Restoration and Risk Reduction of Lead Mining Waste by Phosphate-Enriched Biosolid Amendments

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Abstract

Lead (Pb) contamination in environment has been identified as a threat to human health and ecosystems. In an effort to reduce the health and ecological risks associated with Pb mining wastes, a field study was conducted to stabilize Pb using phosphate (P)-enriched biosolid amendments in contaminated mining wastes (average of 1004 mg Pb kg⁻¹) located within the Jasper County Superfund Site, southwest Missouri. Experiments consisted of six treatments, including Mizzou Doo (MD); Spent mushroom compost (SMC); Turkey litter compost (TLC); Composted chicken litter (CCL); Composed sewage sludge (CSS); and Triple superphosphate (TSP). Tall fescue seeds were planted following treatments and soil and plant samples collected and analyzed 8-10 years post treatment. Results indicated that all biosolid treatments resulted in effective reductions of bioaccessible, leachable and phytoavailable Pb in the treated waste. The treatments had no toxicological effect to soil microbial community. Analysis of the Pb fractionation revealed that the Pb risk reduction was accomplished by transforming labile Pb to relatively stable species through chemical stabilization reactions as induced by treatments. The solid-phase microprobe analysis confirmed the formation of pyromorphite or pyromorphite-like minerals after treatment. Among the six amendments examined, SMC and MD treatments were shown most effective in context of Pb stabilization and risk reduction. This study demonstrated that the efficacy of Pb stabilization and risk reduction by P-enriched biosolid amendments was long-term and environmental-sound, which could be potentially applied as a cost-effective remedial technology to restore contaminated mining site and safeguard human health and ecosystems from Pb contamination.

Introduction

Heavy metal contamination in natural environments such as lead (Pb) resulting from various human operations has been identified as a serious threat to human health and ecosystem because of its human toxicity and persistence in environment¹. In Jasper County, southwestern Missouri of the United States, a survey indicated that 14% of children under the age of 7 years living in the mining community were found to have an elevated blood Pb level higher than 100 µg L⁻¹, which was directly associated with Pb contamination in soil and mining waste resulting from mining and smelting activities². The Pb contamination in environment has also shown adverse impacts on wildlife³, surface and groundwater quality, and vegetation⁴.

The health and ecological risks of Pb in environments were found strongly associated with Pb bioavailability in the gastrointestinal (GI) tract and mobility in ecosystems, which were highly dependent on the chemical or mineralogical forms of soil Pb and their solubility^{5,6}. It was believed that the transformation of soil Pb from labile species to insoluble forms would substantially reduce the Pb health and ecological risks.

In situ soil treatment using phosphate or organic materials has been evaluated as a cost-effective and environmental-sound remedial technology for stabilizing heavy metals in contaminated soil and reducing

the health and ecological risks. Pyromorphites $[\text{Pb}_5(\text{PO}_4)_3(\text{OH}, \text{Cl}, \text{F}...)]$ or pyromorphite-like minerals were considered biologically stable and chemically insoluble under the surface soil conditions⁷. Previous studies of soil Pb remediation have been much focused on inducing the transformation of labile soil Pb to pyromorphites through phosphate-based amendments, including phosphate rocks⁸, synthetic hydroxapatite^{9,10}, and phosphoric acid^{11–13} and proven effective for soil Pb immobilization and risk reduction. The formation of pyromorphites in Pb-contaminated soil as induced by phosphate amendments has been confirmed. Applications of biosolids such as municipal sewage sludge, composts, manures, or peats have also shown to effectively stabilize Pb and reduce the Pb bioavailability in soil through the mechanisms of immobilization, adsorption or complexation reactions^{14–17}. As said, in situ Pb immobilization was an approach that converts soil Pb to relatively insoluble Pb species induced by amendments, without Pb removal from soil ecosystem. The chemically and biologically stable Pb species formed after treatment would be the key for assessing the efficacy of this remedial technology. Thus, the long-term assessment of the immobilized Pb stability and treatment effectiveness under field conditions, specifically plant growing soil conditions, would be critically needed for ensuring the success of this cost-effective technology and its large-scale application.

In an effort to restore or remediate the Pb-contaminated mining waste sites in the Jasper County Superfund Site of the historical tri-state lead mining district, southwestern Missouri, the goal of this field demonstration study was to assess the treatment effectiveness of six P-enriched biosolids and evaluate their long-term efficacy for stabilizing Pb and reducing the health and ecological risks of the mining waste. Specific objectives were to: i) assess the health risk reduction by the biosolid treatments through in vitro bioavailability test; ii) evaluate the mobility or stability of the stabilized Pb by leachability assessment; iii) determine the treatment impacts on plant Pb uptake with a tissue analysis; iv) investigate the microbial toxicity effect of the treated waste using bacteria-based assay; and v) examine the Pb species responsible for the risk reduction by sequential chemical fractionation and solid-phase speciation post 10 year treatments.

Materials And Methods

2.1. Site description

An abandoned mining site located in 1.6 km north of Webb City within the Jasper County Superfund Site of southwestern Missouri was selected for this study. The site was on 18.2 ha floodplain and 4.1 ha uplands of Center Creek, consisting of a mixture of chat and tailing in the size ranging from fine sand to gravel (0.6 cm diameter). Both areas were completely or mostly barren with a few islands of vegetation occurring along small waterways and depressions where surface water runoff accumulated. The mining waste on the site contained an average of $1004 \text{ mg Pb kg}^{-1}$, with spatial variations ranging from 230–3800 mg Pb kg^{-1} across the site, as determined by the EPA standard XRF method. Lead carbonate (PbCO_3), a relatively soluble and highly bioavailable Pb species, was identified as primary solid Pb

mineral by XRD in the waste. Tailings, fine mining waste, were found containing higher Pb contents than chats. In addition, the waste also contained average of 3492 mg Zn kg⁻¹ and 68 mg Cd kg⁻¹.

2.2. Experimental procedures

Six soil amendments used for treatments included 1) Mizzou Doo® (MD), a locally manufactured propriety blend of animal waste, post consumer paper, sawdust and other patented ingredients, containing 0.08% P; 2) Spent mushroom compost (SMC) having 0.36% P; (3) Composted sewage sludge (CSS), municipal sewage sludge composted with sawdust with 1.93% P; (4) Composted chicken litter (CCL), chicken litter composted with sawdust and peanut skins with 1.73% P; (5) Turkey litter compost (TLC) with 1.5% P; and (6) Triple super phosphate (TSP). Physiochemical characterization of the amendments can be found in the report by Mosby et al¹⁸. The biosolid materials used were attempted to improve the physiochemical properties of the mining waste and facilitate the vegetation establishment, while the enriched P content intended to enhance the Pb stabilization or immobilization on the mining waste site.

The field experiment consisted of seven 5–10 acre plots arranged randomly across the site. Five biosolid materials were applied on each plot respectively at a rate of 50–100 tons (dry weight) per acre, based on waste Pb concentration measured, and TSP was applied in the high Pb plot at a rate of 1.3 tons per acre. Untreated plot was included and served as control. The amendments applied were incorporated into the top 15 cm by a tiller, and the grass seeds of Kentucky tall fescue planted one week post treatment for vegetation establishment on the site.

Topsoils (0–15 cm) and above-ground plant tissue were collected from three randomly-selected spots within each plot every 3-month interval for 2 years post 8 year treatment. The collected soil samples were air-dried and ground to pass through a 0.25 mm sieve, while the plant samples oven-dried at 70°C for 24 h and ground to pass through a 0.1 mm sieve. Both samples were stored in room temperature until analysis.

2.3 Analytical procedures

Bioaccessible Pb is the measurement that assesses the potential exposure risk of soil Pb to human health based on the modified physiology-based extraction test (PBET) that simulates Pb dissolution in the GI tract. Analyses were performed following the procedures as described by Yang et al¹¹. Leachable Pb, an assessment of potential risk of soil Pb or P to water quality or chemical stability of soil Pb or P, was determined using the procedures described by Singh et al¹⁹. Lead content in plant tissues, an indication of phytoavailability or the risk of soil Pb to plant community, was measured following the procedures of USEPA Methods 3050. Microtox™ test, a bacteria-based assay that estimates the soil toxicity to microbial community, was analyzed with the procedures by Yang et al²⁰.

Sequential chemical extraction fractionation of soil Pb, including water-soluble, exchangeable, carbonate, Fe/Mn oxide, organic, and residue fractions, was performed to investigate the Pb transformation as

induced by treatments and identify the chemical species responsible for the Pb immobilization or risk reduction. The solubility of the six Pb fractions extracted was from the most soluble to relatively insoluble. The fractionation analysis followed the sequential extraction procedures by Ma and Rao²¹. In an effort to examine the formation of solid pyromorphites, solid-phase Pb speciation was applied with the microprobe analysis using scanning electron microscopy (SEM) combined with energy dispersive spectroscopy (EDS) as described by Yang et al¹¹.

Inductively coupled plasma–atomic emission spectroscopy (ICP-AES, Varian Vista-Pro) was used to determine Pb or P concentration in the soil or plant samples. All analyses were conducted in triplicate per sample, with a calibration of every 15-sample run using a standard reference material, NIST-SRM 1640 Trace Elements in Natural Water. A synthetic chloropyromorphite standard was included in the analyses for the solid-phase speciation.

2.4 Statistical Analysis

Data analysis was performed by standard analysis of variance (ANOVA) for mean comparisons among treatment, sampling time, and treatment x time interactions using the procedure in Statistix 8.1 software (Analytical Software Co.). Critical values (CV) and least significant differences (LSD) were calculated to separate means among treatments at the 0.05 significance level ($P < 0.05$).

Results And Discussion

3.1 Health risk reduction

As mentioned above, bioaccessible Pb represented the potential toxicity or exposure risk of soil Pb to human health based on the modified physiology-based extraction test (PBET). Measurements presented in Fig. 1 showed that, in all cases, Pb bioaccessibility in the mining waste was significantly reduced by the amendment treatments as compared with untreated control ($p < 0.05$). This finding was consistent with previous studies reported^{22,23}. The averaged reductions by the amendments were in an order: CSS (97.8%) > SMC (97.6%) > TSP (97.4%) > TLC (97.0%) > MD (96.8%) > CCL (96.5%), which was found not significantly differed among the treatments and during the sampling period. The concentrations of bioaccessible Pb in control plot (averaged 1050 mg Pb kg⁻¹) was measured relatively higher in compared with the average of total Pb content (1004 mg Pb kg⁻¹) on the site that was determined by the standard XRF method. This could be due to sampling variation and spatial Pb variability on the site. The waste was heterogeneous across the site (230–3800 mg Pb kg⁻¹) and consisted of a mixture of chat gravels and tailing sands, with about 10% sample volume passing through a 0.25 mm sieve for analysis. The fine particles usually contained higher Pb content than chat and large particles. Thus the samples that were collected and analyzed could contain higher Pb than the average concentration in the waste. Even under the assumption that all > 0.25 mm sample particles contained no or little Pb, the reductions of bioaccessible Pb by the treatments were still estimated at a range from 47.5–92.1%. The treatment effectiveness was found similar to the results on the Pb milling wastes reported by Tang and Yang¹³.

The significant reduction of Pb bioaccessibility or health risks in the mining waste could be resulted from the Pb transformation from labile or bioaccessible forms to less soluble or relatively stable species as induced by the amendment treatments through the immobilization reactions. The reaction mechanisms could include formation of pyromorphites or pyromorphite-like minerals; chelation by organic function groups; and surface adsorption or complexation by organic materials^{24,11}. In addition, the measurements post 8–10 years treatments indicated that the transformed Pb species were relatively stable under the surface soil conditions and the treatment effectiveness was maintained in long-term, with less likely being absorbed into the human bloodstream through the GI tract.

3.2 Ecological risk reduction

The ecological risk assessments used in this study included the measurement of the Pb uptake by plants, the leachability test to water quality, and the microbial toxicity assay to soil microbial communities. After the waste treatments with amendments, grass seeds of tall fescue were planted on all plots one week later for establishing vegetation on the site. The applied biosolid materials would help improve the physiochemical properties of the mining wastes, such as water holding capacity and nutrient status, and facilitate plant establishment and growth. The enriched P content in the used biosolids could induce or enhance soil Pb transformation to less soluble forms through the stabilization or immobilization reactions. After one year post treatments, tall fescue grasses started growing, with about 70–80% plant coverage estimated on the treated plots and none or very few grasses grown on control plot (no data collected).

Analyses of above-ground plant tissues indicated that all amendments significantly lowered Pb uptake by the grasses (Fig. 2, $p < 0.05$). The tissue Pb concentrations were in an order: CSS > TLC > CCL > TSP > SMC > MD, with the highest in CSS (72 mg Pb kg⁻¹) and the lowest in MD (13 mg Pb kg⁻¹). In compared with control (132 mg Pb kg⁻¹), the reductions among the treatments ranged from 45–90%, similar to the measurements of bioaccessible Pb. However, there was no significant correlation found ($r^2 = 0.0055$) between Pb bioaccessibility and plant uptake, which could be attributed to different physiochemical properties of organic matter and solubility or phytoavailability of the Pb species formed through differential stabilizing mechanisms by the treatments. Nevertheless, reduced Pb uptake by plants could be achieved by the immobilization or phytoavailability reduction of soil Pb induced by various treatments.

The microbial toxicity assay (Microtox™ test) was used to assess the potentially toxicological risks of a soil to microbial community. The assay was to measure the effective concentration of a soil that caused 50% death of bioluminescent *V. fischeri* bacteria (EC50%) based on bioluminescence reduction in compared with “none-toxic” conditions²⁵. A higher EC50% value would represent a lower toxicity or lower risk to soil microbial community. The assay measurements presented in Fig. 3 indicated that all amendment treatments resulted in numerically higher EC50% values (69–77%) or lower toxicological effects to soil microbial communities than control plot (63%), but the differences were not statistically significant ($P > 0.05$). The relatively higher EC50% values in treated plots suggested that the amendments could potentially lower the metal risks to soil microbial community through the stabilization reactions

and create soil conditions facilitating microbial activity and growth due to addition of organic matter and improved soil properties in treated mining waste. Data illustrated that there was no adverse impact of the amendments on soil microbial community or soil microbial activities and functions were maintained in long-term after treatments.

Measurements of Pb leachability represented the maximum amounts of soil Pb leachable to surface and groundwater or the potential risks to aquatic ecosystem¹⁹. The sample analyses revealed that the Pb leachability in all treated plots was significantly reduced by over 90% ($p < 0.05$) in compared with averaged 500 mg Pb kg⁻¹ in control plot, which had a similar trend of Pb bioaccessibility measured (Fig. 4). The effectiveness among treatments varied a little and did not significantly differ across the sampling period ($p > 0.05$). The average of leachable Pb concentrations among treatments was in an order: CCL > TLC > TSP > SMC > MD > CSS. Reduced leachable Pb by the amendments in treated plots implied that much less Pb in treated waste could be potentially transportable or leachable to surface and groundwater, thus the risks from the mining waste to aquatic ecosystem were lowered, and water quality near the mining site protected, in safeguarding human health and ecosystem from Pb contamination. This finding was consistent with data reported on the mill wastes treated by soluble P-based treatments¹³. The Pb leachability was found much lower than the Pb bioaccessibility measured. Such discrepancies would be related to the acid conditions of the sample extraction procedures, in which a pH 4 solution was used for Pb leachability test and a pH 2 solution for Pb bioaccessibility. It was well known that soil extractable Pb was largely dependent on the physical and chemical associations and metal solubility, and the Pb dissolution from soil was usually proportional to the acidity of extraction solution^{26,27}. As expected, more Pb could be extracted from soil by strong acid solution than weak acid solution. In previously mentioned, the substantial reduction of Pb leachability by the amendments in the treated waste could be due to the formation of less soluble Pb species induced by the treatments through various stabilization mechanisms^{28,29}.

3.3 Alteration of Pb Speciation

Exploring Pb species and verifying the Pb transformation responsible for Pb stabilization and risk reduction are critical for determining the immobilization mechanisms and better understanding the treatment efficacy. In this study, chemical speciation by sequential extraction procedures in combined with solid-phase speciation by electron microprobe microspectroscopy was used to identify the alteration of Pb species induced by amendments. Analyses of chemical speciation presented in Fig. 5 showed that, in all cases, the residual Pb fractions in treated wastes significantly increased as a result of the treatments ($p < 0.05$). In compared with control plot, the percentages increased among amendments were CSS (59%) > TLC (54%) = MD (54%) > CCL (48%) > SMC (38%) > TSP (6%), which was not significant different across the sampling period. The residual Pb fraction was the least soluble or bioavailable fraction including pyromorphite or pyromorphite-like minerals. Increased residual Pb suggested the enhanced Pb transformation to relatively stable species by amendment treatments. Organic amendments had been reported to increase the insoluble or stable Pb fractions in rice paddy soil²². Data also indicated

that the formation of residual Pb was primarily from transformed labile Pb species including water-soluble, exchangeable, carbonate, and Fe/Mn oxide-associated fractions. As mentioned above, lead carbonate (PbCO_3), a soluble and highly bioavailable Pb species, was identified as primary Pb mineral in untreated waste. This labile Pb mineral would facilitate Pb dissolution and be effectively transformed to stable species. Xian³⁰ and Zhang et al³¹ indicated that water-soluble and exchangeable Pb were highly leachable or bioavailable, and exchangeable and carbonate Pb fractions were considered responsible for Pb uptake by plants^{32,33}. This finding would well account for and support the risk reduction assessments of Pb bioaccessibility, phytoavailability, and leachability discussed earlier in the treated wastes.

Solid Pb particles in selected treated wastes were successfully identified by scanning electron beam microscopy (SEM) in combined with energy-dispersive spectroscopy (EDS). The particles analyzed were found at 20–40 μm size, containing the elements of Pb, P, Si, Ca or Al, with no P present in untreated samples (Fig. 6). This solid speciation analysis verified the formation of solid Pb phosphates or pyromorphite-like minerals as induced by amendments and their association with clay minerals and carbonates present in the wastes. Nevertheless, there were less than 10% of the identified Pb solids that were found associated with Pb phosphates or pyromorphite-like minerals. Scheckel et al³⁴ indicated that pyromorphite formation was not facilitated or enhanced by organic amendment applications. The insignificant formation of pyromorphites in high organic matter (OM) amended soil could be caused by 1) pyromorphite formation might be decreased by Pb-OM complexation; 2) pyromorphite crystal could be coated by organic coats that inhibited further pyromorphite formation; and 3) organic coatings might help pyromorphite crystals move out of soil by enhanced colloidal transport³⁵. Scheckel et al³⁴ also pointed out that it would be very difficult to distinguish the hexagonal crystals of pyromorphite from the arrays of hexagonal minerals. Pyromorphite-like minerals usually were heterogeneously distributed and in amorphous or poorly-crystallinity without clear hexagonal crystal structure¹¹. This solid-phase speciation analysis revealed the formation of crystalline or poor-crystalline pyromorphite-like minerals after treatments, which confirmed the results of chemical speciation or the induced Pb transformation from labile fractions to relatively stable species.

Conclusions

This field study showed that the applications of six P-enriched biosolid amendments would effectively restore vegetation cover and reduce the bioaccessibility, phytoavailability, and leachability of Pb in contaminated mining site. The treatments had no toxicological impact on soil microbial community. The efficacy of the treatments could be maintained in long-term and environment-sound. Among six amendments assessed, SMC and MD treatments appeared most effective in context of the health and ecological risk reductions. The chemical and solid speciation analysis verified the transformation of soil Pb from labile carbonate, exchangeable, and water-soluble fractions to relatively stable fraction and confirmed the formation of pyromorphite-like minerals, as induced by treatments. The immobilization mechanisms identified could be responsible and accounted for the health and ecological risk reductions by amendments. This study demonstrated that *in situ* soil treatments using P-enriched biosolid

amendments could be potentially applied as a long-term effective, economical, and ecological-sound remedial technology that stabilizes toxic Pb in mining waste site and safeguards human health, water quality, and natural ecosystem from Pb contamination.

Declarations

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Figures

Figure 1

Average of bioaccessible Pb in the amendment-treated and untreated (control) mining wastes during the 8-10 year sampling period post treatment. Vertical bars indicate the standard deviation of measurements.

Figure 2

Average of plant tissue Pb in the amendment-treated and untreated (control) mining wastes during the 8-10 year sampling period post treatment. Vertical bars indicate the standard deviation of measurements.

Figure 3

Average of soil microbial toxicity in the amendment-treated and untreated (control) mining wastes during the 8-10 year sampling period post treatment. Vertical bars indicate the standard deviation of measurements.

Figure 4

Average of leachable Pb in the amendment-treated and untreated (control) mining wastes during the 8-10 year sampling period post treatment. Vertical bars indicate the standard deviation of measurements.

Figure 5

Average of Pb chemical fraction in the amendment-treated and untreated (control) mining wastes during the 8-10 year sampling period post treatment.

Figure 6

EDS patterns of Pb solids in selected amendment treated (SMC, left) and untreated (control, right) mining wastes during the 8-10 year sampling period post treatment.