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Original Research

Using Phosphorus and Zeolite to Immobilize Lead in Two Contrasting Contaminated Urban Soils

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Abstract

Lead (Pb) contamination of urban soil is a threat to human health, and reducing the risk of Pb-contaminated soil is a continuing international concern. Soil stabilization technique has been considered as a promising remediation technique to facilitate the immobilization of Pb in soil. The purpose of this study was to evaluate the effects of different amendments, including H_3PO_4, $Ca(H_2PO_4)_2$, H_3PO_4+$Ca(H_2PO_4)_2$, and zeolite on Pb levels in two naturally contaminated urban soils. Pb speciation and bioavailability was evaluated by the sequential extraction test (SET) and the toxicity characteristic leaching procedure (TCLP) after a two-month incubation. The application of phosphorus amendments significantly reduced the TCLP-Pb concentration in two soil types and the SET-Pb in Soil 1 (alkaline but with high Pb level), whereas the zeolite amendment diminished the SET-Pb in two soil types and the TCLP-Pb in Soil 1. Nevertheless, regardless of the soil type, the application of phosphorus amendments resulted in a significant increase of residual Pb. These phosphate amendments may be a viable strategy in the *in situ* remediation of Pb contamination in urban soils.

Keywords: amendments, bioavailability, immobilization, Pb, urban soils

Introduction

Heavy metal contamination of urban soils has attracted considerable attention around the world because of their toxicity and threat to human life and the environment [1-4]. The United Nations [5] has documented that more than half (54%) of the world population lives in urban areas as of 2014 and the proportion is expected to increase, reaching 66% by 2050, thereby further strengthening concern about heavy metal contamination of urban soil. Lead (Pb), known as one of the most toxic elements to human health, can impair intellectual development in young children [6]. The potential of various amendments to reduce mobility and bioavailability of Pb in soils is an ongoing applied research pursuit [7].

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The selection of the most suitable amendments for *in situ* Pb immobilization is a key factor [8] . Henry et al. [9] demonstrated that the *in situ* remediation with phosphate amendments based on bioaccessibility assessments is the best approach. Phosphate (P) amendments are known to form stable Pb-P minerals (i.e., pyromorphite) [10]. Although previous studies have addressed the effect of different forms of phosphate on the immobilization of metals, there is still limited information regarding bioaccessibility assessments of their effectiveness. Therefore, quantifying the Pb speciation – particularly of its bioavailable form – under the applied chemical amendments is of utmost importance in risk assessment and remediation [8] . Research is urgently needed to increase confidence in using these approaches in risk-based decision making in the context of natural urban soils [9]. In this study, we conducted batch incubation experiments with amendments (H_3PO_4, $Ca(H_2PO_4)_2$, H_3PO_4 + $Ca(H_2PO_4)_2$, and zeolite) in two contrasting contaminated urban soils. The objective of this study was to evaluate Pb immobilization effectiveness using the toxicity characteristic leaching procedure (TCLP) test and sequential extraction test (SET) following stabilization treatment.

Materials and Methods

Soil Collection and Analysis

Two soil types used in this study, representing different levels of lead, were collected from the respective steel industrial area and roadside in the urban districts of Guangzhou, China [2]. The composite soil samples collected at a depth of 0-10 cm were obtained by mixing subsamples from five random points within 2 m^2 in each sampling site. Soil samples were air-dried, crushed to pass through a 2-mm nylon sieve, and homogenized, which were then used for the incubation experiment and determination of soil pH and particle size distribution.

The sub-samples were further ground with an agate grinder to go through a 0.15-mm nylon sieve, which were then used to determine soil Pb, soil organic matter, and total phosphorus (TP). The soil Pb was determined by digesting soil sample with a mixture of concentrated HNO_3, HF, and $HClO_4$ in a polyvinyl-fluoride crucible, followed by graphite furnace atomic absorption spectrophotometry (GFAAS-AA800, PerkinElmer Inc.) [11]. The recovery of analyzed Pb in a reference material was within ±10% of the certified value, and the relative standard deviation of duplicate measurements was less than 10%. Soil pH was measured using a 1:2.5 (w/v) ratio of soil to distilled water, the organic matter was determined using the wet oxidation method, particle size distribution was measured using the pipette method, and TP was determined by the molybdenum blue method [11]. The basic physico-chemical properties and the total concentration of Pb for two soil samples prior to immobilization are summarized in Table 1.

Incubation Experiment

The amendments included two pure chemical reagents, H_3PO_4 and $Ca(H_2PO_4)_2$, as well as ground zeolite (<0.2 mm). Both H_3PO_4 and $Ca(H_2PO_4)_2$ were added to 2.5 kg of soils in solution forms as the stabilizing additives at a 2.5:1 molar ratio of P/Pb [12], and zeolite was added with a mass fraction of 1% (w/w) [13]. The amended soils were thoroughly homogenized in large plastic containers prior to use. Soils without amendment were designated as control. All the treatments, including control, were performed in triplicate and incubated for two months in plastic containers with soil moisture content of 25% (Table 2).

Assessment of Pb Bioavailability

The TCLP test and the chemical partitioning of Pb were performed in accordance with the U.S. EPA protocol [14] and the sequential extraction procedure described by Li et al. [15], respectively, to evaluate the effectiveness of the immobilization treatment for these two contaminated urban soil types. The sequential extraction method [16] operationally defines the metals in four chemical forms: HOAc extractable, reducible, oxidizable, and residual fractions. The values of four fractions summed up were compared with total concentration to check the recovery, and the recovery values were found to be satisfactory (data not shown).

Statistical Analysis

A descriptive analysis was made with the SPSS V13.0 for Windows. A probability level of $p < 0.05$ was considered as significantly different.

Table 1. Concentrations of Pb and physico-chemical properties for studied soils.

Soil	Pb mg/kg	pH	TP g/kg	Organic matter g/kg	Fe g/kg	Mn mg/kg	Particle size distribution (%)		
							2-0.05 mm	0.05-0.002 mm	<0.002 mm
S1	3805.5	8.4	0.48	93.7	90.5	856.3	62.7	24.4	12.9
S2	272.6	6.5	0.43	70.9	49.0	467.0	25.5	45.0	29.5

Table 2. Soil treatments.

Treatment	Additive type	Dose of additive (g/kg)	
		Soil 1	Soil 2
T1	H_3PO_4	4.5041	0.3226
T2	$Ca(H_2PO_4)_2$	5.3784	0.3852
T3	$Ca(H_2PO_4)_2 + H_3PO_4$	2.2520 + 2.6892	0.1613 + 0.1926
T4	Zeolite	10	10
CK (control)	/	/	/

Results and Discussion

Pb-Contaminated Soils

The lead-contaminated soils used in this study were sourced from two locations impacted by distinct anthropogenic activities, namely iron smelting (Soil 1, S1) and historical use of leaded gasoline (Soil 2, S2). S1 was alkaline, sandy clay loam with a Pb concentration of 3,805.5 mg/kg, while S2 was acidic and clay loam containing more than an order of magnitude lower Pb (272.6 mg/kg) than that of S1. Other physicochemical properties are detailed in Table 1. P amendments and zeolite application resulted in reduction and increase in soil pH, respectively (data not shown).

Leachability of Pb in the TCLP Extract

The effects of amendments on the TCLP extractable Pb are shown in Fig. 1. The TCLP-Pb concentration for the soil spiked with Pb (CK, untreated soil) was 3.4 mg/L in S1 and 0.034 mg/L in S2, which are lower than the USEPA limit for soil (5 mg/L). Regardless of H_3PO_4 and/or $Ca(H_2PO_4)_2$, the phosphorus amendments significantly reduced the TCLP-Pb concentration in both soil types: in S1 by 91-93% and in S2 by 56-58%. In comparison, the application of zeolite amendment significantly reduced the TCLP-Pb concentration in S1 (79% reduction), whereas the TCLP-Pb concentration in S2 (0.033 mg/L) was not significantly reduced with the application of zeolite amendment.

In S1, the HOAc extractable Pb was significantly decreased by 82-83% after the application of phosphorus amendments and by 8.1% after the application of zeolite. In S2, however, the phosphorus amendment did not affect the concentration of HOAc-extractable Pb, while the application of zeolite significantly reduced the HOAc-extractable Pb by 26.9%. The decreased pH in S2 could be one of the main factors responsible for the poor effectiveness of Pb immobilization by the phosphorus amendments. The soil pH has been shown to play an important role in increasing the cationic heavy metal retention to soil surfaces, which occurs via adsorption, inner sphere surface complexation, and/or precipitation [7, 17, 18]. Ruby et al. [19] also demonstrated that acidic pH decreases the bioavailability of Pb owing to the formation of anglesite and Pb jarosite, which are stable under the acidic gastric environment. Even though the effectiveness of Pb immobilization has been reported depending on the phosphate amendment, no significant differences were observed among H_3PO_4 and/or $Ca(H_2PO_4)_2$ amendments in the current study. The efficiency of the phosphorus amendment in Pb-contaminated soil has also been reported related to the type of soil and the nature and extent of the contamination [9].

Changes in Pb Speciation

The BCR extraction procedure was applied to evaluate the change of Pb speciation in soil after the incubation with phosphates and zeolite amendments. The proportion of residual Pb was expected to increase after the application of the amendments, and the results of Pb speciation in two soil types are summarized in Fig. 2. The distribution of various Pb speciation showed that the predominant fractions in S1 were the reducible and acid fractions, accounting for about 66.8% and 27.3% of total Pb, respectively, and the application of the amendments significantly reduced the HOAc-extractable Pb (acid fraction) (Fig. 2a). However, all the amendments significantly increased the reducible

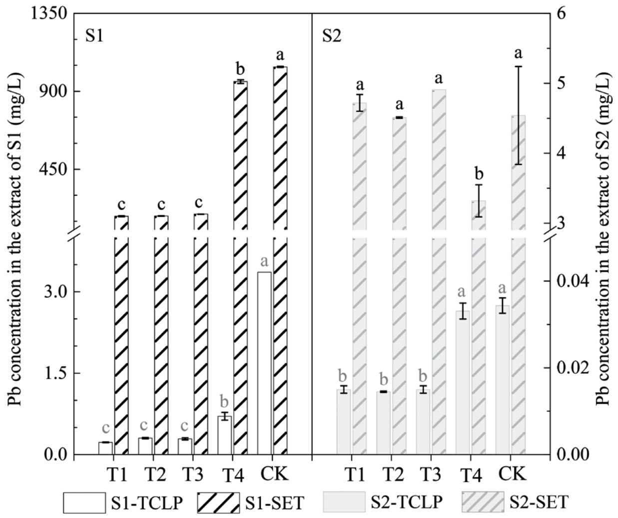

Fig. 1. TCLP extractable Pb and SET extractable Pb in two soils after the application of different amendments. Abbreviations are explained in Table 2.

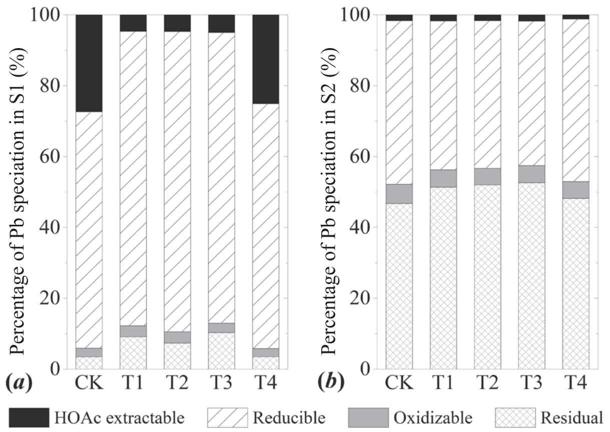

Fig. 2. Variations of Pb speciation in different fractions. Abbreviations are explained in Table 2.

fraction, and the addition of phosphates also increased the oxidizable and residual fractions. In comparison, the greatest proportion of Pb in S2 was associated with the reducible fraction (49.1%), followed by the residual (43.8%) (Fig. 2b). A very small proportion of Pb was found to be HOAc-extractable. The application of all the amendments significantly decreased the reducible and oxidizable fractions of Pb in S2, in contrast to S1, while all the amendments significantly increased the residual fraction of Pb as expected. Although the application of phosphorus amendments did not reduce the acid fraction of Pb in S2, a significant increase of the residual fraction of Pb was observed in both S1 and S2. On the other hand, the application of zeolite slightly decreased the acid fraction of Pb in both soil types.

Conclusions

Results demonstrated that the addition of phosphorus amendments could result in the transformation of non-residual Pb to residual Pb in two contrasting urban soil types after a two-month incubation period. The addition of phosphorus amendments significantly reduced the TCLP-Pb concentration in both, whereas the efficiencies of the phosphorus amendments on the HOAc-extractable Pb were different, probably due to the different soil pHs. The zeolite amendment diminished the TCLP-Pb in both soil types and the HOAc-extractable Pb in S1 (alkaline, high Pb). Results suggest that the application of phosphorus-containing amendments to urban soils would be a useful strategy to induce Pb immobilization.

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