreted as: (i) $\text{EF} < 2$ is minimal enrichment, (ii) $2 < \text{EF} < 5$ is moderate enrichment, (iii) $5 < \text{EF} < 20$ is significant enrichment, (iv) $20 < \text{EF} < 40$ is very high enrichment, and (v) $\text{EF} > 40$ is extremely high enrichment (Kowalska et al., 2018; Gong et al., 2008).

Using the Geochemical background concentrations from the aqua regia digestion the Wilbur series surface samples ($\text{mg}\cdot\text{kg}^{-1}$) and standard deviation ($\text{mg}\cdot\text{kg}^{-1}$) for the following elements are: (i) Ti (344/53), (ii) Fe (15400/2500), (iii) Mn (894/266), (iv) Zn (55/10), (v) Cd (0.19/0.07), (vi) Pb (14.8/3.5). We also sampled a Commerce pedon. The mean and standard deviation concentrations of the Commerce pedon are: (i) Ti (700, 200), (ii) Zn (53, 25), (iii) Cd (0.13, 0.12) and (iv) Pb (15, 8).

The Pollution Index and the Enrichment Factor were calculated using the Wilbur surface horizons for geochemical background initiation. The average pollution index (PI) for the Caruthersville pedons indicate “no pollution” for Zn, Cd

or Pb, whereas these values for the Commerce pedons indicate “low pollution” for Zn and Pb and “moderate pollution” for Cd (**Table 3**). Some horizons in the Commerce pedons have PI values indicating “strong pollution” involving cadmium. The Enrichment Factor values suggest “absent” or “minimal enrichment” for Zn, Cd and Pb in the Caruthersville pedons and for Zn and Pb in the Commerce pedons. The Commerce pedon’s enrichment factors for Cd indicate “moderate enrichment” and a few horizons indicate “strong” enrichment.

Table 3. Pollution index values (averaged across all soil horizons).

Geochemical Background using Wilbur series						
	Caruthersville			Commerce		
PI	Zn	Cd	Pb	Zn	Cd	Pb
Mean	0.55	0.81	0.5	1.43	2.9	1.45
STD	0.09	0.28	0.06	0.18	0.57	0.17
Maximum	0.68	1.37	0.59	1.71	4.26	1.68
EF						
Mean	0.55	0.79	0.13	1.40	2.81	1.4
STD	0.11	0.23	0.03	0.30	0.58	0.23
Maximum	0.70	1.18	0.18	1.969	3.67	1.76
Geochemical Background using the Commerce series						
PI	Zn	Cd	Pb	Zn	Cd	Pb
Mean	0.57	1.18	0.49	1.49	4.24	1.43
STD	0.09	0.40	0.06	0.19	0.83	0.17
Maximum	0.71	2.0	0.59	1.77	6.23	1.65
EF	1.15	2.36	0.28	2.85	5.72	2.86
Mean	0.22	0.68	0.06	0.60	1.17	0.47
STD	1.47	3.5	0.39	3.98	7.46	3.58
Maximum						

PI is Pollution Index, EF is Enrichment Factor.

The Pollution Index calculation using the Commerce pedon geochemical background data provided pollution index values indicating “absent” or “low” pollution impacts for zinc and lead and “moderate” pollution impact for cadmium for the Caruthersville series. For the Commerce series the pollution impacts are considered “low” for zinc and lead and “strong” for cadmium. One horizon indicated very strong “pollution impact” for cadmium.

We exercise caution with respect to the pollution index values inferring that these soils are heavy metal impacted, especially for cadmium. The aqua regia digestion concentrations do not support a significant heavy metal accumulation. The upper range for normal concentrations for (i) zinc is $89 \text{ mg}\cdot\text{kg}^{-1}$, (ii) cadmium is $0.60 \text{ mg}\cdot\text{kg}^{-1}$, and (iii) lead is $90 \text{ mg}\cdot\text{kg}^{-1}$. The mean concentrations for the Com-

merce pedons are (i) zinc is $78 \text{ mg}\cdot\text{kg}^{-1}$, (ii) cadmium is $0.60 \text{ mg}\cdot\text{kg}^{-1}$, and lead is $21.5 \text{ mg}\cdot\text{kg}^{-1}$. The mean cadmium level of the Commerce pedons is precisely equivalent to the upper level for cadmium's typical soil distribution, whereas the Commerce pedon's zinc and lead mean concentrations are below the upper limits for a normal soil presentation. The geochemical background values derived from the Wilbur surface samples exhibited small concentrations: (i) zinc at $55 \text{ mg}\cdot\text{kg}^{-1}$, (ii) cadmium at $0.15 \text{ mg}\cdot\text{kg}^{-1}$, and (iii) lead at $14.8 \text{ mg}\cdot\text{kg}^{-1}$, which lead to implication that annual Mississippi River flood prone soils are more cadmium impacted than the Wilbur pedons. The geochemical background values derived from the Commerce reference pedon demonstrate similar pollution index and enrichment factor values. It remains entirely possible that these Mississippi River floodplain soils are receiving cadmium; however, that amount of cadmium in these soils is not necessarily a significant indication for remediation. Future research involving additional samples and continued monitoring of existing sites is warranted.

7. Conclusion

In Missouri, two soil series located along the Mississippi River were sampled for selected transition, post-transition, and metalloid elements. Aqua regia digestion showed that only cadmium presented elevated concentrations when compared to adjacent floodplain soils that do not experience annual Mississippi River flooding. We conclude that cadmium may be accumulating in annual flood prone soils; however, the intensity of the cadmium accumulation is limited. Other soils may show higher cadmium and other elemental concentrations; thus, more sampling of other locations is warranted.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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