

Assessment of In Situ Immobilization of Lead (Pb) and Arsenic (As) in Contaminated Soils with Phosphate and Iron: Solubility and Bioaccessibility

Yanshan Cui · Xin Du · Liping Weng ·
Willem H. Van Riemsdijk

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Abstract The effect of in situ immobilization of lead (Pb) and arsenic (As) in soil with respectively phosphate and iron is well recognized. However, studies on combined Pb and As-contaminated soil are fewer, and assessment of the effectiveness of the immobilization on mobility and bioaccessibility is also necessary. In this study, a Pb and As-contaminated soil was collected from an abandoned lead/zinc mine in Shaoxing, Zhejiang province of China, which has been treated with three phosphates, i.e., calcium magnesium phosphate (CMP), phosphate rock, and single super-phosphate (SSP) for 6 months in a field study. The ferrous sulfate (FeSO_4) at 20 g kg^{-1} was then amended to the soil samples and incubated for 8 weeks in a greenhouse. The solubility and bioaccessibility tests were used to assess the effectiveness of the in situ immobilization. The result showed that phosphates addition decreased the concen-

trations of CaCl_2 -extractable Pb; however, the concentrations of water-soluble As increased upon CMP and SSP addition. With the iron addition, the water-soluble As concentrations decreased significantly, but CaCl_2 -extractable Pb concentrations increased. The bioaccessibility of As and Pb measured in artificial gastric and small intestinal solutions decreased with phosphate and iron application except for the bioaccessibility of As in the gastric phase with SSP addition. Combined application of phosphates and iron can be an effective approach to lower bioaccessibility of As and Pb, but has opposing effects on mobility of As and Pb in contaminated soils.

Keywords Immobilization · Lead · Arsenic · Solubility · Bioaccessibility

Y. Cui (✉)
College of Resources and Environment,
Graduate University of Chinese Academy of Sciences,
Beijing 100049, People's Republic of China
e-mail: cuiyanshan@gucas.ac.cn

Y. Cui · X. Du
State Key Lab of Urban and Regional Ecology/Department
of Soil Environmental Science,
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences,
Beijing 100085, People's Republic of China

L. Weng · W. H. Van Riemsdijk
Department of Soil Quality, Wageningen University,
Wageningen P.O. Box 8005, 6700EC, The Netherlands

1 Introduction

Arsenic (As) and lead (Pb) are ubiquitous contaminants, which cause serious environmental problems throughout the world. In China, many soils are contaminated with As and Pb (Liu et al. 2005). Arsenic and Pb have been ranked respectively first and second as hazardous substance by the Agency for Toxic Substances and Disease Registry (ATSDR) in America (ATSDR 2007a, b). Arsenic and Pb are toxic and can be taken up from soil by plants and transferred to the food chain, causing potential chronic risks to human health (ATSDR 2007a, b; Zhu et al. 2008). Therefore, it is

important to find a good method to remediate the As and Pb-contaminated soils. Many remediation technologies, including physical, chemical, and biological technologies, have been used in treating As and Pb contamination (Mirsal 2004). The chemical behavior of Pb and arsenic in soil is quite different and it is therefore a challenge to develop an optimal strategy for lowering the risk for the environment as well as for human exposure simultaneously for both contaminants.

In situ immobilization is a cost-effective treatment to remediate As and Pb-contaminated soil and to alleviate the environmental and health hazards (Kim and Davis 2003; Miretzky and Fernandez-Cirelli 2008; Yang et al. 2007). For example, cement, quicklime, bone char, and phosphate are used in immobilizing Pb (Cao et al. 2008a; Chen et al. 2006). In recent years, in situ immobilization of Pb with phosphate has attracted a great deal of attention. A mixture of phosphoric acid (H_3PO_4) and phosphate rock was effective in Pb immobilization, with only a small reduction of soil pH and a small increase in soluble phosphate (Cao et al. 2003). With treatments of hydroxyapatite, phosphate rock, single super-phosphate, and a combination of hydroxyapatite with single super-phosphate, Zhu et al. (2004) found that the hydroxyapatite amendment can lower the mobility and increase the geochemical stability of Pb in soil, and suggested its use for in situ remediation of Pb-contaminated soils. Further research showed that the form of Pb contamination and soil pH also play a role in determining the effectiveness of phosphate-induced Pb immobilization (Cao et al. 2008b). To reduce the mobility of As in soil, lime and cement additions have been proven to be beneficial methods (Bothe and Brown 1999; Dutré and Vandecasteele 1998; Mollah et al. 2004). Some researchers also suggested that iron (Fe) and Fe-oxide were effective in immobilizing As in soil (Kumpiene et al. 2006; Gadepalle et al. 2008).

Many chemical and biological methods have been used to evaluate the effectiveness of immobilization treatments. Oral bioaccessibility test, which is a measure of solubility of heavy metal in the gastrointestinal compartment, is applicable to the soil ingestion pathway (Beak et al. 2006; Ruby et al. 1996). The bioaccessibility of metal has also been used to evaluate the effectiveness of heavy metal remediation in soils (Bosso et al. 2008; Sarkar et al. 2007). Bosso's (2008) study showed that the most efficient phosphate source was NaH_2PO_4 , which reduced Pb solubility by

92% in acidic gastric conditions after the first month. In Pb and As-contaminated soil, Martin and Ruby (2003) found that in situ fixation of As can be achieved by addition of iron amendments, which can also reduce bioaccessibility of As. In Pb and As-contaminated orchard soils, Codling (2007) demonstrated that the addition of Fe was very effective in reducing bioaccessible Pb and water-soluble As and Pb. But the study also suggested that phosphate is not recommended as a reliable Pb remediation strategy for Pb and As-contaminated orchard soils, because As sequestered by Fe addition is desorbed by phosphate application. Regarding As mobility or bioaccessibility, Martin and Ruby (2003) and Codling (2007) have shown contradictory results. Further studies are needed to clarify and to assess the effect of addition of iron and phosphate on the immobilization of soil As and Pb in contaminated soil, and on their bioaccessibility.

The objective of this study is to assess the effectiveness of in situ immobilization measures using a combination of phosphates and iron application. The effectiveness is judged by studying the effect of the amendments on the solubility and bioaccessibility of Pb and As present in contaminated soils. Possible mechanisms that cause the observed effects will also be discussed.

2 Materials and Methods

2.1 Soil Sample and Amendments

The test site is located in an abandoned lead/zinc mine in Shaoxing, Zhejiang Province of China (Xie, et al. 2006), where the soil contains high levels of both Pb and As. The soil has been treated with different phosphates in a field study. The phosphates used in the study were calcium magnesium phosphate [CMP, a citric acid soluble P fertilizer, the main component is $Ca_3(PO_4)_2$], phosphate rock [PR, a water-insoluble P fertilizer, the main component is $Ca_{10}(PO_4)_6Cl_2$], and single super-phosphate [SSP, a water-soluble P fertilizer, the main component is $Ca(H_2PO_4)_2$]. The pH-H₂O of CMP, PR, and SSP is 9.5, 7.4, and 3.1, respectively, whereas the water-soluble P is 14, 1, and 43 mg kg⁻¹ (Xie et al 2006). For each phosphate compound, two additions are used in the field study, i.e., 300 and 500 g m⁻² (P), which is mixed with the topsoil (0~20 cm depth). The treat-

ments are coded as CK, CMP1, CMP2, PR1, PR2, SSP1, and SSP2, in which CK stands for control and 1 and 2 refer to 300 and 500 g m⁻² P treatments, respectively. Xie et al. (2006) have measured water-soluble P in these soils. They found that, in the control soils, water-soluble P is about 1 mg kg⁻¹ soil. Addition of SSP at 500 g m⁻² increased water-soluble P dramatically to about 120 mg kg⁻¹. CMP is less soluble than SSP and in the CMP treatment water-soluble P is up to 30 mg kg⁻¹. PR is the least soluble among the phosphates used and water-soluble P in the PR treatments is up to 6 mg kg⁻¹. Six months after phosphate application, the soil was collected, air-dried, and sieved to 2 mm for the incubation experiment with 20 g kg⁻¹ (2%) ferrous sulfate (FeSO₄) amended (Fe2) or without (Fe0). Plastic cups containing 200 g of soil were used in this experiment and FeSO₄ was applied to the soil as solution. All together, there were 14 treatments: CKFe0, CKFe2, CMP1Fe0, CMP1Fe2, CMP2Fe0, CMP2Fe2, PR1Fe0, PR1Fe2, PR2Fe0, PR2Fe2, SSP1Fe0, SSP1Fe2, SSP2Fe0, and SSP2Fe2. Each treatment had three replicates. Deionized water was added to bring the soil water content to approximately 20% (w/w) and the incubation period is 8 weeks.

2.2 Soil Characterization

The soil without phosphates and FeSO₄ application were collected, air-dried, sieved, and some basic physical and chemical properties were determined. Soil pH was determined in 0.01 M CaCl₂ with a pH meter in a 1:2.5 (w:v) soil-to-suspension ratio after 1 h of equilibration. The content of soil organic matter was determined using the acid dichromate oxidation method described by Bao (2000). The untreated soil has a pH of 4.9, with 22 g kg⁻¹ organic matter content.

2.3 Metal Analysis

The total concentrations of Pb and As in soil were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES; Optima-2000, Perkin-Elmer Co. Lt., USA) and atomic fluorescence spectrometer (AFS; model AFS-2202E; Haiguang, Beijing, China) respectively after being digested with aqua regia (HNO₃-HCl=1:3 in volume) and HClO₄ (1:1 in volume). Water-soluble As and 0.01 M CaCl₂-extractable Pb with 1:10 soil-to-solution ratio were determined with AFS and ICP-OES, respectively.

Total Pb and As content is 11,381 mg kg⁻¹ and 1,957 mg kg⁻¹, respectively.

2.4 Bioaccessibility Test

The bioaccessibility of As and Pb in soil were determined by the physiologically based extraction test. The test was adapted from Ruby et al. (1996) with a modification (Rodriguez et al. 1999; Tang et al. 2006). Artificial gastric solution was prepared by adjusting 0.15 M NaCl solution to pH 1.5 with 12 M HCl and then adding 0.5 g citrate, 0.5 g malate, 0.42 mL lactic acid, 0.5 mL acetic acid, and 1.25 g pepsin (P7000, Sigma Chemical Co., St. Louis, MO, USA) into each liter of solution. Soil (6 g) was added to 600 mL of thus prepared artificial gastric solution in a 1-L glass reaction vessel, which was approximately four-fifths submerged in a temperature-controlled (37°C) water bath. The anaerobic condition of the digestive tract was created by constantly diffusing argon gas at 1 L min⁻¹ through the solution, and solution pH was monitored constantly and adjusted to the selected pH with concentrated HCl or NaHCO₃ powder, if necessary, throughout the procedure. After 1 h incubation, the artificial gastric solution was modified to represent the small intestinal solution by adjusting the pH from 1.5 to 7 with NaHCO₃ powder and adding 1.2 g porcine bile extract (B8631, Sigma Chemical Co., St. Louis, MO, USA) and 0.36 g porcine pancreatin (P1500, Sigma Chemical Co., St. Louis, MO, USA) to each reaction vessel. The duration of the small intestinal phase was 4 h. Constant mixing was performed throughout the procedure using paddle stirrers at a speed of approximately 100 rpm. After each phase, a 10-mL sample of the suspension was collected using a syringe and centrifuged at 4,000 rpm for 20 min before filtering the supernatant through a 0.45 µm cellulose-nitrate filter. Soluble Pb and As concentration in the artificial digestive solution was analyzed using ICP-OES and AFS, respectively. In this experiment, the bioaccessibility is defined as the fraction of total Pb or As that is dissolved in the simulated gastric and small intestinal solutions.

2.5 Statistical Analysis

Statistical analysis was performed using SPSS for Windows (Ver 11.5; SPSS, Chicago, IL, USA). All

data were subjected to ANOVA and subsequently to Duncan's multiple range tests.

3 Results and Discussion

3.1 Soil pH

Addition of both phosphates and iron influenced soil pH. Soil pH increased strongly with the addition of calcium magnesium phosphate, in which $\text{Ca}_3(\text{PO}_4)_2$ is the main component. Addition of phosphate rock increased soil pH slightly, whereas soil pH decreased slightly with the addition of single super-phosphate (SSP, main component $\text{Ca}(\text{H}_2\text{PO}_4)_2$; Fig. 1). The addition of FeSO_4 decreased the soil pH by about 0.6 pH unit on average.

The effects of phosphate addition on pH in soil found in this study are consistent with those found by Xie et al. (2006). Both CMP and PR are alkaline materials and therefore led to an increase of soil pH. The much higher solubility of CMP than PR can explain the stronger pH increase in CMP treatments. The major component of SSP is $\text{Ca}(\text{H}_2\text{PO}_4)_2$, which under the initial pH of the soil will not influence the soil pH significantly. In non-reduced soils, Fe^{2+} in FeSO_4 will be oxidized to Fe^{3+} , whereas the latter forms iron hydroxides at not too low pH (Kumpiene et al. 2008). This process produces protons and thus may lower the pH.

4 Water-Soluble As and CaCl_2 -Extractable Pb

In the control soil (CK), water-soluble As is 0.01 mg L^{-1} , or 0.1 mg kg^{-1} soil, which is 0.005%

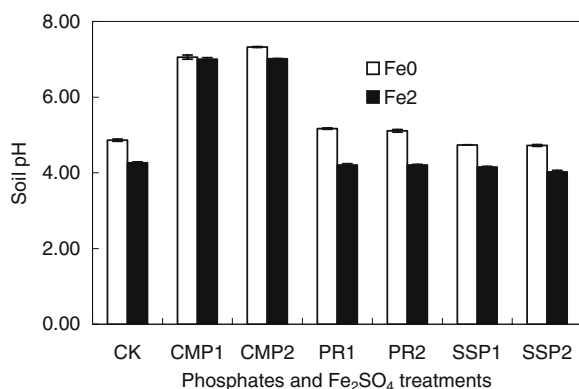


Fig. 1 Changes of soil pH in different Fe_2SO_4 and phosphates treatments

of the total As. The addition of CMP and SSP significantly increased the concentration of water-soluble As ($P < 0.01$). With FeSO_4 addition, the water-soluble As concentrations decreased significantly ($P < 0.01$; Fig. 2). Of all the treatments, the highest water-soluble As concentration is 0.52 mg kg^{-1} in the treatment of CMP2Fe0, which is 4.8-fold that of the control. The lowest concentration, 0.01 mg kg^{-1} , is in the treatments of PR1Fe2 and PR2Fe2, which is 8.0-fold lower than the concentration of CK. This very low As solubility indicates that most of As is present in non-water-soluble forms, such as As-bearing minerals, e.g., arsenopyrite (FeAsS). The relatively small amount of As extracted within the time frame (24 h) of the water extraction can be due to desorption of As from metal (hydr)oxides surfaces, and/or partial dissolution of As-containing minerals.

In Fig. 3, water-soluble As is plotted as a function of pH. Distinction was made between the treatments without (empty symbols) or with (filled symbols) Fe addition. At the same pH, the water-soluble As is in general lower in the Fe treatments than in the corresponding treatments without Fe. For both groups, the data show that water-soluble As tends to increase with increasing pH, although the description of the data with pH is poor ($R^2 = 0.29$ for non-Fe treatments, $R^2 = 0.52$ for Fe treatments).

These observed effects of pH, phosphate, and iron on water-soluble As are in line with effects of these factors that can be expected for As adsorption to oxides (Stachowicz et al. 2008). Adsorption of arsenate to oxides decreases in general with increasing pH. Competition with phosphate for adsorption will lead to desorption of adsorbed As and therefore an increase in soluble As concentration. Added Fe can

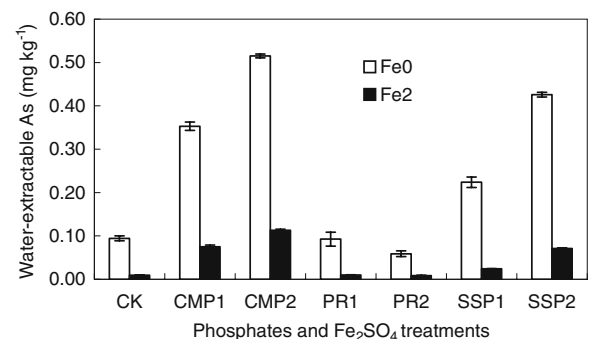


Fig. 2 Water-soluble As in different Fe_2SO_4 and phosphates treatments

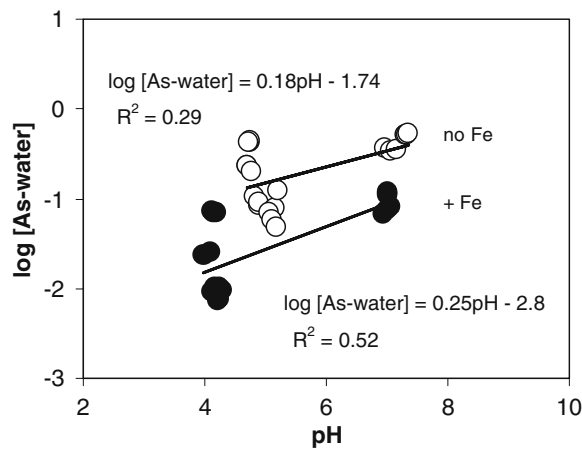


Fig. 3 Concentration of water-soluble As as a function of pH. Symbols are data, in which empty symbols are treatments without iron addition, whereas the filled symbols are treatments with iron addition. Lines are regression lines with the regression equations given in the figure. As-water is in milligrams per kilogram

form iron oxides that provide extra binding surface for As, which leads to more As adsorption and affinity to soil, and induces concentration of water-soluble As decrease. The effects of phosphate treatment on water-soluble As can thus be due to both an increased pH (CMP) and increased phosphate concentration (CMP, PR, and SSP), both lead to increased As solubility. On the contrary, addition of iron will reduce As solubility by both decreasing pH and increasing available binding surfaces.

Solubility of Pb was measured in CaCl_2 extraction. In the control soil (CK), CaCl_2 -extractable Pb is 2.4 mg kg^{-1} , which equals 0.02% of total Pb in soil. The concentrations of CaCl_2 -extractable Pb decreased strongly with the phosphates addition ($P < 0.01$), and increased significantly with the FeSO_4 addition except for the treatment of CMP2 ($P < 0.01$; Fig. 4). The highest concentration of CaCl_2 -extractable Pb was 5.89 mg kg^{-1} in the treatment of PR2Fe2, which is 1.4-fold higher than the concentration in CK. The lowest concentration of CaCl_2 -extractable Pb was 0.06 mg kg^{-1} in the treatments of CMP2Fe0 and CMP2Fe2, 40.6-fold lower than the concentration in CK.

The concentration of CaCl_2 -extractable Pb had an exponential decline with increase in pH of the soils ($R^2 = 0.88$; Fig. 5). Lead is immobilized in the solid phase of soils via adsorption and/or precipitation. Both the adsorption and precipitation will be favored by an increase in pH. The good correlation between soluble Pb

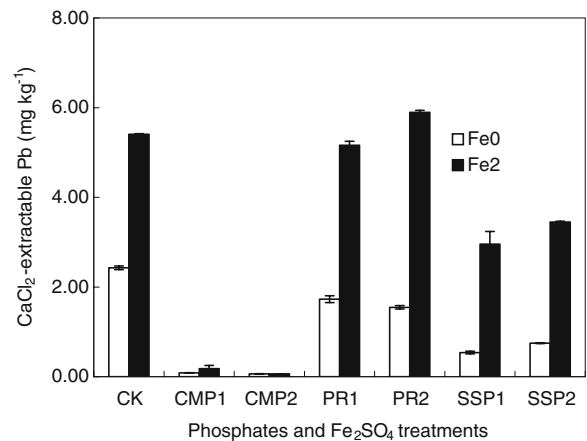


Fig. 4 CaCl_2 -extractable-Pb in different Fe_2SO_4 and phosphates treatments

and soil pH as given in Fig. 5 suggests that pH changes may be the major factor that regulates Pb solubility in both the phosphate treatments and iron treatments. As shown in Fig. 1, addition of CMP increased soil pH by more than 1 U. This much higher pH in the CMP treatment is one of the possible reasons that explain a much lower extractable Pb concentration in the CMP treatments (Fig. 5). On the contrary, addition of iron has led in general to a decrease in pH (Fig. 1). The pH decrease in the iron treatment may be the cause of increased Pb solubility in these soils (Fig. 4).

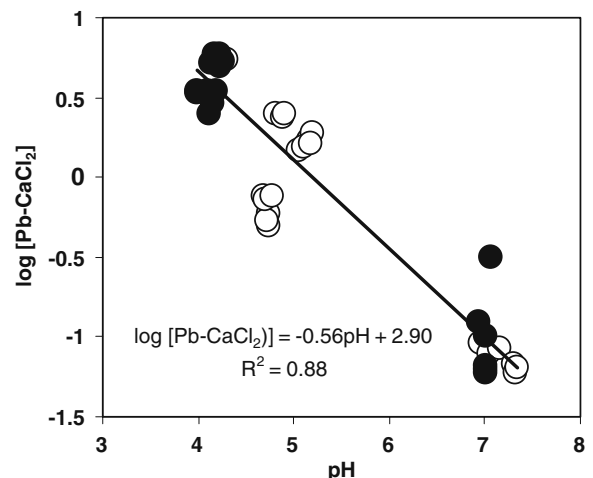


Fig. 5 CaCl_2 -extractable Pb as a function of pH. Symbols are data, in which empty symbols are treatments without iron addition, whereas the filled symbols are treatments with iron addition. Line is the regression line with the regression equation given in the figure. Pb-CaCl₂ is in milligrams per kilograms

In addition to pH effects, addition of phosphate can also influence Pb distribution as a result of increased phosphate concentration. Adsorption of phosphate to metal (hydr)oxides can increase Pb adsorption to metal (hydr)oxides due to synergistic electrostatic effects (Bonten et al. 2008; Genz et al. 2004). On the other hand, phosphate can also form Pb-containing precipitates. Some researchers reported that the formation of pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) type minerals is the cause of reduction of Pb solubility after phosphate application (Ma et al. 1997; Ricardo et al. 2003). Using the water-soluble P measured by Xie et al. (2006) and pH, chloride, and Pb concentration used or measured in CaCl_2 extraction of this study, calculation shows that $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ can be formed for all treatments ($\log K_{\text{sol}} = -83.7$). The PR and SSP treatments did not influence the soil pH to a large extent (Fig. 1). The decrease of Pb solubility in these treatments can be attributed to phosphate effects. The solubility of SSP is larger than PR, which is consistent with the results that show a stronger decrease in Pb solubility in the SSP treatments than in the PR treatments (Fig. 4). Addition of iron to soils can increase the amount of iron oxides content in the soils, which can bind Pb. However, the effects of a decreased pH upon iron addition may reverse the positive effect into a negative effect with increased amounts of Fe oxides used.

Chemical immobilization using phosphate addition is a widely accepted and successful technique to immobilize Pb from aqueous solution in contaminated soils (Cao et al. 2008a; Chen et al. 2006; Xie et al. 2006). However, in soils that contains high levels of As as well, phosphate addition enhances release of As to the soil solution phase probably via competitive anion exchange or an increased pH. Enhanced solubility and bioavailability of As upon phosphate amendments have been reported in many studies (Bothe and Brown 1999; Dutr e and Vandecasteele 1998; Mollah et al. 2004). In the present study, the concentrations of the water-soluble As did not change with the PR addition, but increased in the treatments of CMP and SSP. This indicates that the same kind of phosphate, such as PR, may have different effects on the mobility of As in different soils, depending on the properties of the soils and the concentration and chemical states of the As.

Many forms of iron, such as amorphous iron oxides, can increase As adsorption or form arsenic–iron compounds with low solubility (Lenoble et al.

2005). Ferric sulfate is a good material that can be used to immobilize As in soil. Taylor and Fuessle (1994) discussed the relative merits of Fe(III) and Fe(II) as stabilizing agents for arsenate. In other studies, Kim and Davis (2003) found that ferric sulfate treatment is more effective than that of ferrous sulfate to stabilize the available As in the tailings. Ferrous sulfate is often used as major ingredient for As immobilization. Under oxidized soil conditions, Fe^{2+} can be oxidized to the less soluble Fe^{3+} within a few days. The concentration of As in the first step of a sequential extraction, which included the most labile As fraction, was greatly reduced with the FeSO_4 addition (Yang et al. 2007). Moore et al. (2000) used FeSO_4 to immobilize As in contaminated soils from wood-preserving solution at a timber-framing site and achieved good results. The result of Kim and Davis (2003) also showed that with ferric sulfate or ferrous sulfate addition, the mobility and solubility of Pb did not increase. In the present study, however, with the addition of FeSO_4 , the concentrations of water-soluble As decreased, but the concentrations of CaCl_2 -extractable Pb increased. The response of soil pH to iron addition may be one of the important reasons to explain these contradictory results.

4.1 Bioaccessibility of As and Pb in Soil

The bioaccessibility of As and Pb was estimated by measuring As and Pb solubility in artificial gastric (pH=1.5) and small intestinal solutions (pH=7). In the untreated soil (CK), soluble As equals to more than 9% of the total As, in both the gastric and small intestinal phases (Table 1), which is much higher than in the water extraction (0.005%). The bioaccessibility of As did not change significantly from the gastric phase to the small intestinal phase. With the phosphates addition, the bioaccessible As fraction in the gastric solution showed no significant change except a decrease for the treatment of CMP2. In the small intestinal phase, the bioaccessible As fraction decreased for all phosphate treatments except for the treatment with SSP2 (Table 1). Addition of iron decreased in general As solubility compared to the corresponding treatments without iron. The lowest As solubility was found in the treatment of CMP2, i.e., 4.3% and 4.0% in respectively the gastric phase and small intestinal phase, which equals about 40% of that in the control treatment.

Table 1 Bioaccessibility of As and Pb (%) in different FeSO₄ and phosphates treatments

Arsenic	Gastric phase		Small intestinal phase	
	Fe0	Fe2	Fe0	Fe2
CK	9.7±0.1a*	6.0±1.3b	9.5±0.6ab	5.9±0.3b
CMP1	7.6±0.1ab	4.5±0.1c	8.1±0.3bc	5.3±0.3b
CMP2	5.7±0.3b	4.3±0.5c	4.3±0.1d	4.0±0.2c
PR1	8.2±0.2ab	6.4±1.2b	9.0±0.9ab	7.2±0.2a
PR2	7.3±0.2ab	4.5±1.3c	6.7±0.9c	3.9±0.3c
SSP1	8.6±0.4ab	6.4±0.4b	8.0±0.6bc	6.0±0.2b
SSP2	10.2±0.4a	7.6±0.4a	10.5±0.9a	6.9±0.2a
Lead				
CK	52.3±4.7a	42.0±1.1a	8.1±0.1a	6.5±0.2bc
CMP1	38.4±0.9bc	30.8±0.3c	7.8±1.7a	4.4±0.5d
CMP2	32.8±2.1c	27.4±1.6c	1.7±0.3c	2.7±0.4e
PR1	46.8±4.3ab	41.3±0.4a	7.3±0.3ab	8.5±1.0a
PR2	44.1±5.1abc	36.2±2.0b	6.5±0.4ab	5.5±0.3cd
SSP1	42.2±1.7abc	38.8±1.6ab	7.5±0.1ab	7.2±0.5ab
SSP2	39.6±4.3bc	35.7±1.7b	5.5±0.3b	4.8±0.2cd

* $P < 0.05$, means in the same column followed by different letters differ significantly

The much higher As solubility in the synthetic solutions compared to that in the water extraction was also reported by Pouschat and Zagury (2006). The important factor controlled higher As solubility in the synthetic solutions can be due to the presence of organic ligands (citrate, malate, etc.) in both the gastric and small intestinal solutions, and the synthetic solutions could extract both organic and inorganic arsenic (Mir et al. 2007). In general, dissolved metal (hydr)oxides in the gastric phase decreased with increased adsorbed As (Beak et al. 2006). Competition of organic acids with As for adsorption to oxides may also have contributed to the increase of As in solution, especially in the small intestinal solutions. Studies have shown that competition of organic acids such as citrate with oxyanions like phosphate can lead to strong increase of solution concentration of oxyanions (Geelhoed et al. 1998). The study of Geelhoed et al. also showed that the presence of citrate resulted in a much weaker pH effect on phosphate adsorption compared to when no organic ligands are present. The very small difference of As solubility between the gastric and small intestinal phases observed (Table 1),

despite the big pH difference between these two solutions. Arsenic bioaccessibility was independent of simulated stomach and small intestine pH (from 2 to 7) can be due to little variation in adsorption capacity of arsenic in this pH range (Yang et al. 2003). The presence of organic ligands may be another reason to induce small difference of As solubility between the gastric and small intestinal. Oomen et al. (2002) compared five in vitro digestion models and found that the bioaccessibility of As largely depends on the applied methods (different pH and organic ligands). The influence of phosphate and iron treatment on As solubility in the gastric and small intestinal solutions is much smaller than that on the water-soluble As, which can also be explained by the effects of pH and organic ligands in the artificial solutions.

Similar to As, solubility of Pb also increases dramatically in both the gastric and small intestinal solutions compared to that in the CaCl₂ extraction. In contrast to the situation for As, in the case of Pb there is a big difference between the two types of solutions. In the control (CK), 52% of Pb was dissolved in the gastric solution, whereas in the small intestinal solution it was 8%. The lower bioaccessibility of Pb at higher pH could be explained by their strong pH dependence and adsorption to solid (Yang et al. 2003). The bioaccessibility of Pb is much higher than that of As in the gastric phase. The bioaccessibility of Pb decreased in both the gastric and the small intestinal phase with phosphate addition. The lowest bioaccessibilities of Pb were 32.8% and 1.7% in the gastric and the small intestinal phase, which were 63% and 21% of the CK, respectively. With FeSO₄ addition, the bioaccessible Pb fraction in the gastric phase was decreased and the reduction is maximum 10%. Bioaccessible Pb fraction in the small intestinal phase was also decreased by Fe addition except in the treatment of CMP2.

The very high solubility of Pb can be ascribed to desorption of adsorbed Pb and dissolution of Pb-containing minerals. Both the low pH (pH=1.5) and presence of organic ligands in the gastric may have promoted Pb dissolution and desorption. Compared to the CaCl₂-extraction, pH in the small intestinal phase is higher. Despite of this higher pH, the Pb solubility in the small intestinal solution is much higher than in the CaCl₂-extraction. The relative high concentration of citrate, malate, and bile in the synthetic solution may have caused enhanced dissolution of Pb due to

the formation of Pb-organic ligands complexation. With the bile addition, the bioaccessibility of Pb in small intestinal phase increase from 11% to 23% (Oomen et al. 2003). It is likely that the soluble Pb in the small intestinal phase is mainly present as soluble organic Pb complexes.

This stronger pH dependency of Pb solubility in the gastric and small intestinal solutions led to a weaker correlation between bioaccessibility of Pb in gastric and small intestinal phase ($R^2=0.34$) than the correlation between bioaccessibility of As in the two phases ($R^2=0.83$; Figs. 6 and 7). A much weaker pH dependency of As solubility in the stomach and intestine solutions than solubility of Pb has also been found by others (Ruby et al. 1996).

In Pb-contaminated soil, with the addition of three kinds of phosphates, Tang et al. (2004) found that single super-phosphate showed the best performance in minimizing the bioaccessibility of Pb in gastric phase. However, in the small intestinal phase, SSP appears to be the least effective amendment. Bosso et al. (2008) used the $\text{NaH}_2(\text{PO}_4)_3$, super-phosphate and phosphate rock to immobilize Pb in soil and assessed the risk with the bioaccessibility tests. The results showed that the most efficient phosphate source was NaH_2PO_4 , which reduced Pb solubility to 92% in gastric conditions after the first month of incubation. SP and PR also diminished Pb solubility, but the effect was more time dependent. In the present study, the CMP is the most effective among the three phosphate amendments used to reduce the bioaccessibility of Pb. Sarkar et al. (2007) found that the

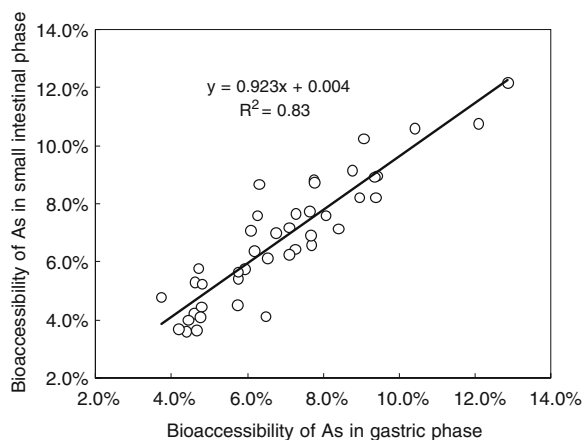


Fig. 6 Relationship between bioaccessibility of As in gastric and small intestinal phase

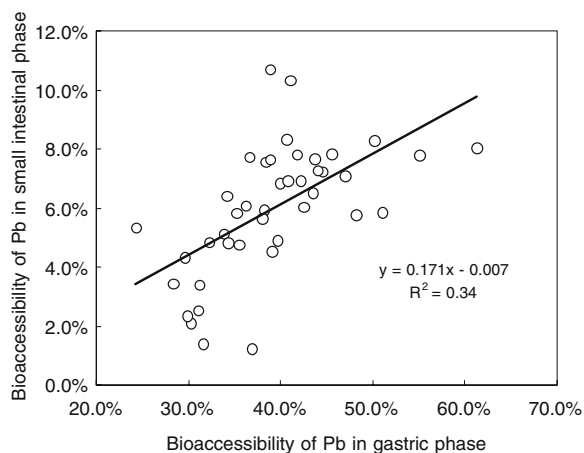


Fig. 7 Relationship between bioaccessibility of Pb in gastric and small intestinal phase

bioaccessibility of soil As in the human stomach was not influenced by the presence or absence of phosphate after considerable equilibration time (12 months). In the present study, the bioaccessibility of soil As did not change except for a small decrease for the treatment of CMP with the addition of phosphate in gastric and small intestinal phase.

Liu and Zhao (2007) found that iron phosphate nanoparticle reduced the bioaccessibility of Pb in soils. Brown et al. (2004) reported a 36% reduction in bioaccessible Pb concentration in a Pb-contaminated soil when 1% of an iron-rich byproduct material (a mineral byproduct produced in the production of TiO_2) was used. In the present study, with the FeSO_4 addition, the concentrations of CaCl_2 -extractable Pb increased, but the bioaccessibility of Pb decreased. Many studies showed that Fe amendments (FeCl_3 , $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, ferrihydrite, Fe^0 , and FeBr_3) may be an effective strategy to decrease As bioaccessibility and bioavailability, and to remediate As-contaminated soils (Martin and Ruby 2003; Subacz et al. 2007). In the present study, FeSO_4 addition decreased the bioaccessibility of soil As in all the treatments in gastric and small intestinal phase.

5 Conclusions

Both the concentrations of CaCl_2 -extractable Pb and the bioaccessibility of Pb decreased with the phosphates addition. Phosphates increased the concentrations of

water-soluble As, but reduced the bioaccessibility of As (CMP and PR). Ferrous sulfate addition reduced the concentrations of water-soluble As, but increased the concentrations of CaCl₂-extractable Pb. Both the bioaccessibility of As and Pb are decreased with ferrous sulfate application. Combined application of phosphates and ferrous sulfate can be an effective approach to lower oral bioaccessibility of As and Pb to human.

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