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The distribution and elevated solubility of lead, arsenic and cesium in contaminated paddy soil enhanced with the electrokinetic field

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Abstract The objectives of this study were to investigate fractionation, solubility and potential bioavailability of Pb, As and Cs in Mississippi River Delta paddy soil under an electrokinetic field (EKF). Effects of EKF on soil pH changes and solid-phase distributions of metal(loid)s were examined. Results showed that fractionation of Pb, As and Cs was largely determined by the nature of elements, loading levels and EKF treatment. Native Pb in the soil was mostly in the amorphous iron oxide, organic matter and residual fractions, native As in the amorphous iron oxide, easily reducible oxide and residue fractions while native Cs in the residue fraction. Added Pb, As and Cs showed distinguished solid-phase distributions: Pb dominantly in the organic matter fraction; As in the amorphous iron oxide fraction, and Cs in the residue with a significant water-soluble plus exchangeable fraction. EKF treatment is effective on lowering soil pH to 1.5 near the anode due to water electrolysis releasing proton which is beneficial for dissolution of metal(loid)s, increasing their overall solubility. The acidification in the anode soil efficiently increased the water-soluble Pb and the exchangeable Cs, implying enhanced solubility and elevated their overall potential bioavailability in the anode region while lower solubility in the cathode area. The building up of water-soluble As in the anode region may be from electromigration of As anion from the cathode. This study shows significant enhancement of redistribution, elevated solubility and overall bioavailability of Pb, As and Cs in Mississippi Delta paddy soil under the EKF.

Keywords Metal(loid) · Distribution · Mobility · Bioavailability · Electrokinetic remediation

Introduction

Soil pollution with heavy metal(loid)s is an increasing global concern due to their persistence, high toxicity and potential carcinogenic characteristics (Davies 1980; Kabata-Pendias 2000; Adriano 2001; Han et al. 2007). Heavy metal(loid)s such as lead (Pb) and arsenic (As) are mainly released to soils from anthropogenic activities such as industrial, agricultural and mining activities (Davies 1980; Kabata-Pendias 2000; Adriano 2001; Cameselle et al. 2013). It was suggested that top soil could be a permanent sink for anthropogenic Pb and As compounds from the atmosphere or hydrosphere (Salazar and Pignata 2014). Pb was largely released to the environment due to coal burning dating from the industrial revolution (Davies 1980; Kabata-Pendias 2000; Adriano 2001; Shotyk et al. 1997). The introduction and combustion of leaded gasoline peaked the Pb emission to the environment during the 1950s–1980s. It was reported that the highest content of Pb was up to 209 mg kg^{-1} in the top roadside soils (Banin et al. 1987). Arsenic is primarily derived from sulfide mining (as As^{5+} in most minerals), tailings (both fully oxidizing tailing with As^{5+} adsorbed on Fe oxides and partially oxidizing tailings with 20 % arsenopyrite, FeAsS and 80 % As^{5+} scorodite, FeAsO$_4$·2H$_2$O), industrial activities such as electronic, fireworks ceramics and glass (Porter and Peterson

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1977; Foster et al. 1998). During the twentieth century, widespread soil pollution with As has been resulted from indiscriminate use of pesticides, herbicides, desiccants and fertilizers in agricultural activities (Mandal 2002). Soils in contaminated sites have been detected with As content as high as more than 1000 mg kg^{-1} (Smith et al. 1998).

On the other hand, as a radionuclide, cesium has been released into soils through nuclear wastes, nuclear power plant accidents, and nuclear weapon testing (Giannakopoulou et al. 2007). 137Cs is a radionuclide of great concern with a half-life of 30.2 years due to its high bioavailability and chemical and biological similarity with potassium, an essential element in living organisms. Chernobyl accident released a huge amount of 137Cs and other radionuclides into surrounding soils (Belarus, Ukraine and Russia) and even spread through the entire Northern Hemisphere (Gommers et al. 2005; Kashparov et al. 2005). Similarly, radionuclides 134Cs and 137Cs) were released during the Fukushima Daiichi nuclear power plant accident in 2011. 137Cs has heavily contaminated the soils in large areas of eastern and northeastern Japan (Yasunari et al. 2011). The soils around Fukushima and neighboring prefectures have been extensively contaminated with depositions of 137Cs in Japan Islands and the surrounding ocean (Yasunari et al. 2011). Radionuclides were reported to be also present and be transported in colloids of groundwater of nuclear ground detonation sites such as the Nevada Test Site (Kersting et al. 1999; Yasunari et al. 2011).

Some current practices for remediating heavy metal(-loid)-contaminated soils relies on "dig-and-dump" or encapsulation, neither of which addresses the issue of soil decontamination. Immobilization or extraction by physicochemical techniques may be expensive and are often appropriate only for small areas where rapid and complete decontamination is required. Other remediation methods, such as soil washing, have an adverse effect on biological activity, soil structure and fertility in addition to significant engineering costs (Pulford and Watson 2003). On the other hand, phytoremediation is an emerging technology that uses various plants to degrade, extract, contain or immobilize contaminants from soil and water (Raskin and Ensley 2000). Phytoextraction is the process of concentrating metals/metalloids in the stems and leaves of accumulating plants (Raskin and Ensley 2000). The development of phytoremediation is being driven primarily due to the high cost of other soil remediation methods as well as the desire to use an environmental benign process. Potential obstacles to a large-scale application of phytoremediation technologies include the time period required for remediation, pollutant levels tolerated by plants and the relative low bioavailability of contaminants.

The water-soluble and exchangeable fractions of metal(loid)s, which are in equilibrium with the solid-phase speciation, are the most bioavailable form to plants (Han et al. 2007; Adriano 2001). The metals and metalloids are present in many solid-phase fractions including exchangeable, carbonate bound, organic bound, iron/manganese oxide bound etc. (Tessier et al. 1979; Han et al. 2007; Han and Banin 1997, 1999; Han et al. 2006, 2008, Han et al. 2012). In order to improve the mobility and bioavailability of heavy metal(loid) in soil, electrokinetic field (EKF) was introduced to enhance phytoremediation efficiency of metal(loid) contaminated soils (Cameselle et al. 2013). EKF involves using a direct or alternating current with electrodes inserted into contaminated soils. When a low intensity electric field is applied, H$^+$ is generated around the anode electrode through the effect of water electrolysis. As a result, more metal(loid)s are demobilized under the acid condition around the anode electrode (Thangavel 2004). In addition, enhanced mobilization processes occur in soils resulting in the transport of metal(loid) ions from the anode to the cathode electrode (Dermont et al. 2008). Electromigration and electroosmosis are two main mechanisms for metal/metalloid transportation (Fig. 1). Water present in soil is able to move toward the cathode through soil pores by electroosmosis, while cations could move to the cathode through electromigration (Cameselle and Reddy 2012). The migration of ions makes it possible for the subsequent removal of soluble metal(loid)s or immobilization with oxides, hydroxides and carbonates during the phytoremediation (Ottosen et al. 2007). However, the detailed mechanisms of releasing/mobilization of metals/metalloids with EKF through transformation of metal/metalloids among various solid-phase components were not clearly understood.

The objectives of this study were: (1) to investigate the fractionation and distribution of Pb, As and Cs among solid-phase components in Mississippi River Delta paddy soil with different input levels, (2) to investigate changes of soil pH influenced by EKF, (3) to determine the redistribution/transformation processes of Pb, As and Cs in soils under EKF from stable fractions into labile fractions, and (4) to evaluate the solubility and overall potential bioavailability of Pb, As and Cs under constant electrical parameters of EKF such as electrical field intensity, mode of voltage, operational time and the distance between the anode and cathode electrodes.
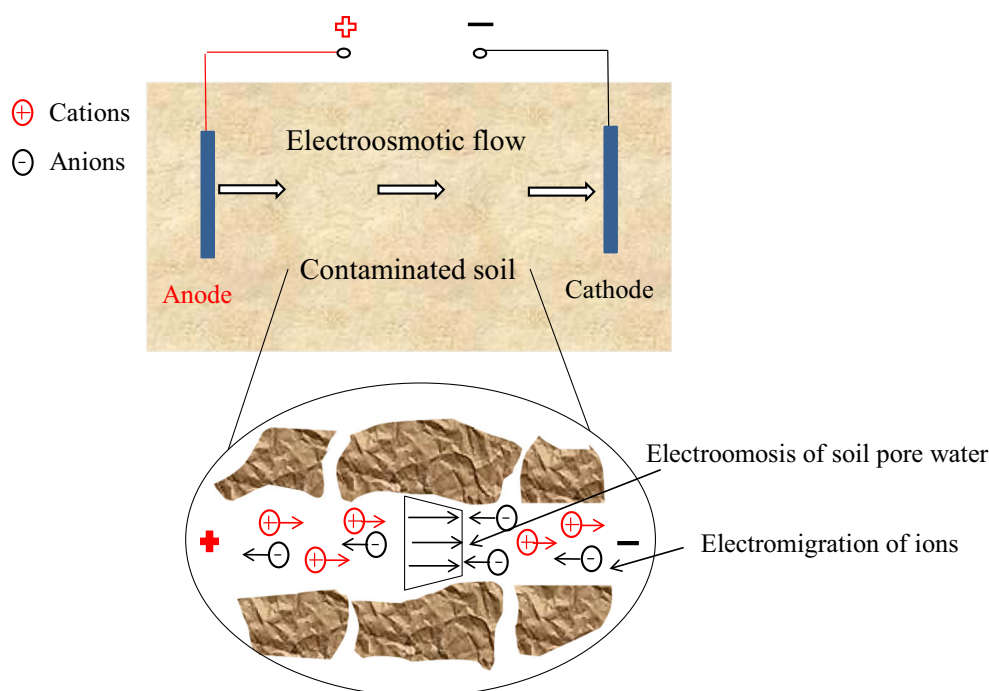
Fig. 1 Diagram of electrokinetic remediation (EKR) of metal(loid) contaminated soils under electrokinetic field (EKF)

Materials and methods

Soil and experimental design

A surface paddy soil (0–15 cm) was sampled from the rice field in the MS River Delta. All soil samples were air-dried and ground to pass 2 mm sieve. Two replicates were set for each treatment (Table 1). About 1 kg of air-dried soil was weighed and placed into each plastic pot with 6 in. (15.2 cm) diameter and 5.4 (13.7 cm) inch height. Chemical grade lead nitrate ($Pb(NO_3)_2$), sodium arsenite ($NaAsO_2$) and cesium chloride (CsCl) were used as Pb, As and Cs sources, respectively. Three content levels were applied for each metal(loid). Pb treatments included the control, 200, 600 and 1000 mg kg^{-1}; As treatments were control, 5, 20 and 100 mg kg^{-1}; and Cs treatments

included the control, 5, 20 and 100 mg kg^{-1}. The control and the middle level treatments for each element were selected for application of EKF: Pb (600 mg kg^{-1}), As (20 mg kg^{-1}) and Cs (20 mg kg^{-1}). Pb, As and Cs salts were ground and mixed with air-dried soil to ensure the homogeneity of mixing the salts with soil. Water moisture was kept at field capacity throughout the incubation period.

EKR setup and determination of metal(loid) speciation

A DC power supplier (0–60 V, 0–3 A) was used as an electrical power source. Graphite electrode rods (0.95 cm diameter, 30.5 cm length) were used as both anodes and cathodes due to their low cost and inertness. A DC electrical field with a constant intensity of 1 V cm^{-1} was applied to soil in plastic pots with a medium concentration level of Pb, As and Cs treatments, respectively. A pair of graphite electrode rods was vertically inserted into both sides of each pot with 13 cm below the soil surface. The copper wire was used to connect the electrode rods with the power source. The electrical equipments were set up after 5 weeks of equilibrium of elements added in soil. In order to study the soil pH and metal(loid) distribution, mobility and bioavailability, the direct current electrical field was applied for 24 h a day. After 15 days of field EKF treatment, surface soil samples (0–5 cm) were collected in the

Table 1 Experimental design of metal(loid) treatments with and without electrokinetic field (EKF)

Treatment	Addition of heavy metal(loid)s (mg kg^{-1})		
	Pb	As	Cs
Without EKF	0	0	0
	600	20	20
	1000	100	100
With EKF	600	20	20

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anode, the middle and the cathode regions of each pot, respectively. The speciation and solid-phase fractionation of metal(loid)s influenced under EKR were examined.

Determination of soil pHs

About 10 g of soil sample was mixed with deionized water at a soil/water ratio of 1:1. Stir the mixture vigorously and allow the slurry to set for about 15 min. A pH meter was used to measure the pH of the slurry after calibration using pH 4, 7 and 10 buffer solutions. The electrode of the pH meter was directly placed into soil slurry, and then pH was read and recorded. Room temperature (20–25 °C) was ensured throughout the pH measurement.

Metal(loid) fractionation and chemical analysis

Lead, arsenic and cesium were assumed to be presented in seven operationally defined fractions (as water-soluble, exchangeable, easily reducible oxide bound, organic matter bound, amorphous iron oxide bound, crystalline iron oxide bound and residual fractions) in soils and obtained with selective sequential dissolution (SSD) which was developed based on sequential extraction procedure proposed by Tessier et al. (1979) and Han and Banin (1997).

Water soluble (SOL)

1.2 g air-dried soil and 25 mL of 0.01 M $CaCl_2$ were added into a 50-mL Teflon centrifuge tube. The mixture were shaken for 30 min at room temperature and then centrifuged for 10 min at 6000 rpm. The supernatant was filtrated through a 0.45-μm filter and kept for the analysis. The soil residue was kept in the Teflon tube for the next extraction procedure. The same centrifugation operation was applied in the following six extraction steps.

Exchangeable (EXC)

Soil residue from the water-soluble fraction was extracted with 25 mL of 1 M neutral NH_4NO_3. The mixture was shaken for 30 min at room temperature.

Easily reducible oxide bound (ERO)

Soil residue was mixed with 25 mL of 0.1 M $NH_2OH.HCL + 0.01$ M HCl and shaken for 30 min.

Organic matter bound (OM)

Soil residue was first mixed with 3 mL of 0.01 M HNO_3 and 5 mL of 30 % H_2O_2. Then, after digestion in water bath for 2 h at 80 °C, another 2 mL of 30 % H_2O_2 was added. After 1 h heating, 15 mL of 1 M NH_4NO_3 was added and the mixture was agitated for 10 min.

Amorphous iron oxide bound (AmoFe)

Soil residue was extracted with 25 mL of 0.2 M $(NH_4)_2C_2O_4$–$H_2C_2O_4$, and the mixture was shaken for 4 h in the dark environment.

Crystalline iron oxide bound (CryFe)

Soil residue was added with 25 mL of 0.04 M $NH_2OH\cdot HCl$ and 25 % CH_3COOH. The mixture was then digested in water bath for 3 h at 95 °C.

Residue (RES)

Soil residue was added with 25 mL of 4 M HNO_3 and digested in water bath for 16 h at 80 °C.

Supernatants collected after centrifugation were filtrated through 0.45 mm filter and further diluted for 20 folds. Pb, As and Cs concentrations in supernatants were determined with inductively coupled plasma mass spectrometry (ICP-MS).

Statistical analysis

The data were processed and the average and the standard deviations were calculated with Microsoft Excel. SPSS 11.5 software was used for statistical analyses. Duncan's multiple range tests were applied for significant analysis of pH changes and metal(loid) speciation under EKF ($P < 0.05$).

Results and discussion

Distribution of Pb, As and Cs in soils with various loading levels

The distribution of Pb, As and Cs among various solid-phase fractions in soils depended upon the nature of elements and their loading levels (Fig. 2). In general, Pb, As and Cs in contaminated soils showed distinguished solid-phase distributions: Pb was dominantly presented in the OM bound fraction (38–52 %); As mainly in the AmoFe bound fraction (40–46 %); and Cs dominantly in the RES fraction (62–68 %) and SOL + EXC (10–17 %). The native Pb, As and Cs in soils showed similar distributions: Pb was dominantly bound to the AmoFe fraction (35 %), followed by the OM fraction (28 %) and RES fraction (18 %); As mainly bound to the AmoFe fraction (57 %), followed by the ERO (14 %) and RES fractions (12 %);
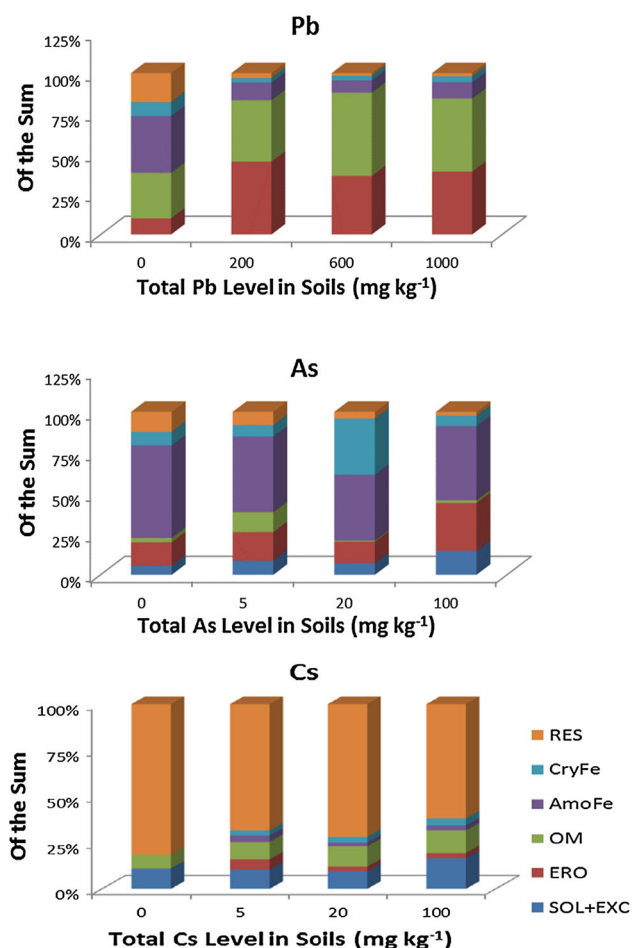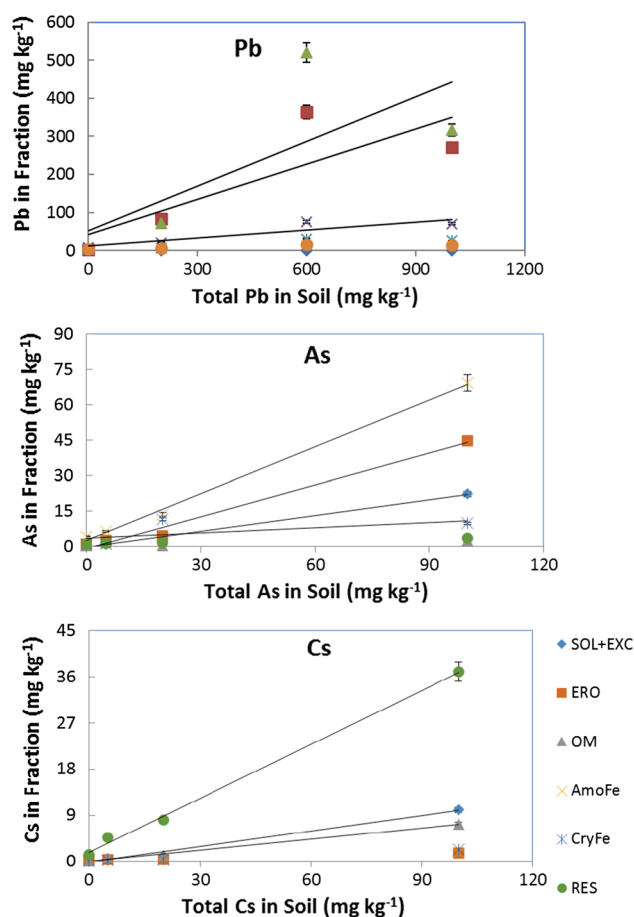
Fig. 2 Distribution of Pb, As and Cs among solid-phase components in Mississippi Delta paddy soils as the increase in Pb, As and Cs loading levels (Day 2 incubation)

Fig. 3 The increases in concentrations of Pb, As and Cs in solid-phase fractions with total Pb, As and Cs loading levels (Day 2 incubation)

and Cs dominantly in the RES fraction (81 %), followed by the SOL + EXC (11 %) and OM bound fractions (7 %).

Obviously, distributions of Pb, As and Cs in soils were significantly influenced by loading levels (Figs. 2, 3). Pb in the OM and ERO fractions, As in the AmoFe and ERO fractions, and Cs in the RES and SOL + EXC fractions all linearly increased with their loading levels. All other solid-phase fractions slowly increased with the loading level as well. This indicates that the organic matter (OM) and Mn oxides (ERO fraction) were major solid-phase components for binding added Pb, the amorphous iron oxides (AmoFe) and Mn oxides (ERO) for added As, and surface exchangeable sites on clay and oxide mineral surfaces (the RES and SOL + EXC fractions) for added Cs. Since Mn/Fe oxides are surface susceptible to redox potential as a change of water regime (Han and Banin 1996), the decrease in redox potential in soil may result in the increase in As and Pb bioavailability. Cesium is

significantly presented in the water-soluble and surface exchangeable fractions, possessing a high solubility and potential bioavailability.

It was reported that distribution of heavy metal(loid)s in soils depended on the nature of elements and their total content (Han et al. 2007). In addition, soil physicochemical properties such as pH, redox potential and organic matter content also influence speciation and binding in soils (Han and Banin 1997; Nyamangara 1998). It was suggested that the water-soluble and exchangeable fraction of metal(loid)s were used to estimate their mobility and bioavailability to plants (Adriano 2001; Kabata-Pendias 2000). Based on the general distribution of metals/metalloids in soil solid components, trace elements are divided into three categories according to their phytoavailability: readily bioavailable (Cd, Ni, Zn, As, Se, Cu); moderately bioavailable (Co, Mn, Fe) and least bioavailable (Pb, Cr, U; Prasad 2003). Pb and As are the two most widespread contaminants in soils. It was reported that exogenous Pb in

agricultural soils was dominantly present in the RES fraction, followed by the OM bound and ERO bound fractions indicating the low bioavailability of Pb (Huang et al. 2014). Arsenic in poultry waste-amended Mississippian soil was mainly present in the RES and Mn/Fe oxide bound fractions (Han et al. 2004a, b). However, arsenic in mined soils was dominantly present in the AmoFe fraction, followed by the CryFe and ERO fractions and a significant increase in the SOL and EXC fractions was observed as the increase in As addition (Marabottini et al. 2013). Not many studies were reported on the distribution of Cs in contaminated soils.

Effect of the electrokinetic field (EKF) on soil pHs

The changes of soil pHs under EKF are shown in Fig. 4. Medium concentration level of Pb (600 mg kg^{-1}), As (20 mg kg^{-1}) and Cs (20 mg kg^{-1}) were used for EKF treatment, respectively. The pHs of different metal(loid) contaminated soils without EKF were all around 6.7, while pHs in the control soil without metal(loid) were around 7.49. This suggested that distribution of metal(loid)s in MS River Delta paddy field soil reduced soil pH. With enhancement of EKF, the pHs of treated soils were significantly polarized upon the electricity current. Sub-region soils near the anode and cathode areas for Pb-, As- and Cs-treated soils were around 1.5 and 10.8, respectively, which significantly changed compared to those without EKF. The data indicated significant acidification and alkalization under operational electrical conditions at DC electrical field intensity of 1 V cm^{-1} for a period of 15 days (24 h a day). It was resulted from the electrolysis of water releasing proton ($2H_2O \rightarrow O_2$ (g) $+ 4H^+ + 4e$ at the anode; $4H_2O + 4e \rightarrow 2H_2$ (g) $+ 4OH^-$ at the cathode) during the EKF. Furthermore, the pHs of soils in the middle region (around 7.5) were larger than those without EKF (around 6.7) indicating the migration of OH$^-$ from the cathode to the anode.

Since most metal(loid)s are solubilized in acid soil environment, lowering soil pH becomes a strategy for increasing bioavailability of most metal(loid)s in soils. Strong acids and weak acids are usually used to neutralize the OH$^-$ in soils with high acid/base buffer capacity (Pérez-Esteban et al. 2013). However, potential risks may be generated in the acidification process. It was reported that, lowering soil pH with HCl may increase the leaching potential of metals and Cl$^-$ to groundwater and the formation of some insoluble salts (i.e., PbCl$_2$; Yeung and Gu 2011). Weak acid such as citric acid and acetic acid are environmental friendly and biodegradable, while their effect on lowering soil pH is not as effective as strong acid (Yeung and Gu 2012). As supported by the present study,
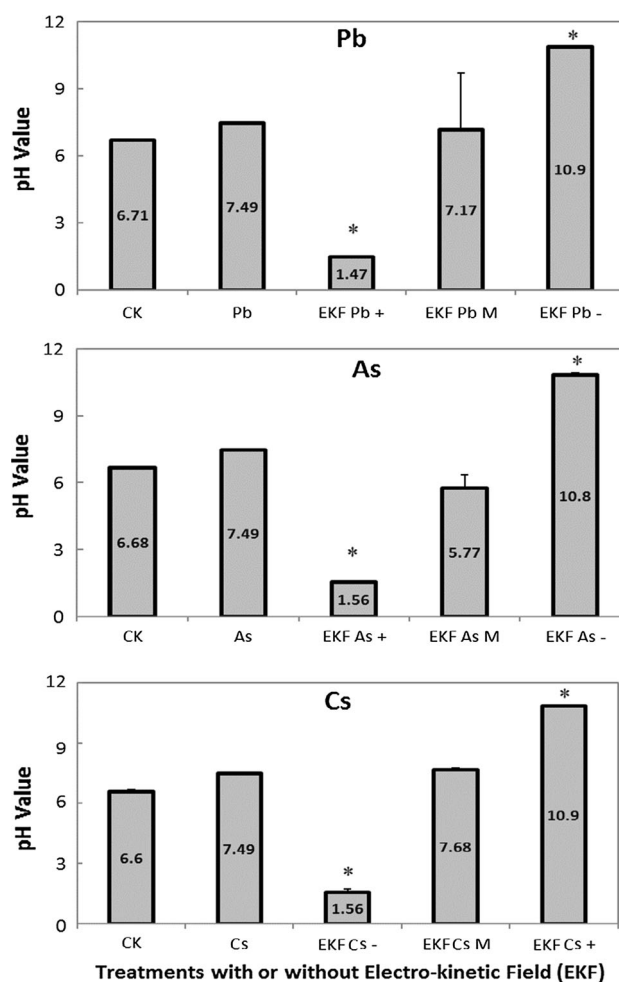
Fig. 4 Effects of EKF on pH changes of Pb-, As-, and Cs-contaminated soil in the anode (+), cathode (−), the middle region (M) between two electrodes, the control soil (CK) and the polluted soils without EKF (Pb, As, Cs). Soil was contaminated with 600 mg kg^{-1} Pb, 20 mg kg^{-1} As and 20 mg kg^{-1} Cs. Means followed by the *asterisk* were significantly different compared with the control soil (CK) at $P < 0.05$

EKF seemed an effective technique to lower soil pH (Puppala et al. 1997). H$^+$ generated by the electrolysis of water decreased the soil pH near the anode region. Through electromigration and electroosmosis, H$^+$ could be transported toward the cathode and naturalize generated OH$^-$ ions to some extent (Kim et al. 2010). Acidification of soil pH was beneficial for solubilization and removal of metal(loid)s such as Pb, Cr, Cd, Cu and Zn (Altin and Degirmenci 2005; Iannelli et al. 2015; Lu et al. 2012; Virkutyte et al. 2002). In addition, addition of organic acids may neutralize the OH$^-$ to some extent and avoided the precipitation of metal(loid)s in the vicinity of the cathode (Lee and Yang 2000; Saichek and Reddy 2003).
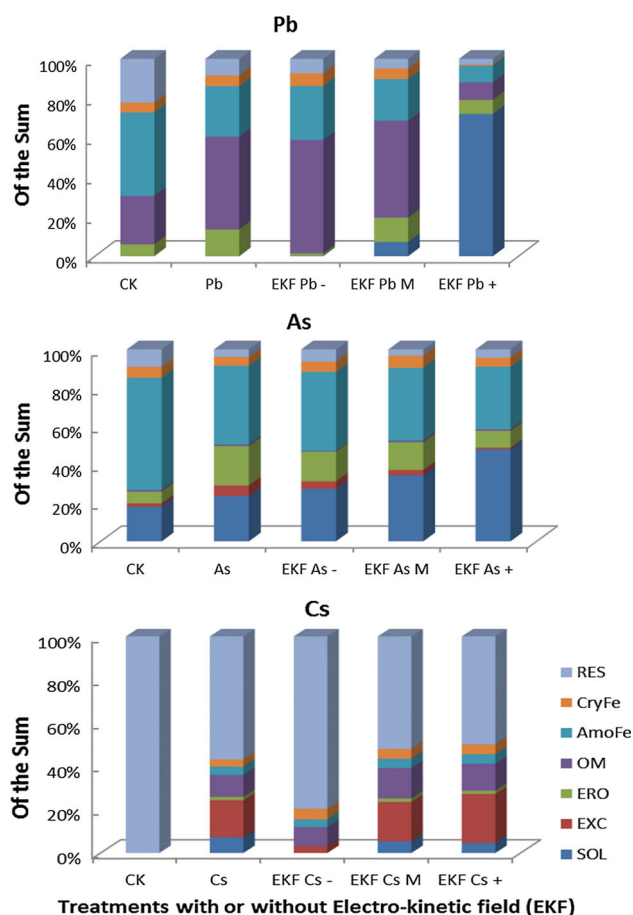
Fig. 5 Distribution of Pb, As and Cs among solid-phase components in contaminated soil with EKF in the anode (+), cathode (−), the middle region (M) between two electrodes, the control soil (CK) and the polluted soils without EKF (Pb, As, Cs). Soil was contaminated with 600 mg kg^{-1} Pb, 20 mg kg^{-1} As and 20 mg kg^{-1} Cs

Distribution of Pb, As and Cs among solid-phase fractions with EKF treatment

The distribution of Pb, As and Cs among solid-phase components under EKF are shown in Fig. 5. With enhancement of EKF, distributions of Pb, As and Cs in soils were dramatically changed. Generally, the native Pb was mainly present in the AmoFe and OM fractions while added Pb at 600 mg kg^{-1} was mainly in the OM, followed by AmoFe and ERO fractions. With EKF, Pb in soil near the cathode and the middle regions was similar to the treated Pb without EKF, but Pb in the soil near to the anode was dominantly in the water-soluble (SOL) form. Pb in the SOL fraction increased from the soil near the cathode, to the middle region, to the soil near to the anode due to the acidification. The OM bound fraction of Pb decreased from the soil in the cathode (57 %) to that in the anode areas

(6.0 %). Same patterns were observed for Pb in the AmoFe (27–5.8 %), CryFe (6.4–0.4 %) and RES (7.1–1.9 %) fractions. On the contrary, the SOL fraction was increased from 1.4 % near the cathode to 86 % near the anode indicating the large potential mobility and bioavailability of Pb enhanced with EKF.

The native and added As was mainly presented in the AmoFe and ERO fractions. With EKF, As in soils near to the cathode and the middle region was similar to As-treated soil without EKF. As in the AmoFe fraction decreased from the cathode (54.7 %), to the middle region (49 %) and to the anode region (46 %). However, the water-soluble As (SOL) in the anode increased to 20.7 % while that in the cathode was 5.7 %.

The native and added Cs in soils was dominantly presented in the RES fraction with a significant amount in the EXC and OM fractions. With EKF, Cs in the EXC fraction increased from the soil near the cathode to the middle region, to the soil near the anode. A large decrease was shown in the RES fraction from the areas near the cathode (82 %) to the anode (65 %). Cs in the EXC fraction increased from the cathode (0.36 %), to the middle region (2.8 %) and to the anode region (3.5 %).

Distributions of Pb, As and Cs in the anode region were more significantly affected than in cathode areas during the EKF. This was the result of strong acidification for solubilization of Pb and Cs around the anode as well as possible electromigration of As anion from the cathode where As was solubilized at high pH. Basically, more water-soluble Pb and As (SOL) were presented in the soil near the anode, while more Cs was found in EXC fraction due to strong acidity. Since acid environment is more beneficial for the transformation of metal(loid)s from the stable forms to the labile forms, Pb, As and Cs in the ERO bound, AmoFe bound and CryFe bound fractions in soils were transferred and redistributed to the SOL and EXC fractions. Furthermore, changes in the solid-phase distribution in soils near the anode were significant compared to those in the middle region and cathode areas, i.e., building up of water-soluble and exchangeable ions in the anode may potentially facilitate the transport of ions such as diffusion processes from the anode to the cathode based on electroosmosis and electromigration. However, the effect of ion transport/diffusion on metal(loid) distribution and alternations of parameters in EKF such as the application of AC electrical field and the distances between the electrodes required further investigation to ensure the homogeneous distribution of metal(loid)s in soil.
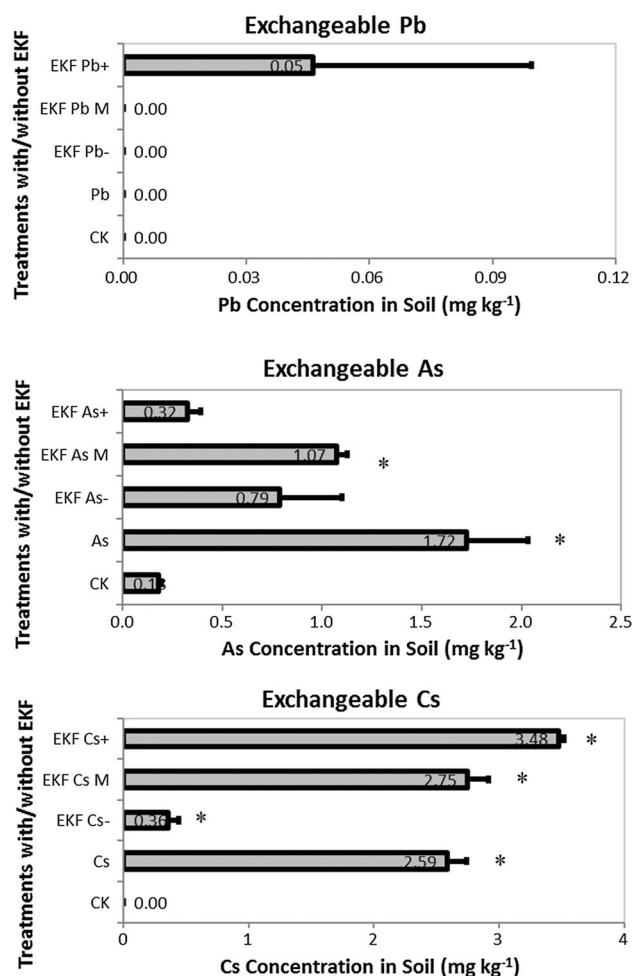
The SOL and EXC fractions of metals/metalloids in soil represent their mobility and bioavailability to plants. Obviously, concentrations of Pb, As and Cs in SOL and
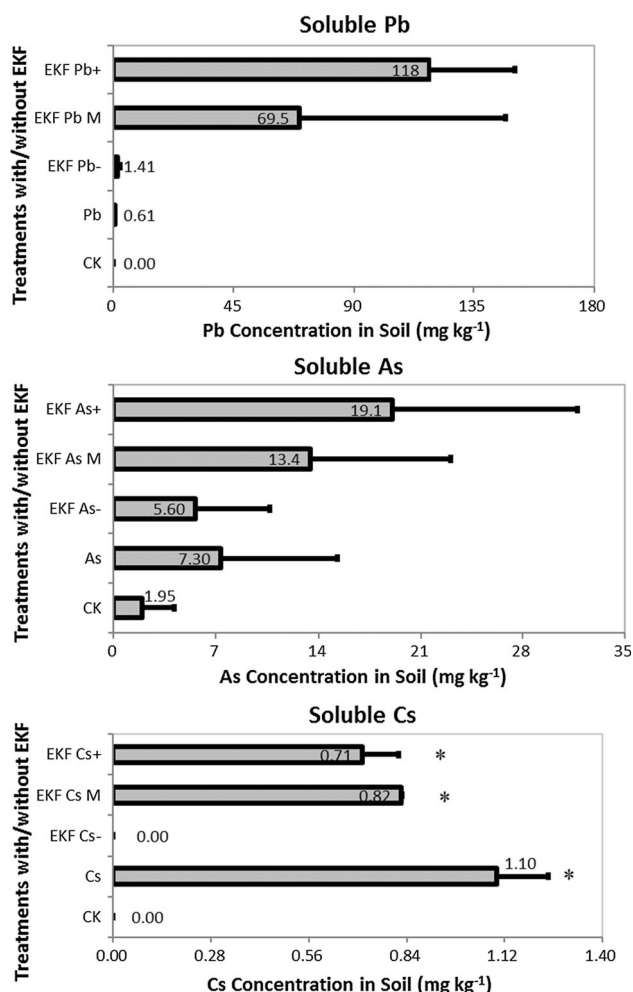
Fig. 6 Changes of soluble Pb, As and Cs in soils with EKF in the anode (+), cathode (−), the middle region (M) between two electrodes, the control soil (CK) and the polluted soils without EKF (Pb, As, Cs). Soil was contaminated with 600 mg kg^{-1} Pb, 20 mg kg^{-1} As and 20 mg kg^{-1} Cs. Means followed by the *asterisk* were significantly different compared with the control soil (CK) at $P < 0.05$
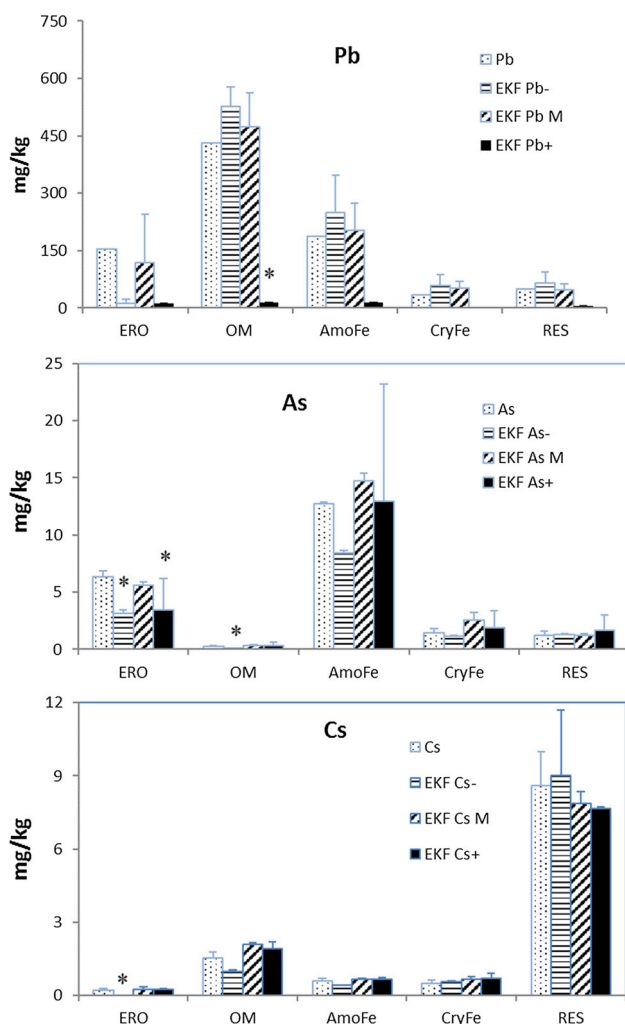
Fig. 7 Changes of exchangeable Pb, As and Cs in soils with EKF in the anode (+), cathode (−), the middle region (M) between two electrodes, the control soil (CK) and the polluted soils without EKF (Pb, As, Cs). Soil was contaminated with 600 mg kg^{-1} Pb, 20 mg kg^{-1} As and 20 mg kg^{-1} Cs. Means followed by the *asterisk* were significantly different compared with the control soil (CK) at $P < 0.05$

EXC fractions were strongly affected by EKF (Figs. 6, 7). At Pb addition of 600 mg kg^{-1}, the SOL fraction of Pb in soil increased from 1.41 mg kg^{-1} near the cathode, to 69.46 mg kg^{-1} near the middle region and 118 mg kg^{-1} near the anode. Slight increase in the EXC fraction was shown (0.05 mg kg^{-1} increase) in the anode area. It was suggested that the native Pb in soil usually is not bioavailable for phytoextraction. However, Pb tends to transfer to the SOL fraction under EKF. With As addition of 20 mg kg^{-1}, the SOL fraction of As in soil increased from 5.6 mg kg^{-1} near the cathode, to 13.4 mg kg^{-1} near the middle region and 19.1 mg kg^{-1} near the anode, while

little decrease in the EXC fraction was shown in all samples. It may indicate that the EXC fraction of As in soil tended to transform to the SOL fraction upon EKF. With Cs addition of 20 mg kg^{-1}, a slight increase in the SOL fraction was found in the middle and cathode areas (0.82 and 0.71 mg kg^{-1}, respectively). However, Cs in the EXC fraction was significantly increased in the anode area (3.48 mg kg^{-1}) compared to that in the cathode (0.36 mg kg^{-1}) which may suggest the Cs was more able to be adhered to adsorption sites of colloids in soil pore influenced by the EKF. Results of the SOL and EXC fractions indicated the comparable higher mobility and

Fig. 8 Changes in selected solid-phase fractions of Pb, As and Cs in soils with EKF in the anode (+), cathode (−), the middle region (M) between two electrodes, and the polluted soils without EKF (Pb, As, Cs). Soil was contaminated with 600 mg kg^{-1} Pb, 20 mg kg^{-1} As and 20 mg kg^{-1} Cs. Means of each metal(loid) fraction followed by *asterisks* were significantly different compared with that of polluted soils without EKF

bioavailability of As and Cs. Larger addition of As and Cs and parameters in EKF such as the electrical field intensity may play important roles in further improving their mobility and bioavailability (Fig. 8).

Moreover, acidification transformed stable fractions (the OM and AmoFe fractions for Pb, the AmoFe fraction for As and the RES for Cs) into the SOL (Pb and As) and EXC (Cs) fractions in soils near the anode (Fig. 8) . Low bioavailability constrains the phytoextraction efficiency of heavy metals (i.e., Pb), while the changes of soil physical–chemical properties may enhance their availability and

mobility. Plants have developed their own strategy for dissolving metals. Secretion of H$^+$ ions by roots will compete binding sites on soil particles with heavy metal cations. As a result, more metals are mobilized under acid condition around rhizosphere (Thangavel 2004). Moreover, activities of rhizospheric microbes significantly increase heavy metal bioavailability which results in the increase in the labile metal in soil (Sheoran et al. 2009). In addition to mobilization by plant itself, the solubility of metal(loid)s could also be enhanced by extraneous soil amendments such as chelating, complexing, organic and microbial agents (Bolan et al. 2014). However, there are still some limitations in applying soil amendments associated with phytoremediation. EDTA was the most common chelating agent for increasing water-soluble metal(loid) in soils (Han et al. 2004a, b). There is no standard for the additive amount of EDTA according to different types of soils and contaminated metal(loid)s. Therefore, excessive addition may cause the leaching of EDTA, plant phytotoxicity and the pollution of groundwater (Han et al. 2004a, b; Wu et al. 2004; Zhao et al. 2011). Engineered microorganisms are usually introduced to soil as microbial agents which effectively increase the mobility of metal(loid)s. However, they may disrupt the ecological balance of the soil environment and lead to species invasion as a consequence of competition with indigenous microorganisms (Roane et al. 2015). It was reported that the SOL fraction of Pb was dramatically increased in soil stimulated by EKR and the phytoremediation could remove 95 % of Pb with an optimization of electrical field intensity and stimulation period (Yang and Lin 1998). EKP treatment also significantly decreased the dominant AmoFe As and CryFe As fractions by 42 and 10 %, respectively, and the removal of total As by phytoremediation increased to 32 % after 4 weeks of EKR (Jeon et al. 2015). In addition, 58 % of Cs was removed after 3 weeks of EKR with electrical field of 5 V (Kim et al. 2015). Without pH maintenance near the cathode, precipitation of metal(loid)s may be generated due to the high OH$^-$ concentration implying the decreased bioavailability of Pb and Cs in soils near the cathode.

However, some limitations appeared over the electrokinetic remediation. Gas species produced during water electrolysis as discussed above may be trapped near the surface of the electrodes thus increasing the resistance and significantly slowing the remediation process (Sah and Chen, 1998). This required initial low voltage with lower resistance in soil and progressive increase in the voltages due to increased resistance developed over the electrokinetic processes. Other possible species such as potential precipitated hydroxides of cations due to the increased pH around the

cathode plugged the soil pores, subsequently hindering the electrical current and decreasing the diffusive flow over time when the voltage is applied (Sah and Chen 1998).

Conclusion

The native Pb in the MS River Delta paddy soils was mostly in the AmoFe, OM and RES fractions, the native As in the AmoFe, ERO and RES fractions, while Cs in the RES fraction. In general, added Pb, As and Cs in paddy soils showed distinguished solid-phase distributions controlled by the nature of the element: Pb was dominantly present in the OM fraction (38–52 %); As in the AmoFe fraction (40–46 %); and Cs in the RES (62–68 %) and SOL + EXC (10–17 %) fractions.

The solid-phase distributions of added Pb, As and Cs were significantly influenced by the electrokinetic field. EKF treatment was efficient on lowering soil pH near to the anode through hydrolysis of water in releasing proton which is beneficial for the dissolution of metal(loid)s. The acidification in the anode region under EKF efficiently increased the SOL Pb (by 193 times) and EXC Cs (by 1.3 times) in the soils while possible electromigration of As anion from the cathode where As was solubilized at high pH may be responsible for building up of SOL As in the anode region (by 2.6 times). In addition, the SOL and EXC fractions progressively decreased from soils in the anode to the cathode areas which implied both acidification of H^+, solubilization/mobilization of elements in the anode and possible precipitation in the cathode due to high OH^- concentration. The bioavailability of Pb, As and Cs may increase upon EKF treatment due to their significant presence in the soluble and exchangeable forms, indicating the EKF treatment might be a good alternative for increasing metal(loid) bioavailability in phytoremediation of Pb-, As- and Cs-contaminated soils. Further studies are required on pH maintenance near the cathode by using organic acids such as acetic acid and citric acid, optimizations of electrical parameters including electrical field intensity, current application mode, the distance between the electrodes and stimulation period and their enhancement on the mobility of bioavailability of metal(loid)s.

Abbreviations

EKF	Electrokinetic field
EKR	Electrokinetic remediation
SOL	The water-soluble fraction
EXC	The exchangeable fraction
ERO	The easily reducible oxide bound fraction
AmoFe	Amorphous iron oxide bound fraction
OM	Organic matter bound fraction
CryFe	Crystalline iron oxide bound fraction
RES	Residual bound fraction
SSD	Selective sequential dissolution
ICP-MS	Inductively coupled plasma mass spectrometry

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