Inhibition of ethylenediaminetetraacetic acid ferric sodium salt (EDTA-Fe) and calcium peroxide (CaO₂) on arsenic uptake by vegetables in arsenic-rich agricultural soil

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ABSTRACT

Chemical immobilization of arsenic (As) in contaminated sites may be achieved through the use of inorganic and organic soil amendments to reduce its bioavailability. The chemical immobilization of As-rich soil by using ethylenediaminetetraacetic acid ferric sodium salt (EDTA-Fe) and calcium peroxide (CaO₂) as stabilizing agents was investigated in Chianan plain of southwestern Taiwan. The As-rich soil was amended with EDTA-Fe, at the rates of 0, 0.35, 0.7 and 1.4 Mg ha^{-1}, or with CaO₂, at the rates of 0, 0.38, 0.76 and 1.52 Mg ha^{-1}, and grown with radish (*Raphanus sativus L.*), lettuce (*Lactuca sativa*), Chinese cabbage (*Brassica rapa*) and Arden lettuce (*Lactuca sativa L.*). Results showed that those amended with EDTA-Fe at 0.35 and 0.7 Mg ha^{-1} can significantly reduce As accumulation in vegetables. Moreover, the uptake of As in vegetables decreased more in soil amended with CaO₂ relative to that amended with EDTA-Fe. The topsoil amended with EDTA-Fe and CaO₂ can significantly increase As chemisorption by oxides and hydroxides of Fe and Al on the soil surface. As indicated, applications of EDTA-Fe at the rate of 0.7 Mg ha^{-1} and CaO₂ at the rate of 1.52 Mg ha^{-1} can obtain optimal effect on suppressing As uptake by vegetables. As a result, both EDTA-Fe and CaO₂ proved to be effective in immobilizing As in the soil and thus can maintain nutrient balance of vegetables grown in As-rich soil, though CaO₂ application obtained a better result.

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1. Introduction

Toxic arsenic (As) was naturally enriched in the aquifers and surficial soil in the Chianan plain of southwestern Taiwan. Peripheral vascular gangrene, also known as Blackfoot disease (BFD), was first reported in the coastal area of Chianan Plain in the 1960s (Tseng et al., 1961), due to the consumption of deep well water with high As concentrations (Tseng, 1977, 1985). Since 1990, As-rich groundwater has no longer been consumed as drinking water in the BFD area, while it is still widely used for irrigation and aquacultural and industrial purposes and hence deserves our continued attention (Chou et al., 2014). In particular, agricultural crops are still irrigated with As-rich groundwater in the BFD area during the dry season period (October–April).

Arsenic is regarded as non-essential elements for plants and its bioavailability depends on species of plant and soil properties (Tao et al., 2006). High As concentration in soil can inhibit plant growth causing visual phototoxic symptoms (Warren et al., 2003; Liu et al., 2005). Previous studies indicated that several crops and vegetables can accumulate As

in substantial quantities (Das et al., 2004; Chatterjee et al., 2010). Crops and vegetables grown in As-rich agricultural soil can accumulate large amounts of As in roots and shoots (Khan et al., 2008). In a study where As-rich soils ranged from 3.5 mg kg^{-1} to 935 mg kg^{-1} (with the mean value of 129 mg kg^{-1}), As accumulation in vegetables measured up to 2.38 mg kg^{-1} (Liu et al., 2010). Arsenic can be easily accumulated in rice. It showed that As concentration reached 7.5 mg kg^{-1} in rice grown in As-rich soils (Liao et al., 2005).

Long-term irrigation with As-rich groundwater can cause the As contamination in soil, resulting in As accumulation in food crops and dietary exposure to As (Alam et al., 2003). Arsenic in soil and groundwater is considered as a major source of contamination via food chain. It is therefore an important issue to remediation of As-rich soil for reducing the risk of human exposures to As (Frankenberger, 2002). The mobility of As in soil depends primarily on processes of desorption/adsorption and co-precipitation with metal oxides (Kumpiene et al., 2008). Stabilization is considered as one of most effective remediation techniques in reducing As mobility and bioavailability (Moon et al., 2004; Gutierrez et al., 2010). Many studies indicated that iron oxides have a high affinity for the adsorption of arsenite and arsenate in soils. Several chelating agents were investigated for the stabilization of As-bearing soils. To

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date, inorganic amendments for soil remediation has been used to reduce mobile As species and As bioavailability (Hartley and Lepp, 2008). As(III) and As(V) are the dominant inorganic As species in the environment and As(III) is more toxic and mobile than As(V). Therefore, stabilization of As(III) is more challenging than As(V) (Liu et al., 2012). Arsenite has to be oxidized to arsenate prior to stabilization (Fuessle and Taylor, 2004).

Iron and lime compounds are common ameliorants used in the amendment of As-rich soil (Leist et al., 2000). The iron compound was effective in reducing mobility of As due to the formation of amorphous iron(III) arsenate ($FeAsO_4 \cdot H_2O$) (Carlson et al., 2002; Gutierrez et al., 2010). Iron (hydr)oxide was used to absorb for stabilization in soil. Previous studies indicated As(III) and As(V) absorption onto ferrihydrite through surface charge reduction and net OH^- release (Jain et al., 1999).

Iron is able to act as an electron donor or reducing agent that has been utilized in the so-called Fenton treatment techniques, whereby Fe^{2+} or Fe^o is used to reduce hydrogen peroxide and generate the highly reactive OH radical, e.g., for Fe^{2+} via reaction (1) (Hong et al., 2007):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \qquad (1)$$

The hydroxyl radical is a strong oxidizing agent capable of non-selectively oxidizing a variety of organic compounds (Villa et al., 2008). Further, zero-valent iron (Fe^o) was applied to effectively remove AsO_4^{2-} and AsO_3^{2-} from the aqueous solutions (Su and Puls, 2001). Therefore, it is an important matter to find the effective and economical techniques to be used in the stabilization of As-rich soil. Iron (Fe) is one of essential trace nutrients and important component of oxidoreductase for plants. The chemical structures of ethylenediaminetetraacetic acid ferric sodium salt (EDTA-Fe) and calcium peroxide (CaO_2) are shown in Fig. 1.

The As bioavailability of lime reducing soil was possibly attributed to the formation of As-Ca complexes (Moon et al., 2004). Calcium peroxide is one of the most helpful and safest modifiers to handle the family of solid inorganic proxy compounds which are considered as "solid form" of hydrogen peroxide (Tieckelman and Steele, 1991). The compound dissolves in H_2O to form H_2O_2 and $Ca(OH)_2$ via reaction (2), and can liberate a maximal amount of 0.47 g H_2O_2 per gram of CaO_2 (Northup and Cassidy, 2008). The As(III) stabilization process will be improved by CaO_2 amendment in soil by means of the reaction of As(III) with H_2O_2 via reaction (3)(Fuessle and Taylor, 2004). In addition, hydrated lime $Ca(OH)_2$, the byproducts of slurry CaO_2, could reduce As mobility due to the formation of low solubility Ca–As precipitates such as $Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O$ and $Ca_5(AsO_4)_3(OH)$ (Bothe and Brown, 1999). Therefore, CaO_2 would be a potential amendment for As-polluted soil remediation.
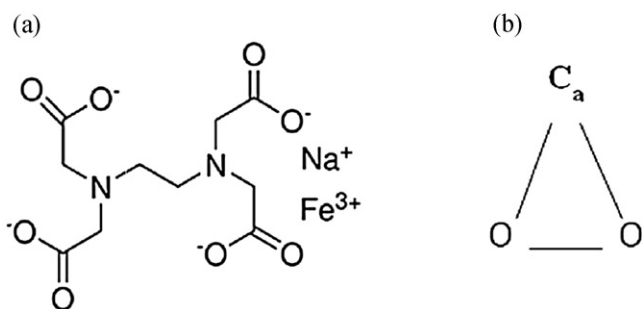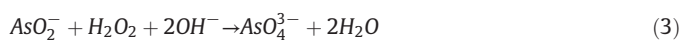
$$CaO_2 + 2H_2O \rightarrow H_2O_2 + Ca(OH)_2 \qquad (2)$$

Fig. 1. The chemical structure of (a) ethylenediaminetetraacetic acid ferric sodium salt (EDTA-Fe) and (b) calcium peroxide (CaO_2).

$$AsO_2^- + H_2O_2 + 2OH^- \rightarrow AsO_4^{3-} + 2H_2O \qquad (3)$$

At present, little is known about the effectiveness that CaO_2 and EDTA-Fe stabilize and remediate As in the soil. In this study, CaO_2 and EDTA-Fe were used as stabilizing additives to immobilize As for remediating As-rich soil in Chianan plain of southwestern Taiwan. The purpose was to evaluate the effectiveness of EDTA-Fe and CaO_2 in reducing As uptake by vegetables in As-rich soil. Radish (*Raphanus sativus*), lettuce (*Lactuca sativa*), Chinese cabbage (*Brassica campestris L. ssp. Chinensis (L.) Mak. Var. communis Tsen et Lee*), and Arden lettuce (*Lactuca sativa L.*) were selected as the target plants in this study. Their roots and/or shoots are edible for human consumption and have been regarded as good model plants in evaluating heavy metal uptake.

2. Materials and methods

2.1. Field experimental design and soil and climatic conditions

The schematic diagram of the inhibition effects of EDTA-Fe and CaO_2 amendments on As uptake by vegetables is graphed in Fig. 2. The experimental field for the study is located in Hsuechia District of Tainan City, the main agricultural area of Chianan plain of southwestern Taiwan and the BFD endemic area in the 1960s. This farm site (23°12′4.02″ N, 120°10′50.7″ E) belongs to the Chianan Irrigation Association (Fig. 3). The climate of this area is hot and humid, with an annual mean air temperature of 25 °C and monthly mean air temperatures of 21 °C in January and 28 °C in July (Table 1). About 80% of the annual rainfall, in the range of 1800–2400 mm, is concentrated in May–October. The soil is mostly composed of alluvium (clay, sand, and silt). Its physical and chemical properties are listed in Table 2.

In this study, different rates of EDTA-Fe (0, 0.35, 0.7, and 1.4 Mg ha^{-1}) and CaO_2 (0, 0.38, 0.76, and 1.52 Mg ha^{-1}) were applied and there were three replicates of each treatment for the individual vegetable species. Both were mixed evenly with the surface soil one week prior to planting. Four vegetable species of short lifespan were selected and denoted as four field experiments. Field layout for each experiment was a completely randomized design with each plot size of 2.25 m^2 (1.5 m × 1.5 m). The growth period for Chinese cabbage, Arden lettuce and lettuce was from February to May 2013, while it was from March to May 2013 for radish. Periodic irrigation with As-rich groundwater was applied during the growth period.

2.2. Cultivation management

Seeds of Chinese cabbage, Arden lettuce, lettuce and radish were sown in a respective area of 10 cm × 10 cm on February 15, March 2, March 5 and March 15, respectively, in 2013. For each vegetable species, fifty most uniform 14-day-old seedlings were selected and were transplanted into field plots. Appropriate amount of composite fertilizer (N:P$_2$O$_5$:K$_2$O = 16:8:12 by weight) was applied after transplanting as basal dose. Ammonium sulfate (21% granule) of 90 g per plot was applied as the second dose at 15 days after transplanting. Hand-weeding was practiced at 7 and 20 days after transplanting and pesticides were sprayed if required.

2.3. Chemical analysis

2.3.1. Sample collection and as analysis

The groundwater was sampled following the standard procedure (Bhattacharya et al., 2010) and was immediately acidified with concentration 6 M HNO_3 until the pH <2 for As analysis. The samples were stored in the dark at 4 °C and were analyzed for total As with an atomic absorption spectrophotometer (GF 5000, GBC Scientific Equipment Pty Ltd., Dandenong, Victoria, Australia). Surface soils and vegetables including Chinese cabbage, Arden lettuce, lettuce and radish were

Table 1

Climatic conditions during the growth period at the Hsuechia experimental site.

Month in 2013	Temperature (°C)		Relative humidity (%)		Average evaporation (mm)[*]	Sunshine (h d^{-1})	Solar radiation (cal cm^{-2}Day^{-1})	Total rainfall (mm/month)
	Max.	Min.	9:00 AM	2:00 PM				
March, 2013	31.0	12.3	85.7	78.0	4.3	5.3	136.5	12.9
April, 2013	31.4	15.5	91.4	88.5	3.2	2.1	104.9	156
May, 2013	33.3	20.3	97.1	96.5	3.8	2.4	135.5	245.1

[a]Source: Work station of Hsuechia Chianan Irrigation Association at Hsuechia District, Tainan City, Taiwan.

[*] Diameter of evaporation pan is 120 mm.

collected from each plot at the experimental site where As-rich groundwater was used for irrigation. The soil samples (0–15 cm depth) were collected and sealed in airtight polyethylene bags in each amendment field before the vegetables were planted. For vegetables, 10 samples were collected from each plot and stored in polyethylene bags. All collected samples were brought back to the laboratory for analyses within five hours. The plant samples were washed by tap water for several times to remove soil and other impurities followed by deionized water cleaning for several minutes. The samples were measured for their fresh weights after air drying and then dried in the hot air oven at 70 °C for 72 h until complete dryness to take dry weights measurements. The soil samples were air dried and ground into powder for further analysis. Soil samples as well as roots and shoots (leaves + stems) of vegetables were processed separately through microwave digestion. Half a gram aliquot of plant samples were placed in a Teflon Material (TFM) vessel, mixed with 7 mL HNO$_3$ (65%) and 1 mL H$_2$O$_2$ (35%), and then placed in a microwave (1000 W) at 200 °C for 20 min. The solution was subsequently diluted to 10 mL with deionized water. Total As concentration of soil was determined after digestion with aqua regia, in which 0.2 g aliquot placed in a clean TFM vessel was added with 3 mL of 37% HCl and 9 mL of 65% HNO$_3$. The vessels were moved into a microwave (1000 W) and heated at 200 °C for 35 min. The solution was then diluted to 50 mL with deionized water. After through with the microwave digestion process, the solution was filtered and analyzed for total As with an atomic adsorption spectroscopy (GF 5000, GBC Scientific Equipment Pty Ltd., Melbourne, Victoria, Australia) (Chou et al., 2014). Each sample was measured in triplicates. For quality control and assurance of soil and plants, two standard reference materials (SRM 2710 for the soil and SRM1570a for the plant samples) were obtained from the National Institute of Standard Materials and Technology,

Gaithersburg, MD. The As concentrations in soil standard materials were 18.95 ± 1.3 mg kg^{-1} and 19.03 ± 1.7 mg kg^{-1}, approximately 95% recovery of the certified value, whereas those in plant standard materials were 120 ± 5 mg kg^{-1} and 118 ± 3 mg kg^{-1}, approximately 99% recovery of the certified value.

2.3.2. Sequential extraction of as from contaminated soil

Sequential extraction of As based on the method of Wenzel et al. (2001) was conducted to understand the fraction of As bound to different solid phases in the soil. The sequential extraction procedure was as follows: (F1)extracting non-specific sorbed phase using 0.05 M (NH$_4$)$_2$SO$_4$, (F2)extracting specifically sorbed phase using 0.05 M NH$_4$H$_2$PO$_4$, (F3)extracting amorphous Fe and Al oxides bound phase using 0.2 M NH$_4^+$-oxalate buffer-extractable, and (F4) extracting crystalline Fe and Al oxides bound phase using 0.2 M NH$_4^+$-oxalate buffer + ascorbic acid, and (F5)extracting residual phase using HNO$_3$/H$_2$O$_2$. Furthermore, major oxides compositions (MgO, Al$_2$O$_3$, SiO$_2$, P$_2$O$_5$, K$_2$O, CaO, MnO, Fe$_2$O, NaO$_2$, and TiO$_2$) of soil were determined using Rigaku RIX 2000 X-Ray Fluorescence Spectrometer (Japan). The analytical analysis was carried out based on the work of Reza et al. (2010).

2.4. Statistical analysis

Statistical analysis was performed with the SPSS package, version 17.0 (SPSS, USA). Arsenic concentrations of soil and roots and shoots of vegetables as well as soil properties were compared by the variance analysis (ANOVA). The significant differences among different parameters were compared by the Fisher's least significant difference (LSD) test.

Table 2

Soil physico-chemical properties of the experimental site in this study for (a) texture analysis, (b) basic characteristics of the soil profile, and (c) major oxides of soil analyzed by X-ray fluorescence.

(a)

Composition	Percentage
Clay	13 ± 1%
Sand	72 ± 2%
Silt	14 ± 1%

(b)

Depth	pH	Ca	Mg	CEC	OC	EC	Fe$_d$	Fe$_o$	Mn$_d$	Mn$_o$	As$_{Tot.}$
cm		cmol kg^{-1}			%	µS cm^{-1}	g kg^{-1}				mg kg^{-1}
0–30	7.27	11.0	1.46	14.5	0.12	450	4.29	2.16	0.17	0.22	14.4
30–50	7.41	13.5	1.71	18	0.53	220	5.51	2.26	0.30	0.32	15.2

Fe$_d$: free Fe; Fe$_o$: amorphous Fe; Mn$_d$: free Mn; Mn$_0$: amorphous Mn.

(c)

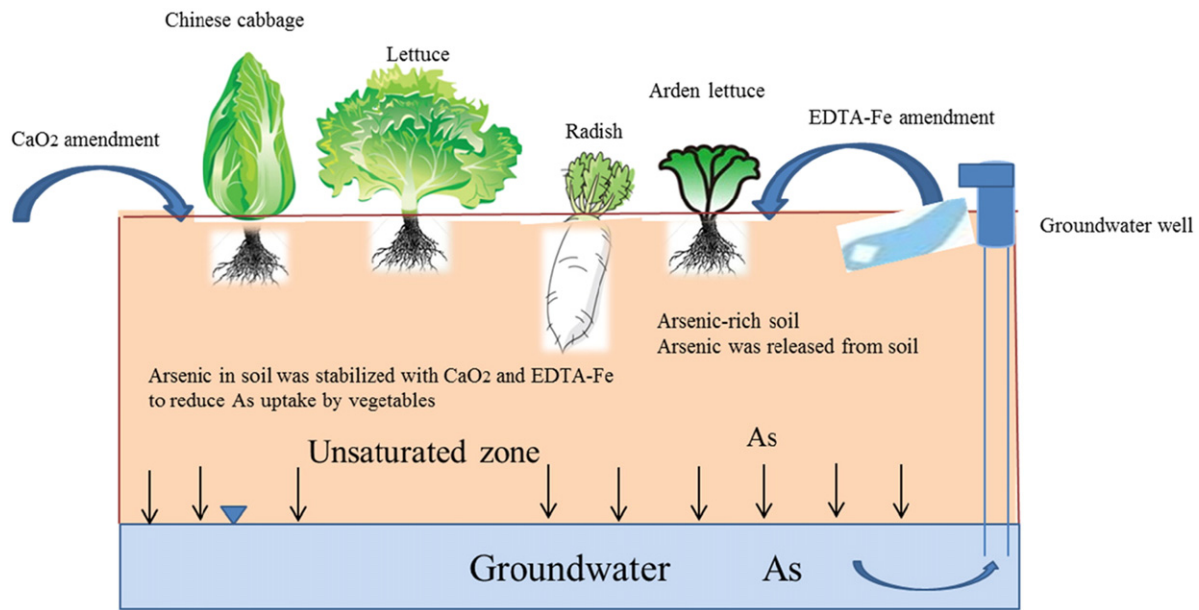| Depth	MgO	Al$_2$O$_3$	SiO$_2$	P$_2$O$_5$	K$_2$O	CaO	MnO	Fe$_2$O$_3$	NaO$_2$	TiO$_2$
cm					wt%					
0–20	2.61	14.6	72.8	0.34	2.95	1.16	0.07	4.05	0.14	0.73
20–40	2.65	15.1	66.7	0.23	2.84	0.76	0.08	3.88	0.13	0.61
40–60	2.67	14.6	66.2	0.18	2.88	0.63	0.07	3.81	0.12	0.63

Fig. 2. The schematic diagram of the inhibition effects of EDTA-Fe and CaO$_2$ amendments on As uptake by vegetables.

3. Results and discussion

3.1. Characterization of groundwater and soil

The characteristics of soil and groundwater are listed in Tables 2 and 3, respectively. The mean of As concentration in the irrigated groundwater was $94.8 \pm 2.1\ \mu g\ L^{-1}$ ($n = 12$) (Table 3), which was higher than the permissible limit for drinking ($10\ \mu g\ L^{-1}$) and irrigation ($50\ \mu g\ L^{-1}$) as recommended by Taiwan Environmental Protection Agency and World Health Organization (WHO) (Shannon and Rodriguez, 2014). The depth of well is 18 m with 2 m water depth at the experimental site. In addition, groundwater is nearly saline-free. The low values of oxidation–reduction potential ($Eh = -74 \pm -13\ mV$) (Table 3) indicated that the aquifers were in reducing conditions corresponding to low dissolved oxygen. The soil is a sandy loam containing high percentages of sand ($72 \pm 2\%$) (Table 2a) with low organic carbon ($OC = 0.12$ to 0.53%) and low cation exchange capacity ($CEC = 14.5$ to $18\ cmol\ kg^{-1}$) (Table 2b). The total As concentration of soils (30–50 cm depth) ranged from 14.4 ± 1.2 to $15.2 \pm 1.6\ mg\ kg^{-1}$. Results of the X-ray diffraction (XRD) analysis

showed that the dominant minerals in the soil of experimental field are quartz, feldspar, mica and clay minerals (Reza et al., 2010). The X-ray fluorescence (XRF) data (Table 2c) revealed that largest ranges of SiO$_2$ and Al$_2$O$_3$ in the soil are 66.2–72.8 wt% and 14.6–15.1 wt%, respectively. In addition, Reza et al. (2010) indicated that magnetite (Fe-oxides) and biotite would be an important source of Fe, which is higher in the upper sand units. The Fe$_2$O$_3$ concentration is 4.05 wt% in the upper layer, slightly higher in the deeper soil layer. The concentration of P$_2$O$_5$ in the soil of experimental field (0.34–0.18 wt%) is slightly higher in the upper layer. The P$_2$O$_5$ concentration correlated with the CaO concentration (Reza et al., 2010). Phosphorous in the soil is fixed in apatite or other Ca-bearing mineral phases.

The results of percentage of solid phase As extracted from surface soil in each plot by sequential extraction method are shown in Table 4. By using the same method, Du et al. (2008) reported that F1 (non-specific sorbed phase) and F2 (specifically sorbed phase) in soil were more labile than other fractions. Further, the results of Tang et al. (2007) also found that sum of As fractions (F1 and F2) was positively correlated with As bioavailability but negatively correlated with F3 (amorphous Fe and Al
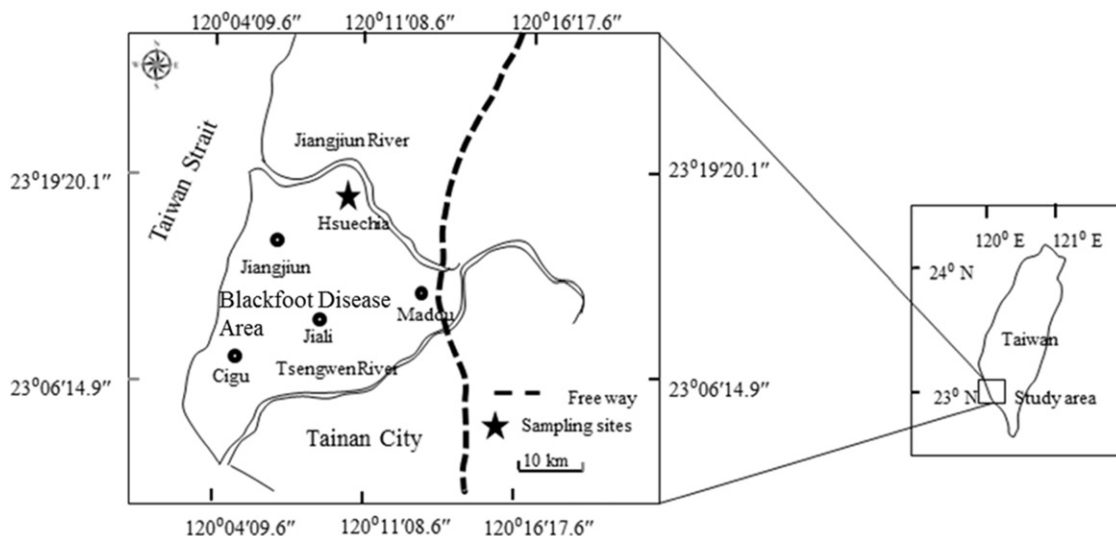

Fig. 3. The experimental sites (sampling sites) at Hsuehchia District of Tainan City in Chianan plain of southwestern Taiwan.
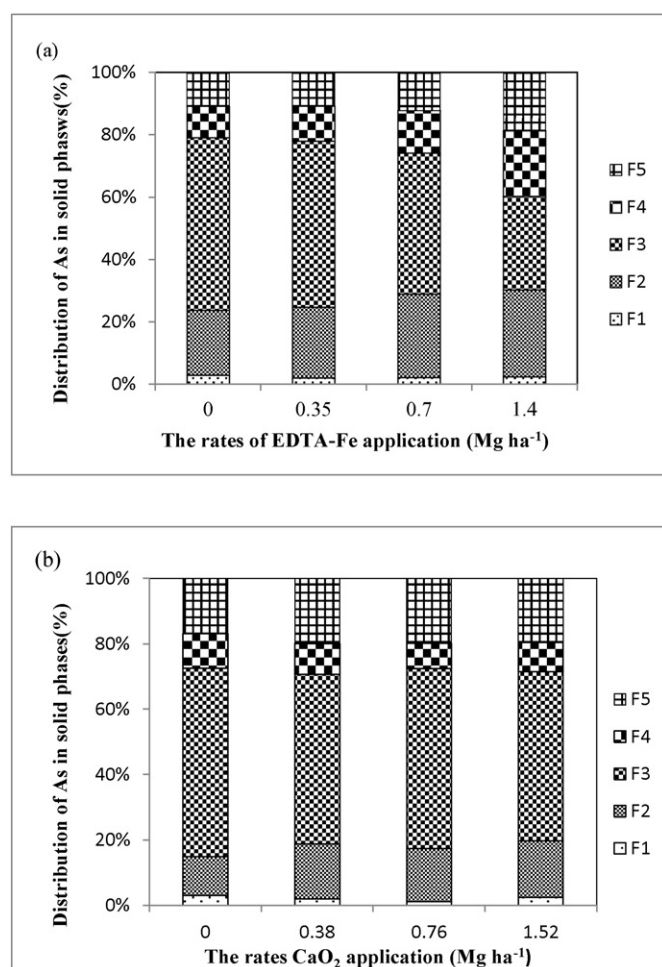
Fig. 4. The As fractions in soil treated with different rates of (a) EDTA-Fe and (b) CaO₂ at the Hsuechia experiment site. F1: non-specific sorbed phase; F2: specifically sorbed phase; F3: amorphous Fe and Al oxides bound phase; F4: crystalline Fe and Al oxides bound phase; F5: residual phase.

oxides bound phase), and F4 (Fe and Al oxides bound phase) and F5 (residual phase). Accordingly, the As fractions of F1 and F2 of the present study are designated as bioavailable As (soluble and exchangeable As), and fractions in F3, F4 and F5 as non-labile As (As bound strongly in soil) (Liu et al., 2012). However, the highest As concentrations were attributed to F2 and F3 in each sampling soil amended with EDTA-Fe and CaO₂ (Table 4a and b). In each plot, the sum of As fractions in F2 and F3 was more than 50% of total As. In the control, the As concentrations of F1 and F2 were 0.27 and 1.98 mg kg⁻¹, which accounted for 1.87% and 13.72% of total As, respectively.

Table 3
Chemical characteristics of groundwater in the rice field of Hsuechia experimental site (n = 12).

Water parameter[a]	Value
pH	6.3 ± 0.2
EC (μS cm⁻¹)	1920 ± 73
TDS (mg L⁻¹)	919.6 ± 46.3
Salinity (‰)	0.88 ± 0.07
DO (mg L⁻¹)	0.45 ± 0.35
Eh (mV)	-74 ± -13
As (μg L⁻¹)	94.8 ± 2.1

[a] EC: electrical conductivity; TDS: total dissolved solids; and DO: dissolved oxygen.

3.2. Amendments of soil with EDTA-Fe and CaO₂

The As fractions in five steps of sequential extraction in soil treated with CaO₂ and EDTA-Fe and values of pH were determined (Table 4). The soil pH slightly reduced with the increase of EDTA-Fe application rates. The lowest pH 6.4 was achieved in the dose of 1.4 Mg ha⁻¹ EDTA-Fe (Table 4a), whereas the soil pH increased with the increase of CaO₂ application rates (Table 4b). The highest pH 8.2 was observed in the treatment of 1.5 Mg ha⁻¹ CaO₂. In the sequential extraction of this study, the potential bioavailable As (soluble As fraction in F1 and exchangeable As in F2) and the non-labile As fractions (As in Fe and Al oxides in F3 and F4 as well as residual held strongly in soil in F5) were determined. The sum of the potential bioavailable As fraction (F1 + F2) of soil was significantly decreased with increasing the rates of two ameliorants (CaO₂ and EDTA-Fe) (Table 4a and b). Potential bioavailable As fraction (F1 + F2) was proportionally and more significantly increased with EDTA-Fe amendment than with CaO₂ amendment. The low recoveries (48–71.3% with EDTA-Fe amendment and 67.8–92.4% with CaO₂ amendment) for As fractions in different solid phases in the sequential extraction are due to (1) HNO₃/H₂O₂ was used to extract As fraction in residual phase (F5) that mainly composed of silicates according to the method of Wenzel et al. (2001); (2) EDTA-Fe and CaO₂ amendments were used to sequester As soil so as to inhibit the uptake of bioavailable As by vegetables.

The results showed that the bioavailable As fraction (F1 + F2) is moderately correlated ($r = 0.74$, $p < 0.05$) with total As in EDTA-Fe amendment, and slightly correlated ($r = 0.81$, $p < 0.05$) with total As in CaO₃ amendment. The results imply that the concentration of potential bioavailable As in soil largely depends on As mobility, soil physics properties and the adsorption/desorption capacity of different mineral phases (Kar et al., 2010; Hsu et al., 2012). However, the non-labile As (F5) was significantly increased by CaO₂ than EDTA-Fe amendment, implying that CaO₂ rate increased with the increase of Ca-associated As fraction (F5). Furthermore, extractable As (F3) was slightly correlated with total As in EDTA-Fe amendment ($r = 0.67$, $p < 0.05$). Similar results were observed in CaO₂, where extractable As (F3) was slightly correlated with total As ($r = 0.62$, $p < 0.05$) (figure not shown).

The As fractions in F1 and F2 decreased with increasing EDTA-Fe rates from 0 to 1.4 Mg ha⁻¹ (Table 4a). The As fraction in F1 was the lowest in the treatment of 0.35 Mg ha⁻¹, whereas that in F2 was found in the treatments of 1.4 Mg ha⁻¹ EDTA-Fe application, about 34% lower than that of the control group. In contrast to the treatment of 1.4 Mg ha⁻¹, As fraction in F4 was 9% higher than that of the control group. The As fraction in F3 displayed a positive trend by the EDTA-Fe application and decreased with increasing EDTA-Fe application from 0 to 1.4 Mg ha⁻¹ (Table 4a). The highest As fraction in F3 was found in the control, whereas the As concentration in F3 fraction in the treatment of 1.4 Mg ha⁻¹ EDTA-Fe was significantly lower than that in the control group ($p < 0.05$). The sum of the bioavailable As fractions (F1 + F2) of soil significantly decreased along with increasing the application rate of EDTA-Fe and CaO₂ (Table 4a and b) which was in agreement with the work by Gutierrez et al. (2010) as applicable to steel-marking slag and Ca(OH)₂ in-situ experiments.

The solubility of As in soil treated with CaO₂ is shown in Table 4b. Among As fractions in five steps (F1 − F5) and sum of each treatment shown in Table 4b and Fig. 4, the highest As concentrations were in the steps of F3 and F5 in each plot. The results were in agreement with the finding of Liu et al. (2012) who reported that the sum of As fractions in F3 and F5 in each plot accounted for more than 50% of the total As. At the control group, the As concentrations of F1 and F2 were 0.29 mg kg⁻¹ and 1.08 mg kg⁻¹ which accounted for 1.9% and 7.5% of the total As, respectively (Table 4b). The As fraction in F1 decreased with increasing CaO₂ application from 0 to 0.76 Mg ha⁻¹. The lowest As fractions in F1 and F2 were found in the treatments of 0.76 and 0.38 Mg ha⁻¹ CaO₂ application. In contrast to 0.76 Mg ha⁻¹ treatment with soil, the As fraction in F3 was 10.4% higher than that of the control.

Table 4

Arsenic extracted by sequential extraction method from surface soil amended with (a) EDTA-Fe and (b) CaO_2 amendments at the different treatment rates, and (c) correlation coefficients (r) between the As concentrations in different solid phases and pH values.

(a)

EDTA-Fe amended		F1	F2	F3	F4	F5	Sum	Total	Recovery (%)
Mg ha^{-1}	pH	mg kg^{-1}							
0	7.2c	0.27 ± 0.02a	1.98 ± 0.3b	5.52 ± 1.5d	0.96 ± 0.12ab	1.04 ± 0.02b	9.77	14.4	67.8
0.35	7.1c	0.15 ± 0.01a	1.72 ± 0.3b	4.03 ± 1.1d	0.86 ± 0.11ab	0.82 ± 0.03ab	7.58	10.6	71.3
0.7	6.7c	0.17 ± 0.01a	1.68 ± 0.2b	2.83 ± 0.4c	0.85 ± 0.1ab	0.77 ± 0.02ab	6.3	9.83	64
1.4	6.4c	0.09 ± 0.01a	1.39 ± 0.3b	1.49 ± 0.5b	1.05 ± 0.2b	0.93 ± 0.12ab	4.95	10.2	48

(b)

CaO$_2$ amended		F1	F2	F3	F4	F5	Sum	Total	Recovery (%)
Mg ha^{-1}	pH	mg kg^{-1}							
0	7.2	0.27 ± 0.02a	1.98 ± 0.3b	5.52 ± 1.5d	0.96 ± 0.12ab	1.04 ± 0.02b	9.77	14.4	67.8
0.38	7.5	0.19 ± 0.02a	1.64 ± 0.3bc	5.05 ± 1.2d	0.91 ± 0.1ab	1.94 ± 0.67cb	9.73	10.5	92.4
0.76	7.7	0.12 ± 0.01a	1.73 ± 0.2bc	5.89 ± 1.2d	0.84 ± 0.12ab	2.12 ± 0.87c	10.7	11.8	90.7
1.52	8.2	0.23 ± 0.01a	1.63 ± 0.4bc	4.89 ± 1.0d	0.83 ± 0.1ab	1.86 ± 0.68bc	9.44	10.7	88.4

F1: non-specific sorbed phase; F2: specifically sorbed phase; F3: amorphous Fe and Al oxides bound phase; F4: Fe and Al oxides bound phase, and F5: residual phase.
*There was significant difference ($P < 0.05$ or less) in As concentrations among of sequential extraction procedure of soil from different sampled treatment fields. Mean ± standard deviation (n = 3) within each column followed by the same letter are not significantly different ($P > 0.0.5$) according to the Fisher's least significant difference (LSD) test.

(c)

Amendment	Parameter	As fraction				
		F1	F2	F3	F4	F5
EDTA-Fe	pH	−0.31	−0.65	0.76	0.55	0.16
CaO$_2$	pH	−0.43	−0.72	0.56	0.81	0.23

In addition, variation of soil pH value could be attributed to reaction with hydrated lime via CaO_2 application. Iron oxide already existed in soil can form $FeAsO_4$ with As. In addition, pH was positively correlated with soluble As fractions (F1 and F2) in both two amended soils, but positively correlated with strongly bound As fractions (F4 and F5) in the two amended soil (Table 4c). This agrees with the work by Magalhães (2002), who found that the As was labile due to the As adsorption or co-precipitation depending on pH conditions of soil.

3.3. Amendments of soil on As uptake by vegetables

Gutierrez et al. (2010) indicated that high As concentration in the soil (>20 mg kg^{-1} of exchangeable As) could inhibit plant growth. Arsenic concentration in the soil at the experimental site in the present study was lower than 20 mg kg^{-1}, thus the vegetables were non-stunted in this study. Crops can uptake toxic elements via the roots from contaminated soils, and even leaves can absorb toxic elements that can accumulate in various parts of plants. Corn and potato (+ skin) grown in a volcano-influenced location of Talabre (Northern Chile) contain very high As concentration in the edible parts (Queirolo et al., 2000). The As concentrations in various parts of vegetables after harvesting were shown in Tables 5 and 6. Comparing the results between the EDTA-Fe amendment and control group, the As concentrations of various vegetables after harvesting are shown in Table 5a. The As concentrations in all vegetables decreased significantly with increasing rate of EDTA-Fe application from 0 to 0.7 Mg ha^{-1} (Table 5b, c and d). In addition, the As concentration displayed a reverse trend by the EDTA-Fe application at 1.4 Mg ha^{-1}. The mean As concentrations in the roots and shoots ranged from 5.89 ± 0.47 mg kg^{-1} to 1.13 ± 0.11 mg kg^{-1} and 3.59 ± 0.13 mg kg^{-1} to 1.01 ± 0.02 mg kg^{-1},

Table 5

Arsenic concentration in the various parts of vegetables under the conditions of (a) control group (no amendment), (b) 0.35 Mg ha^{-1} EDTA-Fe added, (c) 0.7 Mg ha^{-1} EDTA-Fe added, and (d) 1.4 Mg ha^{-1} EDTA-Fe added. Data are presented as mean ± SD.

	Vegetable	Scientific name	Arsenic concentration in plants (mg kg^{-1} of dry weight)			
			Roots	Shoots	Diff.	Average
(a)	Radish	*Raphanus sativus*	5.89 ± 0.47d*	3.59 ± 0.13c	2.30bc	4.74d
	Lettuce	*Lactuca sativa*	3.34 ± 0.31c	2.66 ± 0.04b	0.68a	3.0c
	Chinese cabbage	*Brassica rapa*	3.04 ± 0.56c	2.69 ± 0.3b	0.35a	2.87b
	Arden lettuce	*Lactuca sativa L.*	3.15 ± 0.25c	2.63 ± 0.06b	0.52a	2.89b
(b)	Radish	*Raphanus sativus*	5.35 ± 0.37d	2.88 ± 0.14c	2.47bc	4.12d
	Lettuce	*Lactuca sativa*	2.54 ± 0.32b	1.97 ± 0.1a	0.57a	2.26b
	Chinese cabbage	*Brassica rapa*	2.26 ± 0.06b	1.27 ± 0.07a	0.99b	1.77ab
	Arden lettuce	*Lactuca sativa L.*	2.7 ± 0.17b	1.25 ± 0.04a	1.5b	1.98ab
(c)	Radish	*Raphanus sativus*	3.13 ± 0.95c	1.41 ± 0.17a	1.72b	2.27b
	Lettuce	*Lactuca sativa*	1.23 ± 0.08a	1.07 ± 0.09a	0.16a	1.15a
	Chinese cabbage	*Brassica rapa*	1.27 ± 0.04a	0.93 ± 0.03a	0.34a	1.1a
	Arden lettuce	*Lactuca sativa L.*	1.13 ± 0.11b	1.01 ± 0.02a	0.12a	1.07a
(d)	Radish	*Raphanus sativus*	4.45 ± 0.17d	2.12 ± 0.15b	2.33b	3.28 cd
	Lettuce	*Lactuca sativa*	1.9 ± 0.07a	1.72 ± 0.02a	0.18a	1.81a
	Chinese cabbage	*Brassica rapa*	1.98 ± 0.06a	1.48 ± 0.07a	0.50a	1.73a
	Arden lettuce	*Lactuca sativa L.*	1.61 ± 0.18b	1.39 ± 0.02a	0.22a	1.5a

* There was significant difference ($P < 0.05$ or less) in As concentrations among various parts of vegetables from different sampled treatment fields during harvesting. Mean ± standard deviation (n = 5) within each column followed by the same letter are not significantly different ($P > 0.0.5$) according to the Fisher's least significant difference (LSD) test.

Table 6

Arsenic concentrations in the various parts of vegetables under the conditions of (a) control group (no any amendment), (b) 0.38 Mg ha^{-1} CaO$_2$ amended, (c) 0.76 Mg ha^{-1} CaO$_2$ amended, and (d) 1.52 Mg ha^{-1} CaO$_2$ amended. Data are presented as mean ± SD.

	Vegetable	Scientific name	Arsenic concentration in plants(mg kg^{-1} of dry weight)			
			Roots	Shoots	Diff.	Average
(a)	Radish	*Raphanus sativus*	5.89 ± 0.47d*	3.59 ± 0.93c	2.30bc	4.74c
	Lettuce	*Lactuca sativa*	3.34 ± 0.31c	2.66 ± 0.04b	0.68a	3.0c
	Chinese cabbage	*Brassica rapa*	3.04 ± 0.56c	2.69 ± 0.3b	0.35a	2.87b
	Arden lettuce	*Lactuca sativa L.*	3.15 ± 0.25c	2.63 ± 0.06b	0.52a	2.89b
(b)	Radish	*Raphanus sativus*	4.92 ± 0.05d	2.53 ± 0.35b	2.39bc	3.73c
	Lettuce	*Lactuca sativa*	2.04 ± 0.05b	1.68 ± 0.08ab	0.36a	1.86ab
	Chinese cabbage	*Brassica rapa*	2.42 ± 0.16b	1.67 ± 0.08ab	0.75a	2.05b
	Arden lettuce	*Lactuca sativa L.*	2.62 ± 0.19b	1.99 ± 0.03ab	0.63a	2.31b
(c)	Radish	*Raphanus sativus*	3.53 ± 0.19c	1.98 ± 0.3ab	1.55b	2.76b
	Lettuce	*Lactuca sativa*	1.78 ± 0.07ab	1.51 ± 0.05a	0.27a	1.65ab
	Chinese cabbage	*Brassica rapa*	1.93 ± 0.06ab	1.34 ± 0.12a	0.59a	1.64ab
	Arden lettuce	*Lactuca sativa L.*	1.17 ± 0.1a	1.14 ± 0.02a	0.03a	1.17a
(d)	Radish	*Raphanus sativus*	2.98 ± 0.08b	1.14 ± 0.28a	1.84b	2.06b
	Lettuce	*Lactuca sativa*	0.82 ± 0.01a	0.76 ± 0.04a	0.06a	0.79a
	Chinese cabbage	*Brassica rapa*	0.94 ± 0.06a	0.72 ± 0.03a	0.22a	0.83a
	Arden lettuce	*Lactuca sativa L.*	0.96 ± 0.1a	0.83 ± 0.01a	0.13a	0.89a

  * There was significant difference ($P < 0.05$ or less) in As concentrations among various parts of vegetables from different sampled treatment fields during harvesting. Mean ± standard deviation (n = 5) within each column followed by the same letter are not significantly different ($P > 0.05$) according to the Fisher's least significant difference (LSD) test.

respectively. The lowest As concentrations in various vegetables were observed in the EDTA-Fe amendment with 0.7 Mg ha^{-1} in the experimental site. In comparison with the control group, the supply of 0.35, 0.7 and 1.4 Mg ha^{-1} EDTA-Fe led to the decrease of As in the vegetables by 52% (radish), 61% (lettuce), 61% (Chinese cabbage) and 62% (Arden lettuce) in average. The optimal rate of EDTA-Fe amendment was 0.7 Mg ha^{-1}, and at this rate vegetables were found with lowest As concentrations (0.93 mg kg^{-1}). Furthermore, for the amendment with CaO$_2$, the mean As concentrations in roots and shoots ranged from 5.89 ± 0.47 mg kg^{-1} to 0.82 ± 0.01 mg kg^{-1} and 3.59 ± 0.93 to 0.72 ± 0.03 mg kg^{-1}, respectively. The lowest As concentrations in various vegetables were observed in the CaO$_2$ amendment with 1.52 Mg ha^{-1} in the field. In comparison with the control group, the supply of 0.38, 0.76 and 1.52 Mg ha^{-1} CaO$_2$ led to a decrease in As concentrations of these 4 vegetables by 56% (radish), 73% (lettuce), 71% (Chinese cabbage) and 69% (Arden lettuce) in average. The optimal rate

of CaO$_2$ amendment was 1.52 Mg ha^{-1}, and at this dosage vegetables were found with lowest As concentrations (0.72 mg kg^{-1}).

The present study demonstrated that the effects of EDTA-Fe and CaO$_2$ on stabilization of As in the soil were relative to those of zero-valent iron reported by Ascher et al. (2009). The treatment with 1% zero-valent iron decreased As concentration in the shoots of lettuce by 59% at the experimental site. Similar results were reported by Gutierrez et al. (2010) who applied 2 Mg ha^{-1} steel-making slag (SMS), leading to the decrease of As in radish roots by 50% in the field experiment. In addition, the amendments of EDTA-Fe and CaO$_2$ were more effective than that of limestone reported by Lee et al. (2011), whereas the rate of 2% limestone decreased As concentration in lettuce shoots by 23%.

The two-way ANOVA on Tables 5 and 6 resulted in Tables 7 and 8. It showed that there were significant differences among the control group and EDTA-Fe and CaO$_2$ treatments in roots. The correlation coefficients

Table 7

Results of analysis of variance (ANOVA) based on Table 5 for As among different treatments of control group, 0.35 Mg ha^{-1}, 0.7 Mg ha^{-1} and 1.4 Mg ha^{-1} EDTA-Fe for (a) roots and (b) shoots in the tested vegetables.

Interrelationship	F-value significant level	Two-way ANOVA
Control group × 0.35 Mg × 0.7 Mg × 1.4 Mg (Roots)	10.73	b
Control group × 0.35 Mg × 0.7 Mg × 1.5 Mg (Shoots)	0.34	NS
(a) Roots in the tested vegetables		
Control × 0.35 Mg	4.11	NS
Control × 0.7 Mg	15.27	NS
Control × 1.4 Mg	8.58	a
0.35 Mg × 0.7 Mg	144.87	c
0.35 Mg × 1.4 Mg	23.05	a
0.7 Mg × 1.4 Mg	54.94	c
(b) Shoots in the tested vegetables		
Control × 0.35 Mg	0.23	NS
Control × 0.7 Mg	1.05	NS
Control × 1.4 Mg	0.49	NS
0.35 Mg × 0.7 Mg	0.2	NS
0.35 Mg × 1.4 Mg	0.02	NS
0.7 Mg × 1.4 Mg	0.11	NS

NS not significant.
[a]Significant at the 95% level.
[b]Significant at the 99% level.
[c]Significant at the 99.9% level.

Table 8

Results of ANOVA based on Table 6 for As among different treatments of control group, 0.38 Mg ha^{-1}, 0.76 Mg ha^{-1} and 1.52 Mg ha^{-1} CaCO$_2$ for (a) roots and (b) shoots in the tested vegetables.

Interrelationship	F-value significant level	Two-way ANOVA
Control group × 0.38 Mg × 0.76 Mg × 1.52 Mg (Roots)	4.39	a
Control group × 0.38 Mg × 0.76 Mg × 1.52 Mg (Shoots)	0.7	NS
(a) Roots in the tested vegetables		
Control × 0.38 Mg	0.82	NS
Control × 0.76 Mg	4.28	NS
Control × 1.52 Mg	13.38	a
0.38 Mg × 0.76 Mg	0.32	NS
0.38 Mg × 1.52 Mg	6.7	a
0.76 Mg × 1.52 Mg	2.64	NS
(b) Shoots in the tested vegetables		
Control × 0.38 Mg	0.2	NS
Control × 0.76 Mg	0.47	NS
Control × 1.52 Mg	0.05	NS
0.38 Mg × 0.76 Mg	0.2	NS
0.38 Mg × 1.52 Mg	1.11	NS
0.76 Mg × 1.52 Mg	0.59	NS

NS not significant.
[a]Significant at the 95% level.
[b]Significant at the 99% level.
[c]Significant at the 99.9% level.

Table 9
Correlation coefficients (r) between the As concentrations of soil fraction and those in (a) radish, (b) lettuce, (c) Chinese cabbage, and (d) Arden lettuce.

(a)

Amendment	EDTA-Fe		CaO_2	
Radish plant	Roots	Shoots	Roots	Shoots
As in solid phase				
F1	0.47	0.98[c]	0.88[c]	0.87[c]
F2	0.98[c]	0.66[a]	0.72[a]	0.83[c]
F3	−0.12	−0.28	−0.15	−0.36
F4	0.25	0.17	−0.99[c]	−0.96[c]
F5	−0.7[b]	−0.79[b]	−0.69[a]	−0.63[a]

(b)

Amendment	EDTA-Fe		CaO_2	
Lettuce plant	Roots	Shoots	Roots	Shoots
As in solid phase				
F1	0.64[a]	0.6[a]	0.83[c]	0.83[c]
F2	0.67[a]	0.6[a]	0.89[c]	0.89[c]
F3	−0.34	−0.37	−0.45	−0.47
F4	0.2	0.34	−0.92[c]	−0.91[c]
F5	−0.83[c]	−0.86[c]	−0.64[a]	−0.63[a]

(c)

Amendment	EDTA-Fe		CaO_2	
Chinese cabbage plant	Roots	Shoots	Roots	Shoots
As in solid phase				
F1	0.61[a]	0.72[b]	0.94[c]	0.82[c]
F2	0.61[a]	0.63[a]	0.75[b]	0.88[c]
F3	−0.38	−0.69[a]	−0.42	−0.38
F4	0.33	0.44	−0.92[c]	−0.95[c]
F5	−0.86[c]	−0.99[c]	−0.49	−0.68[a]

(d)

Amendment	EDTA-Fe		CaO_2	
Arden lettuce plant	Roots	Shoots	Roots	Shoots
As in solid phase				
F1	0.63[a]	0.78[b]	0.87[c]	0.87[c]
F2	0.7	0.68[a]	0.64[a]	0.74[b]
F3	−0.21	−0.74[b]	−0.02	−0.15
F4	0.03	0.38	−0.99[c]	−0.99[c]
F5	−0.71[b]	−0.99[c]	−0.68[a]	−0.7[b]

[a] Significant at the 95% level.
[b] Significant at the 99% level.
[c] Significant at the 99.9% level.

(r) between As concentration of soil fractions and different parts of vegetables are shown in Table 9. In the case of Chinese cabbage, a positive correlation ($r = 0.61$, $p < 0.01$) between the As concentration of roots and bioavailable As (F1) was observed in the EDTA-Fe amended soil. A positive correlation ($r = 0.94$, $p < 0.01$) between the As concentration of roots and bioavailable As (F1) in soil was observed in the CaO_2 amended soil. In addition, As concentration in Chinese cabbage roots showed negative correlations with Al_2O_3 ($r = -0.88$, $p < 0.01$) and Fe_2O_3 ($r = -0.78$, $p < 0.01$). Similar trends were observed in Chinese cabbage shoots (figure not shown). The As concentration in Chinese cabbage shoots showed negative correlations with Al_2O_3 ($r = -0.65$, $p < 0.01$) and Fe_2O_3 ($r = -0.51$, $p < 0.05$). Arsenic concentrations in roots and shoots of four various vegetables were significantly and positively correlated with labile As in the two treatments (EDTA-Fe and CaO_2). These results are in agreement with the work by Gutierrez et al. (2010), who applied steel-making slag (SMS) and $Ca(OH)_2$ to the field experiment. Arsenic concentrations in these four various vegetables were negatively correlated with stable As fractions (F3 and F5) of CaO_2 amendment, and were also negatively correlated with As fractions (F3 and F5) of EDTA-Fe amendment (Table 9). EDTA-Fe and CaO_2 amendments could increase the amount of vegetable bioavailable As immobilized in soil, resulting in decreasing As uptake by vegetables.

3.4. Significance of major findings

Results revealed that the increase in amounts of calcium and ferric oxides in soil can change the soil characteristics after the EDTA-Fe and CaO_2 amendments, leading to the formation of amorphous Al- and Fe-oxides that bound As in the soil (As fraction in F3). Results also indicated that the amendments of As-rich soil with EDTA-Fe and CaO_2 were very effective in reducing As uptake in some vegetables. In this field experiment, EDTA-Fe and CaO_2 amendments could stabilize As in soil and thus significantly decreased the As concentration in the roots and shoots of vegetables. Furthermore, it was found that the application of the optimal rates of EDTA-Fe (0.7 Mg ha^{-1}) and CaO_2 (1.52 Mg ha^{-1}) could reduce the As concentration in edible parts to the level significantly lower than that in the control group (no amendment). It suggests that EDTA-Fe and CaO_2 might be potential amendments for As stabilization in As-rich soil, in which CaO_2 is more effective than EDTA-Fe in remediation of As-rich soil.

4. Conclusions

The results of present study show that the amendment of As-rich agricultural soil with CaO_2 was more effective in reducing As uptake by the tested vegetables than that of the EDTA-Fe amendment, mainly attributed to the formation of stable Fe- and Al-oxides bound As that decreases labile fractions in soil. Iron and calcium compounds are common ameliorants used in the amendment of As-rich soil. The iron compound was effective in reducing mobility of As due to the formation of amorphous iron (III) arsenate ($FeAsO_4 \cdot H_2O$). Calcium reducing As bioavailability in soil was possibly attributed to the formation of As-Ca complexes. As a result, EDTA-Fe and CaO_2 are proved to be potential amendments for phytostabilization of As-rich agricultural soil. The further work is needed to study the effectiveness of amendments caused by the impact of the soil, such as soil texture, chemical components of soil, and soil ecology. These soil properties can change the agricultural environment so as to affect their effectiveness to remediate metal contaminated soil.

References

Alam, M.G.M., Snow, E.T., Tanaka, A., 2003. Arsenic and heavy metal contamination of vegetables grown in Samta Village, Bangladesh. Sci. Total Environ. 308, 83–96.
Ascher, J., Ceccherini, M.T., Landi, L., Mench, M., Pietramellara, G., Nannipieri, P., Renella, G., 2009. Composition, biomass and activity of microflora, and leaf yields and foliar elemental concentrations of lettuce, after in situ stabilization of an arsenic-contaminated soil. Appl. Soil Ecol. 41 (3), 351–359.
Bhattacharya, P., Samal, A.C., Majumdar, J., Santra, S.C., 2010. Accumulation of arsenic and its distribution in rice plant (*Oryza sativa* L.) in Gangetic West Bengal, India. Paddy Water Environ. 8, 63–70.
Bothe, J.V., Brown, P.W., 1999. Arsenic immobilization by calcium arsenate formation. Environ. Sci. Technol. 33, 3806–3811.
Carlson, L., Bigham, J.M., Schwertmann, U., Kyek, A., Wagner, F., 2002. Scavenging of as from acid mine drainage by schwertmannite and ferrihydrite: a comparison with synthetic analogues. Environ. Sci. Technol. 36, 1712–1719.
Chatterjee, D., Haider, D., Majumder, S., Biswas, A., Nath, B., Bhattacharya, P., Bhowmick, S., Mukherjee-Goswami, A., Saha, D., Hazra, R., Maity, P.B., Chatterjee, D.,

Mukherjee, A., Bundschuh, J., 2010. Assessment of arsenic exposure from groundwater and rice in Bengal delta region, West Bengal, India. Water Res. 44, 5803–5812.

Chou, M.-L., Jean, J.-S., Sun, G.-X., Hseu, Z.-Y., Yang, C.-M., Das, S., Teng, J.-H., 2014. Distribution and accumulation of arsenic in rice plants grown in arsenic-rich agricultural soil. Agron. J. 106, 945–951.

Das, H.K., Mitra, A.K., Sengupta, P.K., Hossain, A., Islam, F., Rabbani, G.H., 2004. Arsenic concentrations in rice, vegetables, a fish in Bangladesh: a preliminary study. Environ. Int. 30, 383–387.

Du, X., Cui, Y.S., Weng, L.P., Cao, Q., Zhu, Y., 2008. Arsenic bioavailability in the soil amended with leaves of arsenic hyperaccumulator, Chinese brake fern (Pteris vittata L.). Environ. Toxicol. Chem. 27 (1), 126–130.

Frankenberger Jr., W.T. (Ed.), 2002. Environmental Chemistry of Arsenic. Marcel Dekker, New York.

Fuessle, R.W., Taylor, M.A., 2004. Stabilization of arsenite wastes with prior oxidation. J. Environ. Eng. ASCE 130, 1063–1066.

Gutierrez, J., Hong, C.O., Lee, B.H., Kim, P.J., 2010. Effect of steel-making slag as a soil amendment on arsenic uptake by radish (raphanus sativa L.) in an upland soil. Biol. Fertil. Soils 46, 617–623.

Hartley, W., Lepp, N.W., 2008. Effect of in situ soil amendments on arsenic uptake in successive harvests of ryegrass (Lolium perenne cv elka) grown in amended as-polluted soils. Environ. Pollut. 156 (3), 1030–1040.

Hong, S., Zhang, H.C., Duttweiler, C.M., Lemley, A.T., 2007. Degradation of methyl tertiary-butyl ether (MTBE) by anodic Fenton treatment. J. Hazard. Mater. 144, 29–40.

Hsu, W.M., Hsi, H.C., Huang, Y.T., Liao, C.S., Hseu, Z.Y., 2012. Partitioning of arsenic insoil–crop systems irrigated using groundwater: a case study of rice paddy soils in southwestern Taiwan. Chemosphere 86, 606–613.

Jain, A., Raven, K.P., Loeppert, R.H., 1999. Arsenite and arsenate adsorption on ferrihydrite: surface charge reduction and net OH- release stoichiometry. Environ. Sci. Technol. 33 (8), 1179–1184.

Kar, S., Maity, J.P., Jean, J.-S., Liu, C.-C., Nath, B., Yang, H.-J., Bundschuh, J., 2010. Arsenic-enriched aquifers: occurrences and mobilization of arsenic in groundwater of Ganges delta plain, barasat, West Bengal. India. Appl. Geochem. 25, 1805–1814.

Khan, S., Cao, Q., Zheng, Y.M., Huang, Y.Z., Zhu, Y.G., 2008. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. Environ. Pollut. 152, 686–692.

Kumpiene, J., Lagerkvist, A., Maurice, C., 2008. Stabilization of as, Cr, Cu, Pb and Zn in soil using amendments - a review. Waste Manag. 28, 215–225.

Lee, S.H., Kim, E.Y., Park, H., Yun, J., Kim, J.G., 2011. In situ stabilization of arsenic and metal-contaminated agricultural soil using industrial by-products. Geoderma 161, 1–7.

Leist, M., Casey, R.J., Caridi, D., 2000. The management of arsenic waste: problems and prospects. J. Hazard. Mater. 76, 125–138.

Liao, X.-Y., Chen, T.B., Xie, H., Liu, Y.R., 2005. Soil as contamination and its risk assessment in areas near the industrial districts of chenzhou city, southern China. Environ. Int. 31 (6), 791–798.

Liu, H.Y., Probst, A., Liao, B.H., 2005. Metal contamination of soils and crops affected by the chenzhou lead/zinc mine spill (Hunan, China). Sci. Total Environ. 339, 153–166.

Liu, C.P., Luo, C.L., Gao, Y., Li, F.B., Lin, L.W., Wu, C.A., Li, X.D., 2010. Arsenic contamination and potential health risk implications at an abandoned tungsten mine, southern China. Environ. Pollut. 158, 820–826.

Liu, C.P., Luo, C.L., Xu, X.H., Wu, C.A., Li, F.B., Zhang, G., 2012. Effects of calcium peroxide on arsenic uptake by celery (Apium graveolens L.) grown in arsenic contaminated soil. Chemosphere 86, 1106–1111.

Magalhães, M.C.F., 2002. Arsenic. An environmental problem limited by solubility. Pure Appl. Chem. 74, 1843–1850.

Moon, D.H., Dermatas, D., Menounou, N., 2004. Arsenic immobilization by calcium-arsenic precipitates in lime treated soils. Sci. Total Environ. 330, 171–185.

Northup, A., Cassidy, D., 2008. Calcium peroxide (CaO2) for use in modified Fenton chemistry. J. Hazard. Mater. 152, 1164–1170.

Queirolo, F., Stegen, S., Restovic, M., Paz, M., Ostapczuk, P., Schwuger, M.J., Munoz, L., 2000. Total arsenic, lead, and cadmium levels in vegetables cultivated at the Andean villages of northern Chile. Sci. Total Environ. 255, 75–84.

Reza, A.H.M.S., Jean, J.-S., Lee, M.-K., Liu, C.-C., Bundschuh, J., Yang, H.-J., Lee, J.-F., Lee, Y.-C., 2010. Implications of organic matter on arsenic mobilization into groundwater: evidence from northwestern (chapai-nawabganj), central (manikganj) and south-eastern (Chandpur) Bangladesh. Water Res. 44 (19), 5556–5574.

Shannon, R., Rodriguez, J.M., 2014. Total arsenic in rice milk. Food Addit. Contam. B Surveill. 7, 54–56.

Su, C., Puls, R.W., 2001. Arsenate and arsenite removal by zero-valent iron: kinetics, redox, transformation and implications for in situ groundwater remediation. Environ. Sci. Technol. 1 (35), 1487–1492.

Tang, X.Y., Zhu, Y.G., Shan, X.Q., McLaren, R., Duan, J., 2007. The ageing effect on the bioaccessibility and fractionation of arsenic in soils from China. Chemosphere 66, 1183–1190.

Tao, Y.Q., Zhang, S.Z., Jian, W., Yuan, C.G., Shan, X.Q., 2006. Effects of oxalate and phosphate on the release of arsenic from contaminated soils and arsenic accumulation in wheat. Chemosphere 65, 1281–1287.

Tieckelman, R.E., Steele, R.E., 1991. Higher-assay grade of calcium peroxide improves properties of dough. Food Technol. 45, 106–112.

Tseng, W.P., 1977. Effects and dose–response relationship of skin cancer and Blackfoot disease with arsenic. Environ. Health Perspect. 19, 109–119.

Tseng, W.P., 1985. Blackfoot disease and skin cancer in an endemic area of chronic arsenicism in Taiwan. In: Tseng, W.-P. (Ed.), Proceedings of the Seminar on Environmental Toxicology, Taipei. 26 Mar.-2 Apr. 1985. Natl. Taiwan Univ. Hospital, Taipei, Taiwan, pp. 142–155.

Tseng, W.P., Chen, W.Y., Sung, J.L., Chen, J.S., 1961. A clinical study of Blackfoot disease in Taiwan: an endemic peripheral vascular disease. Proc. Semin. Environ. Toxicol. 3, 1–8.

Villa, R.D., Trovo, A.G., Nogueira, R.F.P., 2008. Environmental implications of soil remediation using the Fenton process. Chemosphere 71, 43–50.

Warren, G.P., Alloway, B.J., Lepp, N.W., Singh, B., Bochereau, F.J.M., Penny, C., 2003. Field trials to assess the uptake of arsenic by vegetables from contaminated soils and soil remediation with iron oxides. Sci. Total Environ. 311, 19–33.

Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. Anal. Chim. Acta 436, 309–323.