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Lead Immobilization Using Triple Superphosphate in Impacted Floodplain Soils in East-Central Missouri (USA)

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Abstract

East-central Missouri has a legacy of lead (Pb) mining and ore processing. Localized landscapes show the impact of these mining and ore processing activities, with multiple soils having high concentrations of Pb and associated ore-bearing heavy metals. Lead-bearing soil samples amended in 2015 with four rates of triple superphosphate (TSP) were again assessed in 2019 for plant uptake using tall fescue (*Schedonorus arundinaceus*; Kentucky 31). Tall fescue was greenhouse grown, harvested, digested and analyzed with inductively coupled plasma emission -mass spectroscopy (ICP-MS). Lead plant tissue concentrations show smaller Pb concentrations with increasing TSP amendment rates. Zinc and cadmium also show reduced plant tissue concentrations with increasing TSP-amendment rates. The plant uptake reduction observed for Pb was most likely associated with Pb-P soil chemistry interactions, whereas the observed Cd and Zn plant tissue reductions were more likely associated with root uptake antagonism mechanisms. This manuscript reports that Pb:P molar ratio = 1:4 is an optimal compromise to (i) reduce TSP induced Pb-bioavailability and (ii) reduce the specter of surface water eutrophication that would be expected with greater TSP amended rates.

Keywords: Lead, Cadmium, Zinc, Big River, Missouri Valley Types Lead Ores

INTRODUCTION

In east-central Missouri, Aide [1] investigated soils receiving atmospheric deposition of Pb-Zn-Cd mine tailing dust and documented that these soils required remediation. Lead (Pb) concentrations were in excess of 2,000 mg/kg in the A horizons of the Caneyville and Hildebrecht soil series. Cui et al [2] established soil column experiments

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involving Pb-bearing soil amended with hydroxyapatite or KH_2PO_4 and then leached the soil columns with simulated acid rain. The KH_2PO_4 amended soil decreased the Cu, Pb and Cd leachate concentrations, whereas the hydroxyapatite amended soil columns demonstrated increased Cu, Pb and Cd leachate concentrations. Both phosphate bearing amendments reduced exchangeable Pb, Cu and Cd. Yoon et al [3] employed soil column experiments with amendments of phosphate rock and phosphoric acid. The Pb/P molar ratio was established at 1:4. Phosphate amendments reduced the leachate Pb concentrations below the USEPA drinking water standard of 15 µg Pb L^{-1}. Reduced Pb soil column migration was reduced within a range of 73 to 79%. Jalali and Moharami [4] constructed soil columns having soils amended with diammonium phosphate (DAP). The DAP amendment increased the mobility of Cd, Cu, Ni and Zn, whereas the mobility of Pb was reduced. Selective extraction protocols demonstrated that the more bioavailable exchangeable and carbonate soil fractions showed reduced Pb concentrations, which was proposed as the cause of the reduced Pb mobility.

Molina et al [5] performed a batch experiment featuring a Chilean Mollisol having single component and multi-component (Cd, Cu, Ni, Pb and Zn) soil-solution equilibria. All metal adsorption isotherms conformed to a Langmuir expression. Multi-component systems expressed decreased maximum adsorption capacities and reduced partition coefficients relative the single component systems. The differences were attributed to species competition. Lead and Cu showed higher selectivity than Cd, Ni and Zn. Similarly, in a column experiment Devesa-Rey et al [6] observed Pb and chromium(III) sorption in soils. The metal:P ratios were 1:0, 1:0.1 and 1:1. The effect of P was to increase Pb adsorption. Kilgour et al [7] performed a column leaching experiment using Pb, antimony (Sb) and arsenic (As) impacted soils derived from a fire-arms range. Using triple superphosphate, the leachate exhibited increased concentrations of Sb, As and Pb; however, the Pb bioavailability was reduced. Karathanas et al [8] applied biosolids to undisturbed soil monoliths to assess whether these biosolids influenced subsurface soil leaching. Metal leaching of Zn and Cu were similar, and both were more likely to leach than Pb. Metal leaching was more pronounced with increasing soil acidity; however, greater applications of biosolids supported greater metal leaching.

Kim and Lee [9] investigated the role of chelates on the phytoextraction potential of barnyardgrass (*Echinochloa crus-galli)*. The presence of EDTA (ethylenediaminetetraacetic acid) increased Cd, Cu and Pb uptake by barnyardgrass and supported greater Cd, Cu and Pb leaching; however, citric acid also supported Cd, Cu and Pb uptake by barnyardgrass but leaching of these elements did not occur. Thus, citric acid may be preferred when metal leaching is not desired. Michopoulos [10] observed multiple forested sites for forest floor leaching of Pb to deeper soil horizons. He observed that low molecular weight organic matter from humic horizons did not promote Pb leaching. The low pH of these forest floors supported fulvic acid binding to the inorganic constituents and thus limited the fulvic acid-Pb leaching potential.

Kalsi et al [11] cultured Indian Mustard (*Brassica juncea* (L.) Gern) in Pb-bearing soil with (i) silt and clay, (ii) agriculture lime, (iii) and farmyard manure amendments. Increasing additions of these amendments reduced the Pb uptake, with the greatest uptake reductions associated with silt/clay followed by agriculture lime. Yuan-jie et al [12], in a column leaching project and a field soil leaching project, added $MnFe_2O_4$ microparticles and observed that the leaching Cu, Pb, Zn and As was reduced.

Yang et al [13] cultured rice (*Oryza sativa* L.) in a Pb impacted paddy soil that was amended with $CaCO_3$, metakaolin, and fused Ca-Mg-phosphate. The soil exchangeable concentrations of Pb and Cd were smaller because of the amendment and the brown rice Pb, Cd and As concentrations were similarly reduced. Huang et al [14] treated Pb-bearing soil with (i) bone meal, (ii) phosphate rock, (iii) superphosphate, and (iv) $CaCO_3$. The phosphate treatments and the $CaCO_3$ treatment supported an increase in the soil's residual fraction and reduced the Pb content associated with the Toxicity Characteristic Leaching Procedure Leachate test.

Liang et al [15] developed a "pump and treat" protocol for groundwater improvement; wherein, dairy-manure biochar and phosphate rock immobilized Pb and Cd. Brown et al [16] in Oklahoma employed and evaluated diammonium phosphate (DAP), biosolids, biosolid compost and Al- and Fe-water treated residues as soil amendments for immobilizing Pb. All treatments were demonstrated to be effective Pb immobilizing amendments. Similarly, in Idaho, Strawn et al [17] investigated soils impacted by mining activities and which were demonstrated to be enriched in noncrystalline Fe- and Mn-oxides. Lead solubility was shown to be undersaturated with respect to chloropyromorphite and plumbogummite, a result attributed to the large surface area and adsorption properties of the Mn-oxides.

Aide and Braden [18] 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 [19] amended the Pb-impacted alluvial Kaintuck soil, located on floodplain of the Big River with triple superphosphate [$Ca(H_2PO_4)_2$] to estimate the effectiveness of P application rates on: (i) P and Pb loss rates from surface runoff, (ii) Pb accumulation in tall fescue (*Schedonorus arundinaceus*; Kentucky 31), and (iii) soil Pb speciation and the precipitation likelihood of pyromorphite and plumbogummite. Rainfall simulation on both unvegetated and vegetated sites provided evidence for phosphorus surface transport, especially for unvegetated sites and for sites with greater P amendment rates. Phosphorus losses attributed to runoff were substantial after 6 months and one-year after P amendment application. Total P and dissolved P were greater for the 1:16 Pb:P TSP-amended sites. Phosphorus treatments reduced the Pb uptake by the tall fescue, with an observed 50% reduction for the Pb:P 1:4 amended rate. The most optimum Pb:P 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. Scheckel et al [20] provided an impressive review of promoting Pb mitigation using various phosphate sources.

The objectives of this research were: (i) to continue to document the lead, cadmium, and zinc contamination on floodplain soils along Big River in east-central Missouri, and (ii) prepare a scenario for triple superphosphate amendment to reduce lead soil bioavailability and design mitigation strategies to reduce phosphate transfer to fresh water resources. The soil materials were from the initial study by Weber et al [19].

MATERIALS AND METHODS

Study Area

The study area is in east-central Missouri and has a century-long legacy of lead mining. Big River in one of several flood-prone tributaries within the Mississippi River watershed that has been impacted by lead-bearing alluvial deposition. Atmospheric deposition of lead-bearing dust from non-vegetated tailing piles and Pb-ore processing is also a concern. The climate is continental humid with annual rainfall averaging 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 sampling of the Kaintuck soil was performed by Weber et al [19]. The soil samples that were amended with triple superphosphate from Weber's [19] project was subsequently provided to the authors of this manuscript to replicate some of the data after a five-year equilibration interval.

Methodology

A routine soil test involving (i) soil organic matter by loss on ignition, (ii) phosphorus by the Bray 1 test, exchangeable Ca, Mg, K and Na by ammonium acetate (pH 7) extraction followed by atomic absorption spectrophotometry, sulfate-S extraction with 2 molar KCl, pH and total acidity. The routine soil analysis was performed by the soil testing laboratory at the University Missouri-Columbia.

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 used 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 a cool-season perennial C3 grass species called tall fescue variety "K-31" (*Schedonorus arundinaceus*; Kentucky 31). The experimental design was a completely randomized design involving four treatments, each with four replications, based on the Pb:P molar ratios (untreated check, 4, 8, and 16). The treatments were performed by Weber et al [19] for their research project, subsequently stored and provided to the authors of this manuscript for investigation after an equilibration interval of five years. The tall fescue was harvested after two months of post-emergence growth. Plant tissue analysis consisted of N, P, K, Mg, Ca, S, Fe, Mn, B, Cu, Zn, Pb and Cd and was determined by 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). Plant tissue sufficiency levels for tall fescue were selected from Bell and Kovar [22].

RESULTS AND DISCUSSION

Routine Soil Characterization

Routine soil chemical characterization (Table 1) provides a neutral to slightly alkaline pH, consistent with the pH values reported by Weber [19]. Soil organic matter ranges from 3.7 to 3.5%. The total acidity is zero or 0.5 cmol/kg, as expected given the neutral to slightly alkaline pH levels. Exchangeable Ca is typical for the Kaintuck series, whereas exchangeable Mg is substantially greater for the Pb:P ratios of 1:8 and 1:16. Bray 1 P values reflect the phosphorus amendments, with the Pb:P ratios substantially greater with increasing phosphorus amendment rates. The highest rate of soil P was in excess of 2,242 kg/ha (2,000 lbs/ac). Sulfate-S concentrations are greater in phosphorus amended samples, suggesting the phosphorus may have displaced adsorbed sulfate or PbS oxidation yielded sulfate.

Table 1. Routine soil chemical properties for the soil samples from the Kaintuck series.

Pb:P	pH	Acidity	SOM	Bray-1 P	Ca	Mg	K	Na	CEC	SO4-S
1:0		cmol/kg	%	mg/kg	--------------- mol/kg	--------------------				mg/kg
1:4	7.6	0	3.7	33	11.55	3.77	0.30	0.40	16.0	85
1:8	7.5	0	3.5	422	10.80	3.97	0.34	0.47	15.6	161
1:16	7.5	0	3.4	698	11.90	19.83	0.32	0.52	32.6	147
1:0	7.0	0.5	3.6	1037	10.33	19.99	0.33	0.58	31.7	182

Soil 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

Aqua Regia Digestion

The aqua regia digestion revealed elevated zinc, silver, cadmium and lead soil concentrations (Table 2). Manganese had a mean concentration of 1,695 mg/kg, corresponding with a Mn concentration of 1980 mg/kg for Weber et al (2015) [19]. The mean Pb concentration was 1,900 mg/kg and the mean Cd concentration was 8.8 mg/kg, both metal values implying the samples are strongly impacted. The mean Zn concentration was 604 mg/kg, indicting the soil samples were impacted. Similarly, Weber et al [19] had mean concentrations of 634 mg/kg, 10.6 mg/kg, and 2,190 mg/kg for Zn, Cd and Pb, respectively. Uranium soil concentrations increase from 0.8 mg/kg for the untreated check to 6.9 mg/kg for the Pb:P =1:16 amended samples, suggesting that U was present in the TSP.

Table 2. Aqua regia digestion of selected transition metals and U (mg/kg)

Pb:P	Mn	Fe	Co	Ni	Cu	Zn	Mo	Ag	Cd	Pb	U
1:0	1,750	21,900	22	25	67	615	0.7	0.9	8.1	1,930	0.8
1:4	1,710	21,400	21	27	61	604	0.7	0.9	8.3	1,890	2.5
1:8	1,640	21,600	20	25	60	594	0.7	0.8	8.7	1,890	4.3
1:16	1,680	20,900	21	26	60	605	0.8	0.8	10.3	1,900	6.9
Mean	1,695	21,460	21	26	62	604	0.7	0.8	8.8	1,900	3.6
STD	46	420	1	0.7	3.5	8.6	0.06	0.04	1	19	2.6
Detection	1	100	0.1	0.1	0.2	0.1	0.01	0.002	0.01	0.1	0.1

STD is standard deviation, Detection is the ICP-MS detection limit.

The aqua regia digestion soil concentrations for selected alkali, alkaline earth and P are presented in Table 3. Sodium, Mg, K, and Ba concentrations do not significantly vary because of the TSP amendments. Barium has a mean sample concentration of 940 mg/kg in Weber et al [19], slightly greater than our sample mean of 740 mg/kg. Phosphorus demonstrates a regular concentration increase in accordance with phosphorus rate additions.

Table 3. Aqua regia digestion of selected alkali, alkaline earth and phosphorus (mg/kg)

Pb:P	Na	Mg	Ca	K	Sr	Ba	P
0	230	18,000	34,700	1,500	18	740	500
4	270	16,700	34,700	1,700	28	785	1,940
8	320	18,100	37,300	1,700	36	728	3,340
16	410	18,600	38,900	1,800	50	706	5,710
Mean	310	17,900	36,400	1,700	33	740	2,900
STD	80	800	2,100	200	14	33	2,200
Detection	10	100	100	100	0.5	0.5	10

STD is standard deviation

Water Extract Concentrations

The water extract protocol estimates the intensity of soil release of an elemental species to the aqueous phase, thus to a first approximation it is a measure of plant availability. We realize that this protocol does not estimate the soil's capacity to buffer the soil solution. The water leach concentrations for Mn, Fe, Cu, Zn, Cd, and Pb do not show a consistent trend based on the Pb:P ratio, whereas Co, Ni, Mo and U tend to show concentration increases that correspond to TSP amendment rates (Table 4). Similarly, the Na, Mg, Ca, K show concentration increases that correspond to TSP amendment rates, whereas Sr shows no relationship and Ba shows reduced concentration concentrations with increasing TSP amendment rates (Table 5).

Table 4. Water extract of selected transition metals and U (µg/kg) (ppb)

Pb:P	Mn	Fe	Co	Ni	Cu	Zn	Mo	Cd	Pb	U
1:0	1,900	6,000	37	82	487	1,630	7	27.3	3,700	0.7
1:4	2,000	9,000	51	231	587	1,930	9	30.8	4,060	15.3
1:8	1,460	7,000	21	119	455	1,550	12	29.0	3,270	25.5
1:16	2,870	6,000	163	207	396	1,522	32	32.2	3,560	29.4
Mean	2,058	7,000	68	160	481	1,658	15	30	3,648	17.7
STD	590	1,400	65	71	80	188	12	2.1	328	12.8
Detection	1	1,000	1	3	3	10	1	0.2	1	0.1

STD is standard deviation, Detection is the ICP-MS detection limit.

Table 5. Water extract of selected alkali, alkaline earth (mg/kg)

Pb:P	Na	Mg	Ca	K	Sr	Ba
1:0	51	54	167	36	0.21	1.11
1:4	71	58	142	36	0.25	0.71
1:8	98	130	241	45	0.38	0.49
1:16	128	237	259	44	0.29	0.31
Mean	87	120	202	40	0.28	0.66
STD	33	86	57	5	0.08	0.35
Detection	5	2	5	5	0.001	0.001

STD is standard deviation

The mean: standard deviation for Li, Rb, and Cs are 8: 2 µg/kg, 27: 3 µg/kg, and 0.2: 0.1 µg/kg, respectively.

Tall Fescue Plant Tissue Concentrations

Tall fescue plant tissue concentrations are presented in Tables 6a and 6b. The plant tissue sufficiency levels for tall fescue are 2.8 to 3.8% for N, 0.26 to 0.40% for P and 2.5 to 3.5% for K [22] and these values imply that the presented N, P and K concentrations are not plant growth limiting. Analysis of variance ($\alpha = 0.05$) suggests that N, K, Mg, S, Fe, Mn, B, and Cu do not show significant differences; whereas P, Ca (P-value = 0.0019), Zn (P-value = 0.0004), and Cd (P-value = 0.001) show at least one treatment is different at the $\alpha = 0.05$ level of significance. As expected, plant tissue P concentrations increase with greater TSP amendment rates (P-value = 6.7 E-8), whereas Ca, Zn and Cd plant tissue concentrations demonstrate smaller plant tissue concentrations, especially at the Pb:P ratios of 8 and 16. Given that Ca is the dominant cation in TSP, then root uptake antagonism rather than soil chemistry is likely involved to explain the reduced plant tissue Ca concentrations at the greater Pb:P ratios.

Zinc and Cd may show reduced tall fescue concentrations at the higher Pb:P amendment rates because of plant root uptake physiology and reduced root to shoot transmission rather than soil availability. Watts-Williams et al [23] observed phosphorus and zinc antagonism on Tomato (*Solanum lycopersicum* L). They documented that Zn and P uptake was enhanced by zinc phosphate-carbonate and that mycorrhizal associations supported preferential P uptake, whereas the lack of mycorrhizal associations supported the preferential uptake of zinc. Eissa and Ahmed [24] observed nutrient uptake of four species of *Atriplex* plants after applications of urea and superphosphate. Superphosphate applications suppressed Zn, Cd and Pb uptake, whereas urea increased stem concentrations of Zn and P. Enhanced root P and Ca concentrations limited the translocations of metals into the stem. Zhu et al [25] investigated growth chamber grown cultivars of wheat (*Triticum aestivum* L) to assess the antagonistic influence of P on Zn uptake. Zinc had little influence on P uptake; however, increased P availability supported Zn uptake reduction. Wang et al [26] observed that foliar Zn applications reduced Cd uptake in rice (*Oryza sativa* L).

Plant tissue Pb concentrations show significant analysis of variance ($\alpha = 0.06$) differences, in that at least one treatment is different. Weber et al [19] showed that tall fescue cultured in the same amended soils demonstrated Pb concentration reduction of 50% in the Pb:P = 4 samples when compared to the untreated check. However, their mean Pb concentrations in tall fescue were 4.2, 2.0, 1.7 and 0.5 for the Pb:P amended rates of untreated check, 4, 8 and 16, respectively. Thus, the observed plant tissue concentration differences between Weber [19] and this study may be attributed different greenhouse lengths of growing time.

Figure 1 displays the tall fescue plant tissue concentrations by Pb:P treatments with inclusion of the experimental units. The Pb:P = 16 treatment possess one experimental unit with an appreciable tall fescue Pb concentration relative to the other three experimental units. One possible explanation is that when the TSP was surface applied in the field, inadequate mixing occurred because of tractor driven tillage.

Table 6a. Tall Fescue macronutrient content (mean: std in percent)

Pb:P	statistics	N	P	K	Mg	Ca	S
1:0	Mean	4.67	0.33	4.37	0.91	1.33	0.62
	STD	0.27	0.04	0.36	0.08	0.13	0.11
1:4	Mean	4.72	0.62	4.17	1.08	1.36	0.68
	STD	0.27	0.03	0.12	0.16	0.31	0.24
1:8	Mean	4.68	0.65	4.15	1.01	0.95	0.47
	STD	0.43	0.04	0.16	0.03	0.05	0.06
1:16	Mean	4.27	1.05	4.38	1.01	0.83	0.62
	STD	0.23	0.13	0.17	0.09	0.06	0.07

Note: STD is standard deviation

Table 6b. Tall Fescue micronutrient content (mean: std in mg/kg)

Pb:P	statistics	Fe	Mn	B	Cu	Zn	Pb	Cd
1:0	Mean	159	754	12	20	229	19.9	4.8
	STD	11	238	1	2	32	6.9	0.8
1:4	Mean	196	927	10	26	259	12.3	3.9
	STD	100	84	1	4	19	9.6	0.4
1:8	Mean	140	765	9	21	188	4.6	2.8
	STD	27	43	1	0	9	2.8	0.3
1:16	Mean	150	605	11	22	180	7.3	3.4
	STD	46	13	2	3	15	9	0.6

Note: STD is standard deviation

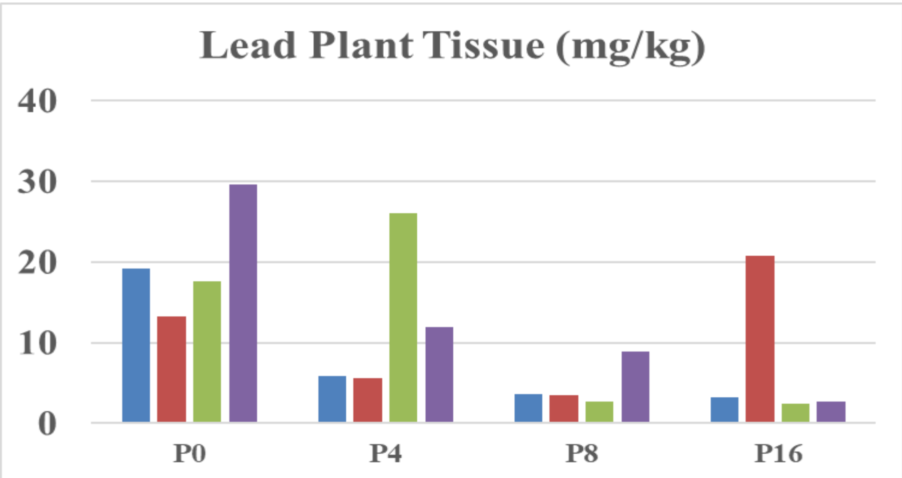

Figure 1. Lead plant tissue concentrations in tall fescue cultured in soil having Pb:P ratio of 1:0, 1:4, 1:8, and 1:16, respectively

CONCLUSION

The aqua regia digestion of soil samples indicates that the soil is strongly Pb, Zn and Cd impacted. The uptake of Pb by tall fescue is generally reduced with TSP amendments. Our assessment is that the Pb:P amendment rate of 1:4 is suitable as a first approximation for reducing Pb bioavailability in these soils and limiting the specter of surface transport of P to adjacent fresh-water resources.

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