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Soil and Plant Tissue Analysis for Lead, Cadmium and Zinc on Impacted Floodplain Soils in East-Central Missouri (USA)

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Abstract

The soil landscape at Washington State Park (Missouri) along the floodplains of the Big River has been documented to be impacted by lead (Pb) generated because of upstream mining activities. Two soil profiles of the Kaintuck soil series at Washington State Park were described for soil morphology and sampled for (i) routine soil characterization, (ii) selected elements using aqua-regia digestion and (iii) a water leach protocol. The aqua regia digestion confirmed that the two soil profiles are Pb impacted; however, the two soil profiles are also impacted with appreciable concentrations of cadmium (Cd), zinc (Zn), silver (Ag), barium (Ba) and possibly copper (Cu). The elements iron (Fe), manganese (Mn), cobalt (Co), nickel (Ni) and arsenic (As) are present in soil concentrations that are considered normal or typical for the Entisol soil order. A water leach protocol was employed to assess the intensity of elemental release to water to infer bioavailability and potential mobility. The elements Pb, Cd, Zn, Ag, Ba and Cu exhibit water release characteristics consistent with impacted soils and the water release concentrations are substantially greater than the reference non-impacted soils. A greenhouse project involving Peas (*Pisum sativm*) was conducted to estimate elemental uptake, including Pb, Zn and Cd. Plant tissue Pb was present at concentrations of 3.0 to 3.6 mg Pb/kg and plant tissue Cd was present at rates of 0.23 to 0.30 mg Cd/kg.

Key words: Lead, cadmium, zinc, Big River, Missouri Valley Types Lead Ores

INTRODUCTION

In the eastern Ozarks of Missouri (USA), Mississippi Valley Type lead ores occur in Paleozoic carbonate rock as galena (PbS), with sphalerite (ZnS) and pyrite (FeS_2) as important auxiliary minerals. On a world-wide basis, lead (Pb^{2+}) abundances vary with the rock type, ranging from 10 to 40 mg Pb kg^{-1} in felsic and argillaceous sediments [1]. Ultramafic and carbonate sediments typically have 0.1 to 10 mg Pb kg^{-1}, whereas the earth's average crustal Pb abundance is 15 mg Pb kg^{-1} [1].

Soil zinc and cadmium concentrations may be a consequence of either anthropogenic activities or mineral weathering of zinc and cadmium bearing minerals and the subsequent migration of zinc and cadmium using geologic and pedogenic pathways. Naturally occurring zinc-bearing minerals include sphalerite (α ZnS), wurzite (β ZnS), zincite (ZnO), smithsonite ($ZnCO_3$), willemite (Zn_2SiO_4) and hemimorphite ($Zn_4Si_2O_7(OH)_2 \bullet H_2O$). Many other zinc-bearing minerals may have small zinc concentrations because of isomorphic substitution; e.g., pyrite (FeS). Naturally occurring cadmium-bearing minerals include: greenockite (CdS), octavite (CdSe), monteponite (CdO). Many other cadmium-bearing minerals may have small cadmium concentrations because of isomorphic substitution; e.g., Zn and Pb ores.

Kabata-Pendias [1] noted that argillaceous sediments generally have greater zinc concentrations (mean of 120 mg Zn/kg) than other sediment types. Zinc concentrations in the surface horizons across soil groups typically range from 60 to 89 mg Zn / kg [1]. Typical global Cd concentrations average near 0.1 mg Cd/kg, with soils from the USA ranging from 0.01 to 2 mg Cd/kg and having a geometric mean of 0.18 mg Cd/kg [1]. Cadmium typically exists in the soil environment, ranging from 0.01 to 0.3 mg Cd/kg in coarse-textured soils and ranging from 0.2 to 0.8 mg Cd/kg in loamy soils [1]. Kabata-Pendias [1] noted that igneous and sedimentary derived parent materials generally have similar cadmium concentrations (mean of 0.1 mg Cd/kg).

LEAD AND SOIL MITIGATION

Aide [2] investigated soils receiving atmospheric deposition of Pb-Zn-bearing mine tailing dust in Missouri. Accumulated soil concentrations of Pb, Cd, Zn, Ag and In were considered impactful and required remediation. Pyrophosphate and EDTA extractions suggested that the vast majority of the Pb and Zn soil pools were not bioavailable; however, given time metal sulfide oxidation should render these elements more bioavailable. Aide and Braden [3] performed simulation of lead immobilization using USEPA software "Minteq", demonstrating the lead precipitation into plumbogummite and other lead-bearing minerals is thermodynamically favored providing the calcium activity is similarly controlled by the solution chemistry.

In southern Missouri, Weber et al [4] amended Pb impacted alluvial soils with triple superphosphate to observe the effectiveness of P application rates on (i) P and Pb loss rates from surface runoff, (ii) Pb accumulation in Tall fescue (*Festuca arundinacea* Schreb; K 31), and (iii) soil Pb speciation. Application rates were P/Pb molar ratios of 0:1, 4:1, 8:1 and 16:1. Rainfall was by rainfall simulation on both unvegetated and vegetated sites. Phosphorus losses attributed to rainfall simulation were greater for the unvegetated sites and for sites with greater P amendment rates. Phosphorus losses attributed to runoff were substantial at 6 months and one-year after P amendment application. Total P and dissolved P remained greater for the 16:1 P:Pb applicate sites. Phosphorus treatments reduced the Pb uptake by the tall fescue. Pyromorphite was shown to be synthesized because of the application amendment. The most optimum ratio for optimizing both (i) pyromorphite synthesis to reduce the Pb bioavailability and (ii) to restrict P runoff was the amendment P/Pb molar ratio of 4:1.

The objective of this research was to document the severity of the lead, cadmium, and zinc contamination on floodplain soils along Big River in east-central Missouri.

MATERIALS AND METHODS

Study Area

The study area is in east-central Missouri, east and southeast of metropolitan St. Louis. The region has a century-long legacy of lead mining and processing within the "lead belt". Big River in one of several tributaries within the Mississippi River watershed that has been impacted by a combination of atmospheric deposition of lead emissions and flood deposition from failed tailing pile retaining walls that permitted massive quantities of lead tailings to enter Big River. The climate is continental humid. Annual rainfall averages 1.14 meters (45 inches). Temperatures are cool in winter (average January high of 6^{0}C) and hot in summer (average June high of 30^{0}C). [https://www.usclimatedata.com/climate/cape-girardeau/missouri/united-states/usmo0144].

The Kaintuck soil series (coarse-loamy, siliceous, superactive nonacid, mesic Typic Udifluvents) consists of very deep, well-drained soils that formed in loamy alluvium on flood plains. The horizon sequence is Ap – C. The site area is in Washington State Park, Missouri, on a broad floodplain adjacent to the Washington State Park's swimming area along Big River (Site 1 (38.08653, -90.68167) and Site 2 (38.08644, -90.68179)). For references purposes four soils of the Wilbur soil series (Coarse-silty, mixed, superactive, mesic Fluvaquentic Eutrudepts) having a total of 20 soil horizons were selected from a non-impacted area at the David M Barton Agriculture Research Center in Cape Girardeau County. The Wilbur series consists of very deep, moderately well-drained soils that formed in silty alluvium. These soils are on flood plains and flood-plain steps.

METHODOLOGY

Two soil profiles of the Kaintuck soil series were excavated, and standard morphology description [5] and chemical characterization was performed (chemical characterization was performed by the University Missouri Fisher Delta Research Center's soil characterization laboratory in Portageville, Missouri).

An aqua regia digestion was employed to obtain a near total estimation of elemental abundance associated with all but the most recalcitrant soil chemical environments. Homogenized samples (0.75g) were equilibrated with 0.01 liter of aqua-regia (3 mole nitric acid: 1 mole hydrochloric acid) in a 35ºC incubator for 24 hours. Samples were shaken, centrifuged and filtered (0.45 µm), with a known aliquot volume analyzed using inductively coupled plasma emission – mass spectrometry (ICP-MS). Selected samples were duplicated and known reference materials were employed to guarantee analytical accuracy.

A water extraction was performed to recover only the most labile or potentially labile fractions. A hot water extraction involved equilibrating 0.5 g samples in 0.02 L distilled-deionized water at 80ºC for one hour followed by 0.45µm filtering and elemental determination using ICP-MS. For the water extraction, selected samples were duplicated, and reference materials were employed to guarantee analytical precession.

The greenhouse project involving the culture of peas in the A horizon extracted from the study area's Kaintuck soil series was conducted. Plants were harvested between the V1 and V2 growth stage. Plant tissue analysis consisted of N, P, K, Mg, Ca, S, Fe, Mn, B, Cu, Zn, Pb and Cd and was determined MidWest Laboratories (Omaha, NB). Plant tissues were oven dried, ground, and digested with a microwave-assisted acid digestion. Analysis was by inductively coupled plasma emission spectroscopy-mass spectroscopy (ICP-MS).

RESULTS AND DISCUSSION

The Kaintuck soil series is predominantly silt loam in texture (49 to 65% silt in Site 1 and 61 to 66% silt in Site 2). Sand content varies from 25 to 42% in Site 1 and 20 to 33% in Site 2 (Table 1). Soil colors are dark brown in the Ap horizon (Site 1) and very dark grayish brown in the Ap horizon (Site 2). Subsurface horizons exhibit dark grayish brown, dark brown and dark yellowish-brown colors, typically with chroma values not typically associated with gleization. Redoximorphic features where present are few fine and faint.

Table 1. Soil morphology for two soil profiles of the Kaintuck soil series

Horizon	Depth (cm)	Texture	Color	Sand %	Silt %	clay %
Site 1						
Ap	13	sil	10 YR 3/3	25	65	10
C1	28	sil	10 YR 3/2	31	60	9
C2	48	sil	10 YR 3/4	32	51	17
C3	69	sil	10 YR 4/3	28	57	15
C4	91	sil	10 YR 3/3	25	59	16
C5	122	sil	10 YR 3/4	35	53	12
C6	135	l	10 YR 4/4	38	49	13
C7	152	sil	10 YR 4/2	42	52	6
Site 2						
Ap	8	sil	10 YR 3/2	33	61	6
C1	14	sil	10 YR 3/2	27	66	7
C2	22	sil	10 YR 3/4	20	66	14
C3	28	sil	10 YR 4/2	20	65	15
C4	36	sil	10 YR 3/3	24	63	13
C5	45	sil	10 YR 3/3	27	64	9
C6	51	sil	10 YR 3/3	28	62	10
C7	60	sil	10 YR 3/4	28	60	12

Sil is silt loam (most of the silt loam values were borderline with sandy loam or loam), l is loam

All soil structures were weak, fine and medium, subangular blocky.

Soil chemical characterization provides neutral to slightly alkaline pH values (Table 2). Soil organic matter is greatest in the Ap horizons and generally declines with increasing soil depth. The soil organic matter contents of the Ap horizons are 3.7% and 3.5% for the respective Ap horizons. Soil phosphorus values are slightly greater than the standard Missouri recommended value of 50.4 kg / ha (45 lbs P / acre) for a 100% fertility index ranking. Phosphorus and SO_4-S are greatest in the Ap horizons and decline somewhat with soil depth, paralleling the soil organic matter contents. For the two combined soil profiles the soil organic matter content (SOM) was strongly correlated with the Bray1 phosphorus content (r^2 = 0.945). The cation exchangeable complex is dominated by calcium and magnesium. Exchangeable potassium levels are appropriate for a well-suited agricultural soil. The total acidity is zero, as expected given the neutral to slightly alkaline pH levels. The cation exchange capacity is generally moderate (12 to 18 cmol/kg).

Table 2. Soil chemical properties for two soil profiles of the Kaintuck soil series

Horizon	pH	SOM	P	SO4-S	Ca	Mg	K	Na	CEC
		%	lbs/ac	mg/kg	------------------cmol/kg---------------				
Site 1									
Ap	7.1	3.7	65	11.3	10.68	3.27	0.61	0.02	14.6
C1	7.4	2.7	47	13.1	11.18	3.60	0.37	0	15.1
C2	7.4	2.0	40	9.5	9.75	3.08	0.26	0	13.1
C3	7.6	2.0	28	7.4	9.95	3.06	0.22	0.01	13.2
C4	7.5	1.5	21	8.0	9.08	2.82	0.20	0	12.1
C5	7.7	1.1	15	5.7	8.03	2.61	0.19	0.01	10.8
C6	7.5	1.1	16	6.8	8.65	2.47	0.19	0	11.3
C7	7.4	1.1	17	11.8	7.90	2.46	0.20	0	10.6
Site 2									
Ap	7.5	3.5	57	10.5	10.78	3.64	0.67	0.02	15.1
C1	7.7	2.2	35	6.4	9.55	3.02	0.32	0	12.9
C2	7.7	1.9	30	6.8	10.25	3.21	0.22	0	13.7
C3	7.6	1.8	24	4.5	9.75	3.03	0.20	0	13.0
C4	7.7	1.7	18	5.5	9.90	2.89	0.22	0	13.0
C5	7.8	1.3	14	4.0	8.65	2.75	0.19	0	11.6
C6	7.8	1.2	12	5.5	8.08	2.39	0.17	0	10.6
C7	7.5	1.1	16	8.5	7.95	2.20	0.18	0	13.3

SOM is soil organic matter by loss on ignition

P is Bray1-Phosphorus

SO4-S is sulfate-S by KCL extraction

Ca, Mg, K, Na are exchangeable cations by ammonium acetate (pH 7) extraction

CEC is cation exchange by summation of exchangeable cations (total acidity was zero for all horizons)

The aqua regia digestion protocol is intended to be a near total elemental estimation. Iron (Fe) and manganese (Mn) in soils are typically associated as oxides and oxyhydroxides; however, Fe and Mn may also occur at lattice constituents of phyllosilicates and other minerals. The soil profile distribution of Fe and Mn in the Kaintuck pedons is rather uniform and somewhat typical for Entisols (Table 3). The total Fe and Mn contents throughout the Kaintuck soil profiles are slightly greater than the non-impacted reference Wilbur soil series and the observed Fe and Mn differences are largely attributed to natural soil heterogeneity.

Cadmium (Cd) and zinc (Zn) concentrations in the Kaintuck pedons are indicative of soil impact and the total Zn and Cd contents decline somewhat with increasing soil depth. Comparison of the near total Zn and Cd contents with the non-impacted Wilbur pedons illustrates the magnitude of the environmental impact. Lead concentrations in the Kaintuck pedons range from 1,590 to 2,710 mg Pb/kg for Site 1 and range from 1,470 to 3,580 mg Pb / kg in Site 2. The reference Wilbur pedons have a mean of 10.8 mg Pb/kg, clearly indicating the intensity of the Pb impact in the Kaintuck pedons. Silver (Ag) concentrations in the Kaintuck pedons are also greater than the non-impacted reference soils; however, the actual concentrations are all less than 1 mg Ag kg^{-1}. Cobalt (Co) varies between 18.4 to 22.5 mg Co kg^{-1}, nickel (Ni) varies between 21.1 to 25.7 mg Ni kg^{-1} and copper (Cu) varies between 58.2 to 80.1 mg Cu kg^{-1}. The concentrations of Co, Ni and Cu are greater than the respective concentrations of the non-impacted reference soils; however, these elemental concentrations do not reach a critical level. Arsenic (As) concentrations range from 6.9 to 9.8 mg As kg^{-1} and are roughly equivalent to those of the non-impacted reference soils. Barium (Ba) is also considered to be present at concentrations greater than typically observed for Entisols and significantly greater than those of the non-impacted reference soils. Interestingly, the highest Ba concentration expressions reside in the C3 to C5 horizons.

Table 3. Soil aqua-regia digestion for selected elements for two profiles (Kaintuck soil series)

Horizon	Fe	Mn	Zn	Cd	Ag	Pb	Co	Ni	Cu	As	Ba
		g/kg	g/kg	---------------------------------mg/kg-----------------------------------							
Site 1											
Ap	21.6	1.86	544	7.32	0.797	1940	20.7	23.3	69.7	7.9	723
C1	21.3	1.92	557	8.41	0.811	1950	22.4	23.8	69.3	9.0	841
C2	22.4	2.04	531	7.43	0.803	1930	22.5	23.8	68.7	8.9	838
C3	22.0	1.84	504	7.15	0.694	1670	21.6	24.7	64.5	9.5	1120
C4	22.6	1.84	466	6.04	0.648	1590	20.9	24.4	62.7	9.8	1300
C5	20.7	1.82	371	4.84	0.525	1670	19.3	21.1	58.7	8.6	988
C6	19.1	1.64	343	4.17	0.481	2030	19.9	23.5	66.7	8.0	878
C7	17.1	1.33	223	2.07	0.304	2710	19.6	25.0	78.2	6.9	484
Site 2											
Ap	21.5	1.94	520	7.60	0.696	1890	21.1	22.6	66.1	8.6	719
C1	22.3	2.00	533	8.15	0.829	1960	22.9	24.3	69.7	8.9	861
C2	21.4	1.90	533	7.60	0.856	1820	22.3	24.4	66.0	8.4	848
C3	22.4	1.89	485	6.91	0.681	1590	21.4	25.4	63.7	9.3	1130
C4	23.6	1.82	449	5.61	0.555	1470	20.2	23.4	59.0	9.6	1350
C5	20.9	1.70	398	5.54	0.549	1650	19.6	22.7	58.2	8.5	1140
C6	19.6	1.62	378	5.09	0.473	1910	18.4	21.7	56.7	7.6	943
C7	17.6	1.45	236	3.28	0.360	3580	20.2	25.7	80.1	7.0	495
Wilbur Soil Series (Reference from 4 profiles having 20 horizons)											
Mean	15.4	0.78	39.2	0.10	0	10.8	7.5	14.9	12.5	4.1	156
CV%	22.0	54.6	27.1	71.0	0	30.3	37.4	27.6	30.7	36.2	33

CV% is the percent coefficient of variation.

The water leach extract protocol is intended to be an estimate of the amount of an element that may be released to water, thus the water leach is an indicator of bioavailability and potential mobility. The release of an element to water may occur as the dissolved species, as an ion-pair, or as an inorganic or organic complex. Iron and manganese are presented simply as reference. Zinc, Cd, Ag, Cu and Pb show substantial release to water (Table 4), suggesting that small portions of the total concentration pools of these elements are bioavailable and potentially mobile. The elements Zn, Cd, Ag, Cu, Ba and Pb exhibit water-release concentrations that are substantially greater than the reference Wilbur pedons. Nickel and As show greater water leach concentrations than the corresponding non-impacted soils; however, the concentration differences are small and for As are not significantly different.

Table 4. Soil water extraction for two soil profiles of the Kaintuck soil series

Horizon	Fe	Mn	Zn	Cd	Ag	Pb	Co	Ni	Cu	As	Ba
	----mg/kg----		---------------------------------μg/kg------------------------------------								
Site 1											
Ap	21	1.17	1410	28.2	0.9	2060	35	177	785	51	892
C1	68	1.80	2810	40.5	1.3	4300	50	222	1010	54	1660
C2	32	1.01	2150	32.9	0.5	3750	22	124	639	39	1420
C3	19	1.03	2060	34.3	0.3	3820	20	102	537	34	1900
C4	18	1.02	1870	31.4	0.3	4150	19	87	465	33	2200
C5	18	1.02	1950	27.8	0.5	5550	19	69	404	28	2180
C6	19	1.32	1610	23.5	0.5	6630	22	74	462	28	2140
C7	15	0.92	800	10.0	0.5	8320	16	66	441	18	1880
Site 2											
Ap	39	1.22	2100	29.0	2.0	3200	31	165	665	51	999
C1	19	1.02	2050	32.6	0.4	3920	21	112	548	35	1340
C2	21	0.96	2060	33.4	0.4	3630	19	100	503	34	1480
C3	18	0.94	2160	31.2	0.2	3730	18	89	483	31	2100
C4	17	0.96	1960	29.7	0.3	4020	29	87	630	31	2290
C5	17	1.16	2070	30.0	0.3	5560	20	73	386	29	2340
C6	15	0.94	1900	30.6	0.5	6710	17	70	356	23	2250
C7	16	0.86	760	16.8	0.5	10900	14	75	511	19	3130
Wilbur Soil Series (Reference from 4 profiles having 20 horizons)											
Mean	--	5.5	56	0.98	ND	33.4	23	69	111	22	760
CV%	--	75	47	70	--	33	43	57	40	41	35

Fe was not determined for the Wilbur pedons, ND is below detection level.

CV% is the percent coefficient of variation.

Greenhouse Culture of Peas to Estimate Plant Availability of Pb, Zn and Cd

The purpose of the greenhouse culture of peas was to assess nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, iron, manganese, boron, copper, zinc, cadmium and lead uptake patterns. The plant tissue nutrient concentrations of nitrogen and phosphorus are considered deficient, whereas potassium is excessive, and Mg, Ca and S are considered sufficient [6] (Table 5). The plant tissue micronutrient concentrations of manganese, boron, and copper are considered deficient, whereas zinc is excessive [6] (Table 5). Lead and Cd concentrations range from 3.0 to 3.6 mg Pb/kg and 0.23 to 0.30 mg Cd/kg, respectively. The total amount of Pb in the plant tissue was substantially less than Zn, the implication is that the plant availability of Pb is significantly less than that of Zn. We speculate that a large portion of the Pb may still reside as PbS.

Table 5. Mean plant tissue composition of peas (*Pisum sativm*) cultured in Pb impacted soil.

N	P	K	Mg	Ca	S	Fe	Mn	B	Cu	Zn	Pb	Cd
--------------------g kg^{-1}----------------------					-------------------------mg kg^{-1}------------------------							
34.3	2.4	47.0	3.5	13.1	2.1	69	30	16	7	48	3.3	0.27

Mean of 4 plants

Coefficient of Variation (CV%) for Pb is 7.3% and for Cd is 10.9%

FUTURE RESEARCH INTENTIONS

We desire to amend these lead impacted soils with triple superphosphate fertilizer [(0-45-0) 15% Ca] at Pb:P molar ratios of (i) 1:0 (untreated check), (ii) 1:4, (iii) 1:8 and (iv) 1:16. Given the magnitude of the P required to render Pb to plumbogummite, protocols are formulated to measure soil P leaching and surface P transport. Lead availability will be estimated using protocols in Weber et al [4].

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