Ecotoxicology and Environmental Safety 125 (2016) 16–24

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Electro-kinetic remediation coupled with phytoremediation to remove lead, arsenic and cesium from contaminated paddy soil

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ARTICLE INFO

Article history:
Received 10 August 2015
Received in revised form
27 October 2015
Accepted 19 November 2015

Keywords:
Metal(loid)
Mobility
Bioavailability
Bioaccumulation
Electro-kinetic remediation
Phytoremediation

ABSTRACT

The objectives of this study were to investigate distribution and solubility of Pb, Cs and As in soils under electrokinetic field and examine the processes of coupled electrokinetic phytoremediation of polluted soils. The elevated bioavailability and bioaccumulation of Pb, As and Cs in paddy soil under an electrokinetic field (EKF) were studied. The results show that the EKF treatment is effective on lowering soil pH to around 1.5 near the anode which is beneficial for the dissolution of metal(loid)s, thus increasing their overall solubility. The acidification in the anode soil efficiently increased the water soluble (SOL) and exchangeable (EXC) Pb, As and Cs, implying enhanced solubility and elevated overall potential bioavailability in the anode region while lower solubility in the cathode areas. Bioaccumulations of Pb, As and Cs were largely determined by the nature of elements, loading levels and EKF treatment. The native Pb in soil usually is not bioavailable. However, EKF treatment tends to transfer Pb to the SOL and EXC fractions improving the phytoextraction efficiency. Similarly, EKF transferred more EXC As and Cs to the SOL fraction significantly increasing their bioaccumulation in plant roots and shoots. Pb and As were accumulated more in plant roots than in shoots while Cs was accumulated more in shoots due to its similarity of chemical properties to potassium. Indian mustard, spinach and cabbage are good accumulators for Cs. Translocation of Pb, As and Cs from plant roots to shoots were enhanced by EKF. However, this study indicated the overall low phytoextraction efficiency of these plants.

1. Introduction

Heavy metal(loid)s and their pollution are an increasing global concern due to their persistence, high toxicity and potential carcinogenic characteristics (Han, 2007). Heavy metal(loid)s such as lead (Pb) and arsenic (As) are mainly released to soils from anthropogenic activities such as industrial, agricultural activities and mining which have become a serious global environmental threat (Han et al., 2004; Cameselle et al., 2013). It was suggested that top soil could be an permanent sink for anthropogenic Pb and As compounds from the atmosphere or hydrosphere (Salazar and Pignata, 2014). Pb was first largely released to the environment due to coal burning dating from the industrial revolution (Shotyk et al., 1997). The introduction and combustion of leaded gasoline peaked Pb emission during 1950–1980s. In terms of As, it is primarily derived from mining and industrial activities such as electronics, fireworks, ceramics and glasses (Porter and Peterson, 1977). During the 20th century, widespread soil pollution with As has been caused by indiscriminate use of pesticides, herbicides, desiccants and fertilizers in agricultural activities (Mandal, 2002). On the other hand, as a radioactive contaminant, cesium has been released into soils through nuclear wastes, nuclear power plant accidents, and nuclear weapon testing (Giannakopoulou et al., 2007). 137Cs is a radioactive pollutant of great concern with a half life of 30.2 years, 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. Similarly, radionuclides (134Cs, 137Cs) were released during the Fukushima Daiichi nuclear power plant accident in 2011 (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).

Phytoextraction, an emerging technology for metal(loid) cleanup, is the process of concentrating metal(loid)s from soil solution

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http://dx.doi.org/10.1016/j.ecoenv.2015.11.021

in the stems and leaves of plants (Raskin and Ensley, 2000). The development of phytoextraction is being driven primarily by the high cost of other soil remediation methods as well as the desire to use an environmental benign process. The success of phytoextraction depends on the tolerance and translocation ability of plants to target metal(loid)s (Lotfy and Mostafa, 2014). Translocation factors (TF), which are ratios of the metal(loid) concentrations in shoots to those in roots, describe the metal(loid) extraction efficiency by plants (Cui et al., 2007). The success of phytoextraction also, is determined by the bioavailability of metal (loid)s in soil. Before metal(loid)s enter into plant systems from soil solution, they must be transported to root surface. This is primarily dependent on the bioavailability of metal(loid)s which are major factors limiting metal(loid) uptake in plant roots (Barber, 1995). The water soluble and exchangeable fractions of metal(loid) s, which are in equilibrium with the solid-phase speciation, are the most bioavailable form for metal(loid)s to plants (Han, 2007). 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, 2007; Han and Banin, 1997, 1999; Han et al., 2012). Secretion of H^+ ions by plant roots improves the mobility and bioavailability of heavy metal(loid)s in soil by competing the binding site of soil particles with metal(loid) cations. As a result, more metals are transformed into bioavailable forms under acid condition around the rhizosphere (Thangavel and Subbhuraam, 2004).

In addition to plant own strategy, electro-kinetic field (EKF) was also recently introduced to enhance phytoextraction 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 and Subbhuraam, 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 the transportation of metals and metalloids (Fig. 1). Water present in soil is able to move towards the cathode through soil pores by electroosmosis while cations 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, hydroxide and carbonates during the phytoremediation (Ottosen et al., 2007). However, the detailed mechanisms of releasing/mobilization of metals/metalloids with EKF coupled with phytoremediation are not clearly understood. Especially coupled electro-kinetic phytoremediation has not been applied to remediate Cs contaminated soils. Moreover, with a rapid global urbanization and metropolitanization, the municipal suburb agricultural land plays an increasing role in supplying fresh vegetables to the metropolitan consumption, especially in the developing world. However, municipal suburb vegetable lands are most vulnerable to be contaminated with anthropogenic activities (Han, 2007). Therefore, understanding bioaccumulation and transport of Cs, Pb and As by vegetable plants under electrokinetic treatment is essential to further prevent pollutants into the food chain.

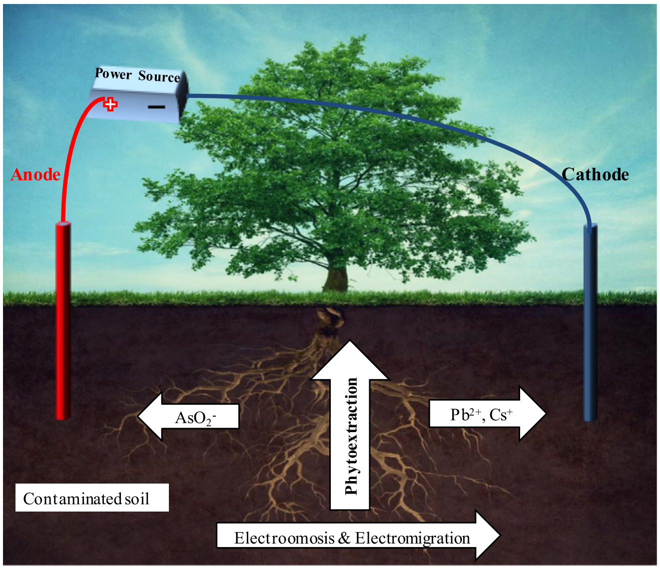

Fig. 1. Schematic diagram of electro-kinetic coupled/enhanced phytoremediation.

The objectives of this study were: (1) To investigate the coupled electro-kinetic remediation with phytoremediation to remove Pb, As and Cs from polluted soils, (2) To study bioavailability of Pb, As and Cs in Mississippi River Delta paddy soil after a growing season enhanced by EKF, and (3) To determine the bioaccumulation of Pb, As and Cs in Indian mustard, spinach and cabbage plants under EKF treatment.

2. Materials and methods

2.1. Soil and experimental design

The surface paddy soils (0–15 cm) were sampled from a rice field in the MS River Delta. All soil samples were air-dried and ground to pass 2 mm sieve. Potted experiment was carried out in greenhouse. Two replicates were set for each treatment. 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 in. (13.7 cm) height. Nitrogen, phosphorous and potassium were added as base fertilizers with a ratio of 1:1:1. 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. Nitrogen brought from lead nitrate was compensated by nitrate fertilizer. Three levels were applied for each metal(loid). Pb treatment included the control, 200, 600 and 1000 mg kg^{-1}; As and Cs treatments were the control, 5, 20 and 100 mg kg^{-1}. The control and the middle level treatment 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 gradually with air-dried soil to ensure the homogeneity of mixing the salts with soil. Indian mustard (*Brassica juncea*), spinach (*Spinacia oleracea*) and cabbage (*Brassica rapa*) were planted in each pot. Ten seeds of each plant were sowed in pots after the selection for uniformity. After 7 days, the seedlings of Indian mustard and spinach were thinned to 3 plants per pot while the seedlings of cabbage were thinned to 1 plant per pot. Water moisture was kept at field capacity throughout 7-week growth period of the experiment. Plastic trays were placed under each pot in case of the loss of nutrients and trace elements. Leaches were collected and put back to the respective pots.

2.2. EKR setup and determination of metal(loid) solubility and bioaccumulation

A DC power supplier (0–60 V, 0–3 A) was used as electrical power source. Graphite electrode rod (0.95 cm diameter, 30.5 cm length) was used as both anode and cathode due to its low cost and inertness. A DC electrical field with constant intensity of 1 V cm^{-1} was applied to soil in plastic pots with a medium concentration level of Pb, As and Cs, respectively. A pair of graphite electrode rods were vertically inserted into both sides of each pot with 13 cm below the soil surface. The copper wire was used to connect electrode rods with the power source. The electrical equipments were set up after 5 weeks of equilibrium of added elements in soil. In order to study the soil pH, metal(loid) solubility and bioavailability in soil and metal(loid) bioaccumulation, the direct current electrical field was applied for 24 h a day. Since soil pH changed with the distance from both anode and cathode systematically under electrokinetic field as showed in the present study, a transect sample line of three sub-regions were employed. Although more subsamples are desired for demonstrating the more detailed gradient distribution of metals/metalloid along the electric field direction, due to the large work load with sample analyses, three subsamples per pot were sampled. After 15-day EKF treatment, surface soil samples (0–5 cm) were collected in the anode, the middle and the cathode areas of each pot, respectively and plant roots and shoots were collected in the middle region. The water soluble (SOL) and exchangeable (EXC) metal(loid)s influenced under EKR were examined.

2.3. *Determination of soil pH*

About 10 g of each soil sample was mixed with deionized water at 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 buffers. 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.

2.4. *Metal(loid) solubility, bioavailability and chemical analysis*

The solubility of lead, arsenic and cesium were examined with water extractability. Both water soluble and exchangeable metal (loid)s indicated their bioavailability to plants.

2.4.1. *Water soluble (SOL) metal(loid)s*

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 was 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 and used in the next extraction procedure. The same centrifugation operation was applied in the exchangeable step.

2.4.2. *Exchangeable (EXC) metal(loid)s*

Soil residue from water soluble fraction was extracted with 25 mL of 1 M NH_4NO_3 which NH_4OH was used to adjust the pH to 7.0 (Kashem et al., 2007; Han et al., 2001; Han, 2007). The mixture was shaken for 30 min at room temperature. Both pH unjustified salt and pH-adjusted neutral salts have been used to extract the exchangeable fraction of trace elements. Since the present study focused on acidification of polluted soils by electrokinetic treatment, a neutral salt with pH adjusted to pH 7.0 was employed.

Supernatants of water soluble and exchangeable forms collected after centrifugation and filtration were diluted for up to 10 folds. Pb, As and Cs concentrations in supernatants were then determined by inductively coupled plasma mass spectrometry (ICP-MS).

2.5. *Determination of metal(loid) bioaccumulation in plant tissues*

Plants shoots were harvested approximately 1 cm above the soil surface after 7-week growth period. Roots were collected and washed with deionized water. All the plant samples were put in paper bags and dried at 80 °C in an oven for 48 h. The dried plant samples were grounded and then weighed. About 0.15 g of dried plant sample was put in a test tube and mixed with 1.5 ml concentrated HNO_3. The tube was covered with Para-film for 24 h and then the plant samples were digested with H_2O_2 (30% w/v) at 95 °C in a hot block (Maruthi Sridhar et al., 2005). The digested solution was diluted to 50 mL and filtered and then analyzed for Pb, As and Cs concentration by using ICP-MS.

2.6. *Determination of translocation factors*

Translocation factor (TF) was the ratio of the metal concentration in shoots to that in roots (Cui et al., 2007). It describes the metal translocation ability in plants from roots to shoots.

$$\text{Translocation factor} = \frac{\text{Metal in shoots(mg/Kg)}}{\text{Metal in roots(mg/Kg)}}$$

Translocation factors were used to evaluate Pb, As and Cs phytoextraction ability of Indian mustard, spinach and cabbage under EKF.

2.7. *Statistical analyses*

The data were processed and the averages the standard deviations were calculated by Microsoft Excel. SPSS 11.5 software was used for statistical analyses. Duncan's multiple range tests were applied for significant analysis of pH changes, metal(loid) solubility/bioavailability, bioaccumulation and TF under EKF ($P < 0.05$).

3. Results and discussions

3.1. *Solubility and bioavailability of As, Cs and Pb in soils*

The SOL and EXC Pb, As and Cs in soils contaminated with different levels of $Pb(NO_3)_2$, $NaAsO_2$ and CsCl after a growing season are presented in Fig. 2. In general, Pb, As and Cs in the SOL and EXC fractions all linearly increased with their loading levels even after a growing season. In soils without plant growing, Pb had 0.78 and 0.006 mg kg^{-1} in SOL and EXC fractions, respectively when added Pb was at 600 mg kg^{-1}. While at 100 mg kg^{-1} loading level, As had 20 and 5.75 mg kg^{-1} in SOL and EXC fractions, respectively and Cs had 0.24 and 7.5 mg kg^{-1} in SOL and EXC fractions, respectively. The SOL and EXC fractions of metal(loid)s, which are in equilibrium with the solid-phase speciation, represent their overall bioavailability in soils (Han et al., 2007). Pb had much less SOL and EXC fractions compared to As and Cs. This indicated the relatively lower solubility of Pb compared to As and Cs. It was reported that, exogenous Pb in agricultural soils was dominantly bounded with organic matter, Mn oxides and carbonates, depending upon the soil properties (Han et al., 2007; Han et al., 2004). Since Fe/Mn oxides are 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 Pb bioavailability. Arsenic in poultry waste-amended Mississippian soil was mainly bounded with Fe and Mn oxides. Thus, lowering soil pH may increase the solubility of As (Han et al., 2004). Not many studies were reported on the distribution of Cs in contaminated soils.

Plants may enhance the bioavailability of metal(loid) in soils to some degrees. No significant increases in the SOL and EXC fractions of Pb were observed in soils with plants indicating that the influence of plants on Pb bioavailability was not as significant as effects of electrokinetic fields-acidification during the growing season. Increases of As and Cs in the SOL and EXC fractions were distinguished in soils with Indian mustard, spinach and cabbage

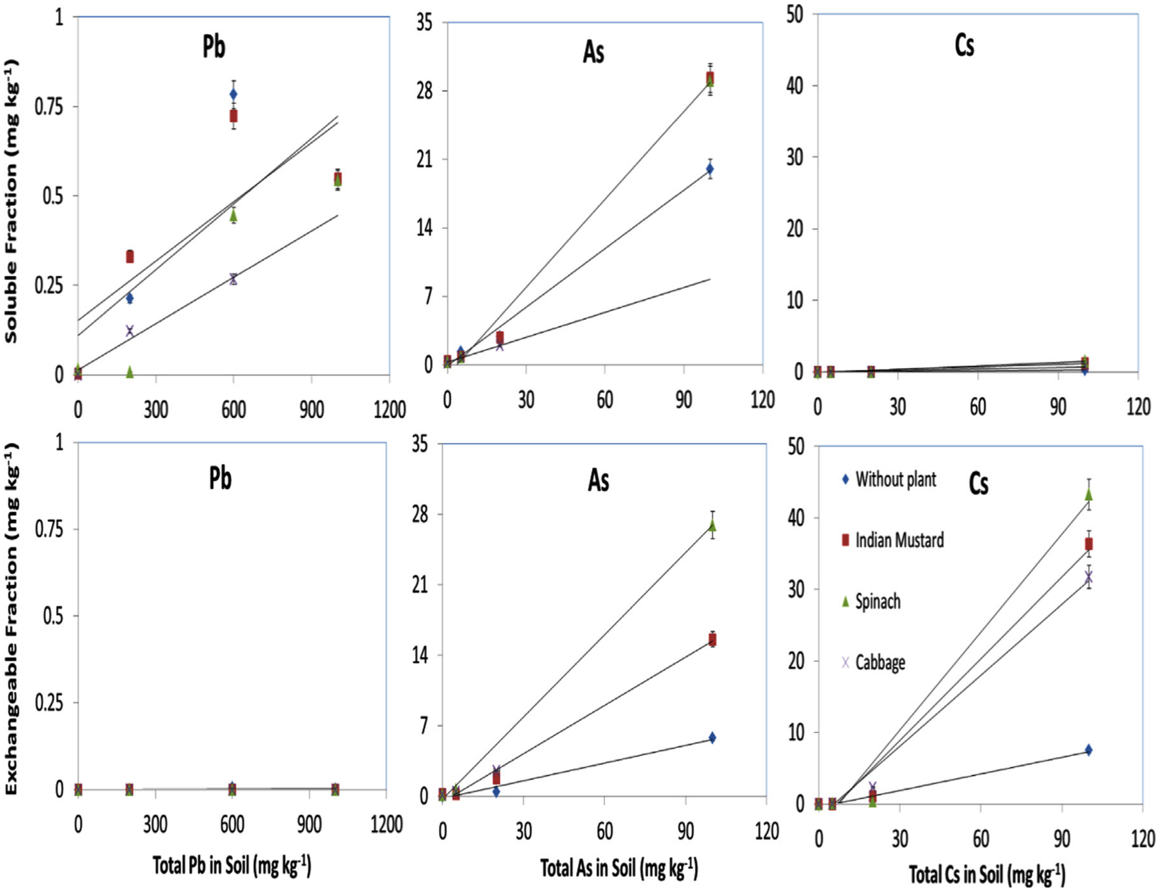

Fig. 2. Increases in concentrations of water soluble and exchangeable Pb, As and Cs with total Pb, As and Cs loading levels in soils.

(Fig. 2). At 100 mg kg^{-1} loading level, As was approximately increased by 9.3–9.1 mg kg^{-1} in SOL fraction and 16–27 mg kg^{-1} in EXC fraction in Indian mustard and spinach treatments. With Cs addition at 100 mg kg^{-1}, slight increases (less than 2 mg kg^{-1}) in the SOL fraction was observed, while significant increases in the EXC (32–43 mg kg^{-1}) was found from all soils with cabbage, Indian mustard and spinach treatments. It was reported that plants indirectly promoted the transport and bioavailability of metal (loid) via plant root exudates and rhizosphere microbial activities (Khan, 2005). Plant exudates, including organic acids, may compete oxides/hydroxides and ion exchange site on soil particles with metal(loid) (Marschner, 1995). Organic acids lower the rhizosphere soil pH which may also increase metal bioavailability (Naidu et al., 2003). In addition, rhizosphere microbes increase metal bioavailability by catalyzing redox reactions and exuding organic ligands (Thangavel and Subbhuraam, 2004). Silva Gonzaga et al. (2012) found great enhancement on As soil bioavailability by using root exuding acids while the mechanisms of rhizosphere effects on Cs bioavailability in soil were not clearly understood.

Bioaccumulation of Pb, As and Cs in plant tissues with loading levels are shown in Fig. 3. The increases in metal(loid)s in plant shoots and roots were observed as the increase in their SOL and EXC fractions in soils. This indicates that the SOL and EXC fractions of metal(loid)s are the bioavailable fractions for the direct uptake by plants. In general, Pb and As were accumulated more in roots than in shoots of Indian mustard, spinach and cabbage. This was resulted from the two-stage process of phytoextraction: metal (loid)s were first taken up by plant roots via the mass flow of water/root surface contact/diffusion process and then transported from roots to shoots (Pettersson, 1976). It was reported that certain metal(loid) ions were transported through the root plasma membrane and potentially accumulated by different plants (Alloway et al., 1990). Indian mustard is a well-known hyperaccumulator of Pb which also has good adsorption capacity of As (Selvaraj et al., 2013). Zaier, et al. (2010) found 340 mg kg^{-1} and $>$ 1000 mg kg^{-1} Pb were accumulated in roots and shoots of Indian mustard, respectively. In addition, spinach and cabbage were reported to be good accumulators of Pb and As (Hara et al., 1977; Selvaraj et al., 2013; Knapp et al., 2013; Saraswati and Watters, 1994). However, Cs showed the higher translocation efficiency in these plants.

3.2. Effect of the electro-kinetic field (EKF) on soil pHs

The changes of soil pHs under EKF are shown in Table 1. 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. The pHs of contaminated soils without EKF were all around 6.7 while pHs in the control soil without metal(loid) were around 7.5. This suggested that these three metal(loid)s 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 11, 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 during the EKF. Furthermore, 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.

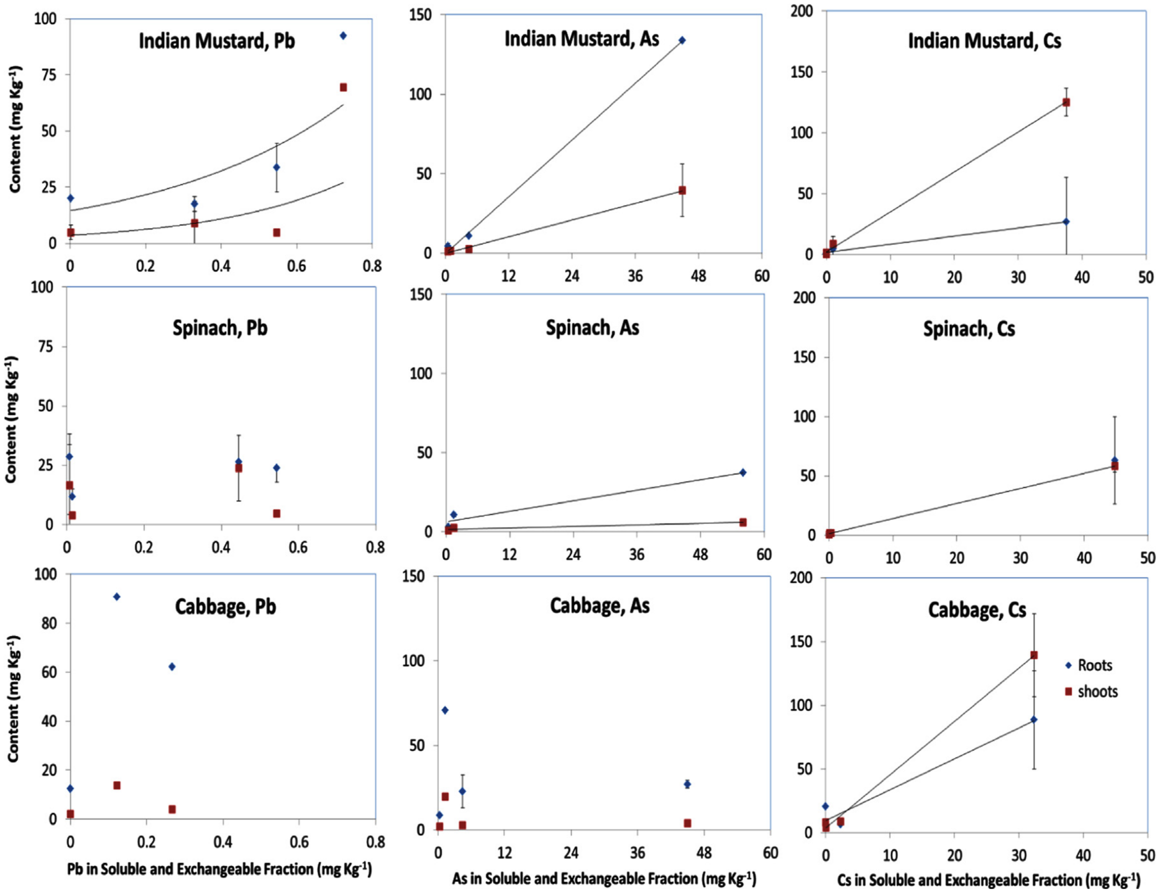

Fig. 3. Pb, As and Cs content in roots and shoots of Indian mustard, spinach and cabbage plants after a growing season with the increases in soluble + exchangeable Pb, As and Cs in polluted soils. Soil was contaminated with 0, 200, 600, 1000 mg kg^{-1} Pb, 0, 5, 20, 100 mg kg^{-1} As and 0, 5, 20, 100 mg kg^{-1} Cs. Means followed by the asterisk (*) were statistically different to the control (for $P < 0.05$).

Table 1
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 Cs.

Treatment		Average soil pH		
		Pb	As	Cs
Without EKF	CK	7.5 ± 0.04	7.5 ± 0.04	7.5 ± 0.04
	Polluted soil	6.7 ± 0.01	6.7 ± 0.03 *	6.6 ± 0.07 *
With EKF	−	11 ± 0.06 *	11 ± 0.09 *	11 ± 0.03 *
	M	7.2 ± 2.6	5.8 ± 0.59 *	7.7 ± 0.12 *
	+	1.5 ± 0.07 *	1.6 ± 0.04 *	1.6 ± 0.18 *

Means followed by the asterisk (*) were statistically different to the control (CK) at $P < 0.05$. Error bars represented ± one standard error ($n = 2$).

3.3. *Effects of EKF on water soluble and exchangeable Pb, As and Cs in soils*

The SOL and EXC Pb, As and Cs in soils planted with Indian mustard and spinach (cabbage was failed in planting) under EKF are shown in Fig. 4. Obviously, concentrations of SOL and EXC Pb, As and Cs were strongly affected by EKF. With Pb addition of 600 mg kg^{-1}, the SOL Pb increased by 4.7 mg kg^{-1} near the cathode, 54 mg kg^{-1} near the middle region and 224 mg kg^{-1} near the anode for the Indian mustard and increased by 12 and 2.6 and 122 mg kg^{-1} for the cathode, the middle region and the anode regions, respectively for spinach treatments. Significant increases in the EXC Pb were observed in the anode (232–277 mg kg^{-1}) and middle regions (291–359 mg kg^{-1}) for both plants. It was suggested that, the native Pb in soil usually are not bioavailable for phytoextraction. However, Pb tends to be transferred to the SOL and EXC fractions with EKF. With As addition of 20 mg kg^{-1}, the SOL As in soil increased by 3.8–7.1 mg kg^{-1} near the anode for Indian mustard and spinach treatments while little decrease in the EXC fraction was shown in all treatments. This indicated that the EXC 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 all treatments. However, the EXC Cs was significantly increased in the anode (2.7–5.4 mg kg^{-1}) and middle areas (3.4–3.9 mg kg^{-1}) for Indian mustard and spinach treatments which may suggest that Cs was more able to be in exchangeable sites of the colloids in soil pore under EKF.

As supported by the present study, EKF seemed a novel and effective technique to mobilize metal(loid)s by lowering soil pH (Puppala et al., 1997). H^{+} generated by the electrolysis of water decreased the soil pH near the anode region. A strong acidification and corresponding solubilization of eletrokinetic treatment occurred in the anode regions where soil pH was as low as 1.5, resulting in a significant solubilization of cation Pb and to some extent Cs. Compared to dominant acidification and solubilization in the anode, electro-transport of Pb^{2+} and Cs^{+} from the anode to the cathode was relatively weak since cations Pb^{2+} and Cs^{+} were bound to the negatively charged clay particles. Overall transport of Pb^{2+}/Cs^{+}-bound negatively charged clay particles were relatively weak under the current electrokinetic field, resulting in the significant building up of soluble Pb to some extent Cs cations in the

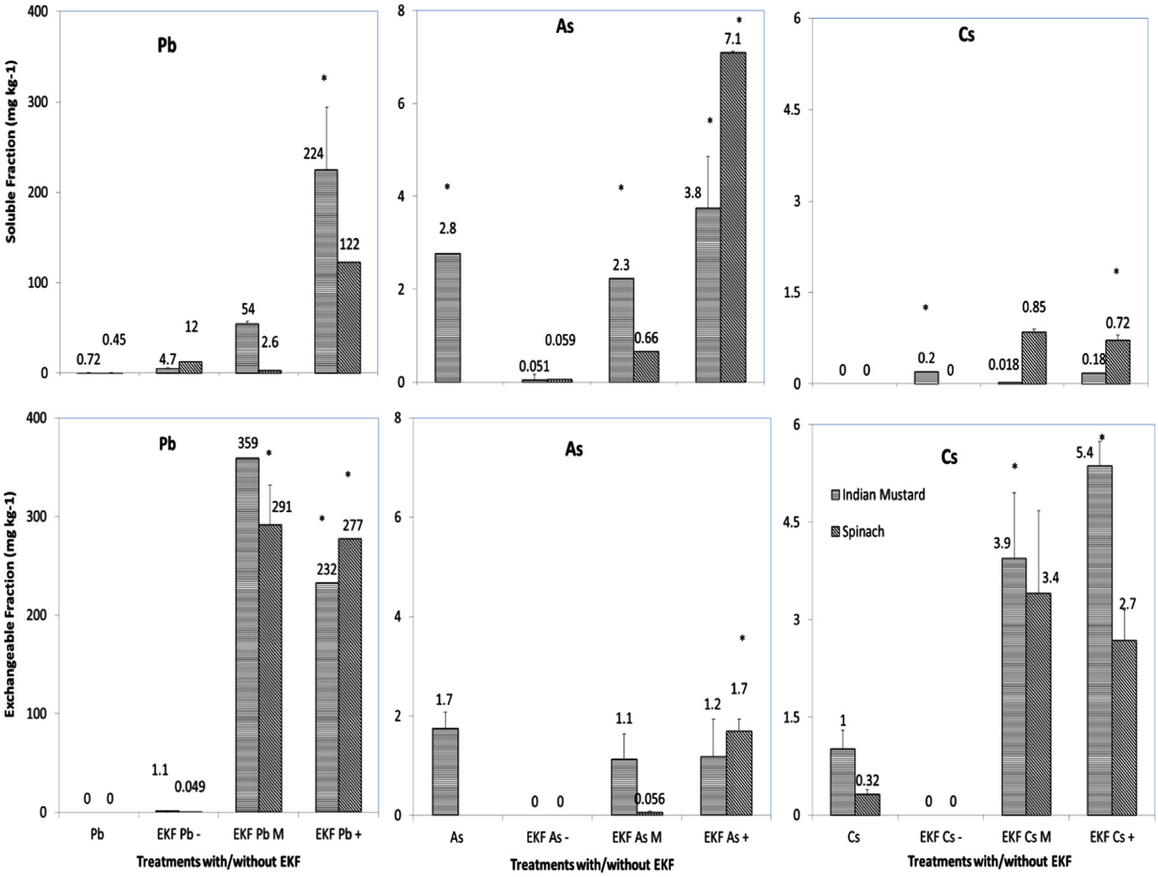

Fig. 4. Changes of soluble and exchangeable Pb, As and Cs in contaminated soil after EKF treatment in the anode (+), cathode (−), the middle region (M) between two electrodes and the polluted soils without EKF (Pb, As, Cs). Soil was contaminated with 600 mg kg^{-1} Pb, 20 mg kg^{-1} As and 20 mg kg^{-1} Cs. Means followed by the asterisk (*) were statistically different to the control (CK) at $P < 0.05$.

anode region than in the cathode region. On the other hand, anion As ion is more soluble in the high pH cathode regions than the low pH anode. However, under electric field, As anion such as arsenate (AsO_4^-) is easily transported from the cathode to the anode region during 14 days of treatment, resulting in the building up of As in the anode region.

Through electromigration and electroosmosis, H^+ could be transported towards the cathode and naturalize the 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, As, Cu and Zn (Altin and Degirmenci, 2005; Iannelli et al., 2015; Lu et al., 2012; Virkutyte et al., 2002). It was reported that the SOL Pb was dramatically increased in soil stimulated by EKF and the phytoremediation could remove 95% of Pb with the optimization of electrical field intensity and stimulation period (Yang and Lin, 1998). Arsenic tended to be transformed to the SOL and EXC fractions and the removal of total As by plants increased to 32% after 4 weeks of EKF (Jeon et al., 2015). In addition, Cs was reported to be largely mobilized in soil and 58% of Cs was removed by plants after 3-week of EKF with electrical field of 5 V (Kim et al., 2015). To increase the efficiency of phytoextraction, organic acids may be added to be coupled with EKF which depolarized 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). Organic acid such as citric acid and acetic acid are biodegradable without risks of plant phytotoxicity and the pollution of groundwater (Han et al., 2004; Wu et al., 2004; Zhao et al., 2011). Without pH maintenance near the cathode, precipitation of metals may be generated due to the high OH^- concentration implying the decrease in their bioavailability in soils near the cathodes.

3.4. Bioaccumulation of Pb, As and Cs under EKF

The contents of Pb, As and Cs in plant tissues under EKF are shown in Fig. 5. In general, EKF significantly increased the contents of metal(loid)s in tissues of both Indian mustard and spinach (cabbage was failed in planting). This indicates higher bioavailable Pb, As and Cs in soils under EKF. At 600 mg kg^{-1}, Pb concentrations in Indian mustard were 581 and 69 mg kg^{-1} in roots and shoots, respectively; while those in spinach were 565 and 381 mg kg^{-1} in roots and shoots, respectively. With addition of 20 mg kg^{-1} As, As concentrations in Indian mustard were significantly increased in both roots (62 mg kg^{-1}) and shoots (35 mg kg^{-1}); While those in spinach were 47 and 14 mg kg^{-1} in roots and shoots, respectively. At 20 mg kg^{-1}, Cs concentrations in both Indian mustard and spinach were 4.2–4.5 mg kg^{-1} in roots and 5.5–8.6 mg kg^{-1} in shoots. Bioaccumulation of Pb and As in roots were higher than shoots indicating the rapid metal(loid) uptake by roots and then slowly transport to other tissues. However, it seemed higher translocation of Cs in both Indian mustard and spinach plants from roots to shoots. It might be related to the similarity of Cs with K transport, an essential element in living organisms (Giannakopoulou et al., 2007).

Obviously, EKF significantly increased the phytoextraction efficiency of Pb, As and Cs. Plant uptake and biomass production are the most important factors for determining the phytoextraction efficiency since shoots are easily harvested and processed (Bi et al., 2011). On one hand, plant uptake is influenced by the nature of elements. Usually, metal(loid) accumulation in roots is higher than that in shoots since metal(loid)s are translocated from roots to shoots (Pettersson, 1976). However, Cs showed a larger

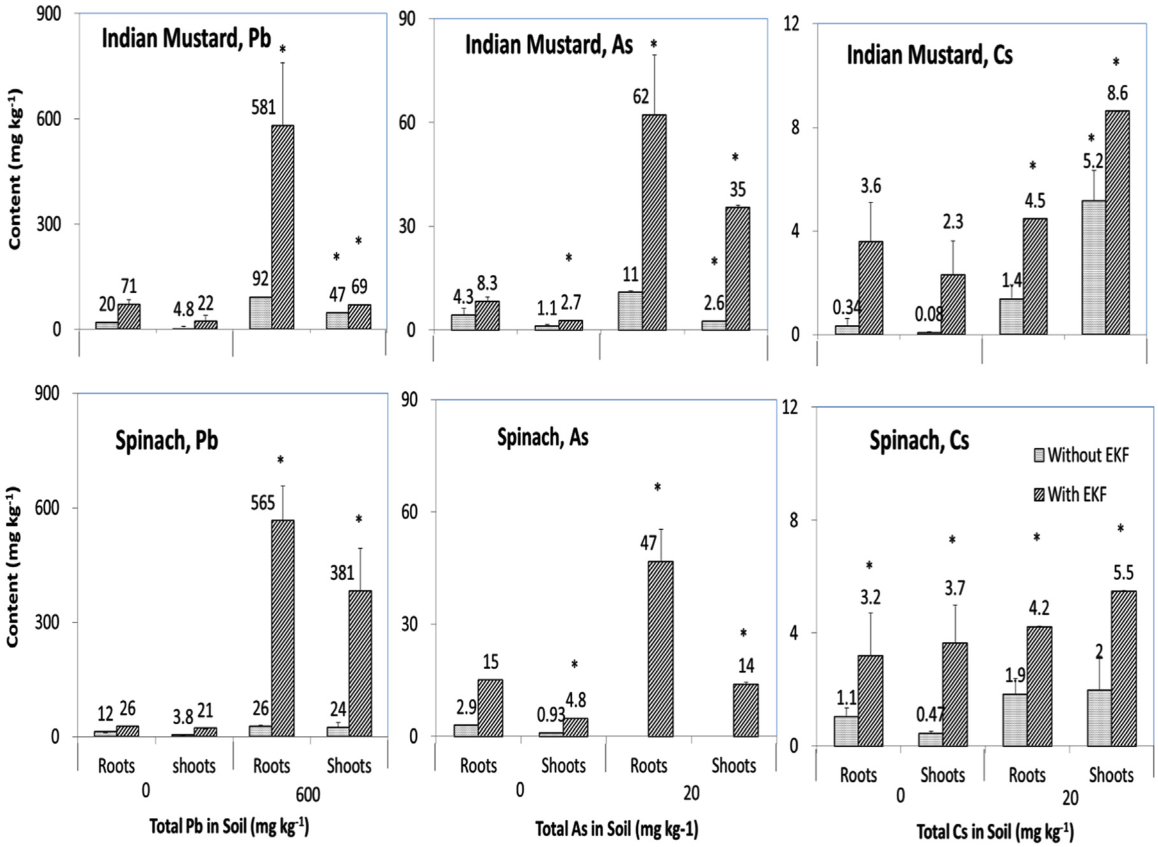

Fig. 5. Effects of EKF on Pb, As and Cs accumulation in roots and shoots of Indian mustard and spinach plants after a growing season in soils with and without pollution. Soil was contaminated with 600 mg kg^{-1} Pb, 20 mg kg^{-1} As and 20 mg kg^{-1} Cs. Means followed by the asterisk (*) were statistically different to the plants planted in soils without EKF at $P < 0.05$.

accumulation in shoots which may be related to the transport process of its root uptake through xylem (Hampton et al., 2005). Since the similarity of chemical properties of Cs to K, Cs uptake might be through proteins catalyzing K$^+$ uptake in plants. In addition, many cation channels in the plasma membrane of root cells catalyzed Cs fluxes across the tonoplast which ensured the quick delivery of Cs to xylem (White et al., 2003; White and Broadley, 2000). The bioavailability of metal(loid)s are influenced by soil physicochemical properties as well such as pH, redox potential and organic matter content (Nyamangara, 1998). Pb, As and Cs were significantly mobilized under EKF through the acidification of soil as indicated by the present study. On the other hand, plant shoot biomass production might be enhanced under EKF. Lemström (1904) found the plants were greener and experienced an increase in biomass under EKF. Muraji et al. (1998) found the electric field had enhancement on plant germination and growth rate. The

Table 2
Roots to shoots translocation factors of Pb, As and Cs in Indian mustard, spinach and cabbage growing in soils with and without EKF. Soil with EKF was contaminated with 600 mg kg^{-1} Pb, 20 mg kg^{-1} As and 20 mg kg^{-1} Cs. Plant tissues were collected in the middle region of each pot.

	Metal addition (mg Kg^{-1})	Without EKF			With EKF	
		Indian mustard	Spinach	Cabbage	Indian mustard	Spinach
Pb	0	0.24 ± 0.17	0.32 ± 0	0.16 ± 0	0.34 ± 0.3	0.79 ± 0
	200	0.57 ± 0.67	0.51 ± 0.17	0.15 ± 0		
	600	0.75 ± 0	0.94 ± 0.64	0.06 ± 0	0.25 ± 0.3	0.73 ± 0.25
	1000	0.15 ± 0.07	0.2 ± 0.07	–		
As	0	0.24 ± 0.01	0.32 ± 0	0.23 ± 0	0.33 ± 0.05	0.32 ± 0
	5	0.79 ± 0	0.21 ± 0.01	0.25 ± 0.04		
	20	0.24 ± 0.02	–	0.14 ± 0.07	0.63 ± 0.29	0.31 ± 0.09
	100	0.52 ± 0.21	0.17 ± 0.12	–		
Cs	0	0.24 ± 0.15	0.44 ± 0	0.38 ± 0	2 ± 2.1*	1.1 ± 0
	5	1.3 ± 0.70	1.2 ± 1.2	0.66 ± 0		
	20	1.9 ± 0.51	1.1 ± 0.40	1.4 ± 0*	3.7 ± 0*	1.2 ± 0.26*
	100	4.7 ± 2.2	1.1 ± 0.55	1.7 ± 0.35*		

Means followed by the asterisk (*) were statistically different to those of unpolluted soils at $P < 0.05$. Error bars represented ± one standard error ($n = 2$). (Data on cabbage with EKF were not available).

operational parameters of EKF such as the electrical field intensity and the mode of electric current (AC or DC) may have impacts on plant growth. Cang et al. (2012) found that low voltage was beneficial for Indian mustard growth while the biomass production was decreased as the increase of voltage. Potato was found to have a 72% increase whereas a 27% decline of biomass production under AC and DC electric field, respectively (Luo et al., 2005). The optimal electric parameters should be included in further study in order to completely understand the effects of electric field on metal(loid) bioavailability and plant biomass.

3.5. Root to shoot metal(loid) translocation factor (TF)

Translocation factors (TF) of Pb, As and Cs by Indian mustard, spinach and cabbage are shown in Table 2. TF is defined as the ratio of metal(loid) concentration in shoots to roots. It describes plant translocation ability of metal(loid)s from roots to shoots (Yoon et al., 2006). Without the treatment of EKF, the TFs of Pb and As were lower than 1 in all treatments indicating low translocation ability of Pb and As in these plants. However, the TFs of Cs were larger than those of Pb and As (4.7, 1.1 and 1.7 in Indian mustard, spinach and cabbage, respectively). EKF treatment did not significantly change the TFs of Pb and As while significantly increased those of Cs in Indian mustard and spinach (cabbage was failed in planting). Plants could be divided into accumulators and excluders according to the responses to elevated concentration of metal (loid)s. Generally, TFs of accumulator species are greater than 1 whereas those of excluder species are typically lower than 1 (Baker, 1981). Most of plants acted as excluders to Pb and As indicated their low translocation ability of Pb and As. However, as a hyperaccumulator of Pb, the TFs of Pb in Indian mustard may be as high as 10 according to previous studies (Lim et al., 2004). The low TFs of Pb in the present study were probably due to the low biomass of Indian mustard. Both Indian mustard and spinach acted as accumulator to Cs and Indian mustard showed better translocation ability. Cs was highly transferable under EKF compared to Pb and As.

4. Conclusions

The native Pb in the MS delta paddy soils was less bioavailable compared with As and Cs. In general, the added Pb, in paddy soils showed lower solubility and bioavailability than As and Cs. Plants growing one season may enhance metal(loid) bioavailability. Increases in SOL and EXC As and Cs were observed due to the potential effects of root exudates and rhizosphere microbial activities.

The solubility and bioavailability of added Pb, As and Cs were significantly enhanced by the electro-kinetic field (EKF). EKF treatment was efficient on lowering soil pH near to the anode which is beneficial for the dissolution of metal(loid)s. Acidification efficiently increased the SOL and EXC Pb, As and Cs in the soils. In addition, the SOL and EXC fractions decreased from soils in the anode to the cathode areas implied both acidification of H^+, solubilization/mobilization of elements in the anode and possible precipitation in the cathode due to high OH^- concentration.

Bioaccumulation of added Pb, As and Cs were also significantly increased upon the electro-kinetic field. With the increase in the SOL and EXC forms, more metal(loid)s were accumulated in plant roots and shoots. Indian mustard, spinach and cabbage are all accumulators for Cs with the TF larger than 1. The bioaccumulation of Pb, As and Cs were all increased upon EKF treatment, indicating the EKF treatment might be a good alternative for increasing phytoextraction efficiency of Pb, As and Cs. Further studies require to focus on soil pH maintenance near the cathode by using organic acids such as acetic acid and citric acid, optimizations of electrical parameters such as electrical field intensity, current application mode, the distance between the electrodes, stimulation period and their enhancement on their mobility and bioavailability.

Acknowledgments

This research was supported by U.S. Nuclear Regulatory Commission (NRC–HQ-12-G-38-0038) and U.S. Department of Commerce (NOAA) (NA11SEC4810001-003499). Mr. Mao was also supported by Jiangsu Scientifical Research Innovation Program of Ordinary Higher Education Graduate (KYZZ0156), Special Fund for Hydro-scientific Research in the Public Interest (201301017), and the Fundamental Research Fund for the Central Universities (2014B04814 and 2015B05814).

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