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Biogeochemical reductive release of soil embedded arsenate around a crater area (Guandu) in northern Taiwan using X-ray absorption near-edge spectroscopy

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Abstract

This study investigates biogeochemical reductive release of arsenate from beudantite into solution in a crater area in northern Taiwan, using a combination of X-ray absorption near-edge structure (XANES) and atomic absorption spectrometry. Total arsenic (As) concentrations in the soil were more than 200 mg/kg. Over four months of laboratory experiments, less than 0.8% As was released into solution after reduction experiments. The 71% to 83% As was chemically reduced into arsenite (As(III)) and partially weathering into the soluble phase. The kinetic dissolution and re-precipitation of As, Fe, Pb and sulfate in this area of paddy soils merits further study.

Key words: agricultural rice soils; arsenic; arsenate; reduction release

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Introduction

The pollution of the environment by metalloid anions may be a consequence of human activities and geochemical evolutions, threatening animal life and causing health problems. Given that most toxic heavy metals can be distinguished from other pollutants, but are not biodegradable, they accumulate in living tissues, causing various diseases and disorders. Hence, humans who endure a heavy dosage of these metallic anions run a high risk of suffering from various diseases, because of the biologically inspired conflicts between their immune system and these threats (Lee et al., 2010). A typical example is the famous Black Foot Disease (BFD), which occurs when there is ingestion of high concentrations of arsenic into the human body. The danger of arsenic (As) lies not only on the fact that it is not bio-degradable, but also in its extremely high toxicity, which can cause the death of many life forms with a small dosage. During the past two decades, this fatal metallic anion has been responsible for many medical problems, following the industrialization of the Chiayi coastal region

in southern Taiwan, China (Tseng, 1989, 2002; Tseng et al., 2005).

An interesting and important finding is the absence of BFD around the crater area in northern Taiwan (the Guandu Plain), where the extent of As pollution in the local soil environment is almost identical to that of the water system in the Chiayi coastal region. The biogeochemical release of embedded arsenate in soil organic matter (SOM) is a long-standing problem for rice plantations and has impacted public health in the crater area of the Guandu Plain, since agriculture first developed in northern Taiwan in 1895. At that time, farmers occasionally irrigated the Guandu agricultural rice soils during periods of drought, using waters from the Huang Gang Creek, which originates in the Beitou Thermal Valley (i.e., an outcrop size of about 0.35 ha). Humans were unaware of the existence of As, Pb and sulfate contaminants in the spring waters (Chiang et al., 2010). A previous survey has shown that the water irrigation pathway caused serious As and Pb contamination of about 842 ha of rice soils in Guandu Plain. The affected rice soil (concentrations higher than 200 mg/g) in the Guandu Plain covers about 128 ha (Chang et al., 1999) (**Fig. 1**). Statistic medical history shows that

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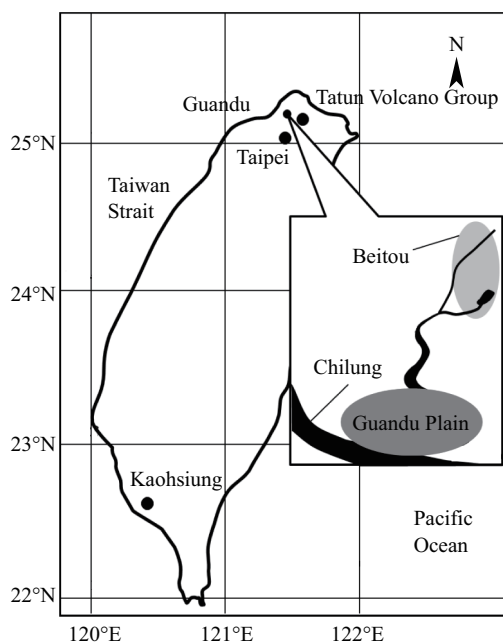


Fig. 1 Location of the Guandu Plain.

As is unlikely to be ingested by human due to the strong chemical stability of As adsorbed in soils.

The origins of heavy metal contamination are of crucial importance in tracing the biogeochemical reductive release of As in this area. It also explains the reason for the low occurrence of As induced medical illnesses in local residents who have contact with highly polluted soil. This was clarified by energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) analysis, combined with microwave-assisted acid digestion chemical analysis. It showed that a large extent of the arsenate pollution in the Guandu agricultural rice soils results from the deposition of beudantite ($\text{PbFe}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6$) particles in the irrigation water from the Huang Gang Creek and spring waters that contain high concentrations of As and Pb from the Chinshan geological fault (Chiang et al., 2010). In addition to forming solid condensates, the arsenate anion also occurs naturally in soils, because of its effective physiochemical adsorption through facet and edge sites at the ferrihydrite surface (Frommer et al., 2011; Manning and Goldberg, 1997; Voegelin et al., 2007). Accordingly, the mechanisms and reaction pathways that explain As release from these physiochemical states are crucial to the development of frontier strategies that reduce the impact of toxic metals on biomedical systems. In previous studies, the release of geo-embedded arsenate has been shown to proceed via three major pathways; bio-inspired reductive relaxation, the reduction induced dissolution of arsenate adsorbed ferrihydrite and the reduction of arsenate into arsenite at a ferrite-rich soil surface (Fendorf et al., 2010; Harvey et al., 2002; Islam et al., 2004; Weber et al., 2010). In these cases, adsorption sites were lost mainly because of the collision of trivalent Fe-hydroxide crystallites in

a system with high reduction potential, leading to arsenate pollution in ecosystems (Dixit and Hering, 2003; Huang et al., 2011; Stachowicz et al., 2008). Although the fundamental arsenate pathways have been extensively studied using chemical dynamics and kinetic methods, the effect of specific critical geochemical conditions (i.e., crater geology of the Guandu Plain) on molecular scale arsenate relaxation in the local soil systems is still being debated.

An efficient strategy for protecting local residents from arsenate poisoning requires a full understanding of the molecular scope of the anions relocated in soil environments. Although soil arsenates in the crater area of the Guandu Plain have been extensively studied during the past decade, the mechanistic pathways for biogeochemical inductive arsenate release are not yet completely understood. The authors' previous works made a preliminary attempt to assess the distribution of arsenate contamination in this area (Chang et al., 1999; Chiang et al., 2010). Given that the local soils remained under reduction conditions, because of the intense agricultural activities common to paddy soil environments, it is difficult to assess the molecular scale reductive dissolution or the relaxation of arsenate/arsenite in this area using conventional chemical characterization techniques (e.g., EDS, ICP-OES, XRF, etc.). X-ray absorption near-edge structure (XANES) and electro-thermal atomic absorption spectrometry (AAS) and high performance liquid chromatography (HPLC) were used to study the ambiguities of the inter-metallic complex interactions that affect the soil arsenate stabilization. This study focused on the management of the soil arsenate distribution to ensure better agricultural practices.

1 Materials and methods

1.1 Background data of soil samples

Two individual soil profiles were collected for this study. Two pedons were close to the Chilung watershed and had a high groundwater table, containing easily exchangeable cations. Pedons 1 and 2 were located at $25^{\circ}07'32.67''\text{N}$, $121^{\circ}29'15.02''\text{E}$ (Pedon 1) and $25^{\circ}07'27.45''\text{N}$, $121^{\circ}29'11.09''\text{E}$ (Pedon 2), in the subtropical Guandu Plain, near Taipei City (Fig. 1). Five horizons were collected with 20 cm depth intervals to form these two soil profiles. They were analyzed to determine their chemical, physical and mineralogical properties, in relation to soil depth. The Guandu soil textures include clay-sandy loam, mixed, mesic, Typic, or Umbric Albaqualls (Soil Survey Staff, 1962, 2010).

The mean pH of the soil was in the range of 5.41 to 6.76. Cation-exchange capacity (CEC) ranged from 18.25 to 20.26 $\text{cmol}_{(+)}/\text{kg}$. Exchangeable K^+ , Na^+ , Ca^{2+} and Mg^{2+} concentrations and base saturation were in the range of 0.16–0.38, 0.20–1.14, 5.70–7.62, 1.14–1.96 $\text{cmol}_{(+)}/\text{kg}$ and 39.8% to 53.8%, respectively (Table 1) (Chiang et al.,

Table 1 As and Pb concentrations in bulk soils and clay fractions digested by aqua regia solution (Chiang et al., 2010)

Soil depth(cm)	Element (mg/kg)	
	As	Pb
Pedon 1		
0–20	259	64
20–40	245	67
40–60	260	63
60–80	265	103
80–100	194	258
Pedon 2		
0–20	252	86
20–40	311	157
40–60	488	774
60–80	374	701
80–100	190	738

2010). These soil textures were clay, clay loam, silt clay loam and sandy loam. As and Pb concentrations ranged from 190 to 488 and from 64 to 774 mg/kg respectively (**Table 1**) (Chiang et al., 2010).

X-ray diffraction (XRD) analysis showed that vermiculite, kaolinite, illite and beudantite exist in the soil profile of the rice fields in the Guandu Plain. Background data for the Guandu agriculture rice soils was previously detailed by Chiang et al. (2010).

1.2 Reduction release experiments

Soils, D(+)-glucose and Milli-Q (18.2 MΩ cm resistivity) water were placed in each centrifuge tube to make up a soil: D(+)-glucose: Milli-Q water ratio of 1000:1:2000 (i.e., 10 g soil:0.01 g D(+)-glucose:20 mL Milli-Q water). Suspensions were continuously shaken at 200 r/min in a reciprocating shaker, for 1 hr and the centrifuge tubes were then placed in an incubator, at 25°C. Each centrifuge tube was taken out of the incubator at 0, 1, 2, 4, 8, 16, 32, 64 and 128 days, in order to measure Eh values using platinum (Pt) electrodes (HI 3131B, Hanna, USA). After measurement of Eh, the samples were centrifuged at 12,000 ×g for 15 min. A sub-sample (5 mL) was filtered through 0.45-μm Millipore filter and the filtrate was used to measure the total concentrations of elemental As, Pb, Fe and Al, using inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 2000 DV, Perkin-Elmer, USA). The procedures for analyzing the As species (i.e., As(III), As(V), monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) were identical to those reported by Huang et al. (2003). As species were separated using an anion column (Nucleosil, 10 μm, 250 × 4.6 mm, Phenomenex, USA), connected to a high performance liquid chromatography (HPLC) (Series 200, Perkin-Elmer, USA), which was connected to an electrothermal atomic absorption spectrometer (AAS) (AA 200, Perkin-Elmer, USA) and a hydride generation (HG) system (FIAS 100, Perkin-Elmer, USA). The recovery rates for As(III) and As(V) were (101.4±3.2)% and (96.7±2.9)%, respectively. The soil in the centrifuge tube was stored in a

refrigerator at –20°C, prior to XANES analysis.

1.3 X-ray absorption spectroscopy (XAS) measurements

The valence states and chemical transformation of As and Fe in different pedons (regions) of the heavy metal-contaminated soil samples were subjected to X-ray absorption near-edges structure (XANES) analysis, before and after the reduction release experiments. The arsenate K-edge, lead L₃-edge and iron K-edge X-ray absorption spectra (XAS) of the soil samples were collected at a wiggler beamline of BL-17C, a super-conductor bending beamline of BL-01C and a tender XAS beamline of BL-16A, in the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. All of the XAS data were collected in fluorescence mode, using a Soller-slits Lytle detector; wherein adequate filters were placed as a window to screen unexpected fluorescence photoelectrons and scattering background. Since the amplification of the Lytle detector was set at the same rank and the samples were prepared with similar surface roughness and uniformity, the edge-jump for each spectrum represents the relative concentrations of the targeting elements in the corresponding samples. The freshly collected soil samples were frozen at –20°C (for transportation), air-dried for 7 days, sieved using a mesh and then pressed into pellets, prior to XAS measurement.

1.4 Analysis of the compositions of the chemical species by fitting the XANES spectra using a linear combination method

The chemical compositions of As and Fe species in soils were quantitatively determined by fitting their corresponding As L₃-edge XANES, using, linear combination analysis, within a range of photon energy from –20 to 20 eV, relative to the absorption edge (E_0) (Koningsberger and Prins, 1987). The data was fitted to the experimental equation using the weighting factors, $a_{i(\text{ox})}$, of a series of standard spectra for i species ($\mu(E)_{i(\text{ox})}$) in different oxidation states as parameters (Eq. (1)):

$$\mu(E)_{(\text{To},i)} = \sum a_{i(\text{ox})} \cdot \mu(E + \Delta E)_{i(\text{ox})} \quad (1)$$

where, $\mu(E)_{(\text{To},i)}$ and ΔE denote the XANES spectra at the absorption edge of i species in soils and the energy shift of the standard spectra of i species (e.g., NaAsO₂ (As(III)), Na₂HAsO₄·7H₂O (As(V)), Fe₂O₃, FeSO₄ and beudantite mineral powder (i.e., < 2 mm).

1.5 Statistical analysis

All statistical analyses were conducted using Microsoft Excel 2007. The parameters for all equations were determined for the soil treatments by fitting a non-linear regression model that optimized the function in all equations. The model for the experimental data was analyzed

graphically and the parameter estimates for all equations were computed by analysis.

2 Results and discussion

2.1 Reductive dissolution/desorption measurements for soils.

The reductive desorption of As and Fe and the Eh values are shown in **Fig. 2**. Desorption curves for As and Fe in Pedons 1 and 2 are shown in **Fig. 2a, b, c, d**, respectively. It is crucially important to note that the maximum extent of As desorption is less than 0.8% of the initial As content, for all soil samples in both pedons. Combining the results

of XAS and HPLC determined As species distribution. The soil samples measured before the reduction release experiments showed that beudantite is the major component of bulk soils. The As(III), As(V) and beudantite components are shown in **Table 2**. As(III) was determined to be 52.0%–43.4% for depths from 40 to 80 cm of Pedon 1 and ca. 38% for depths from 0 to 40 cm of Pedon 2, respectively. As(V) were determined to be 2.1%–32.3% in Pedon 1 and 25.3%–30.1% for depths from 40 to 100 cm of Pedon 2. Beudantite was determined to be 45.9%–74.7% in Pedons 1 and 2. Soil As(III) to total As ratios are above 71.0% in Pedons 1 and 2, after the reduction release experiments (**Table 3**).

The stability of solid-state organic-As complexes or

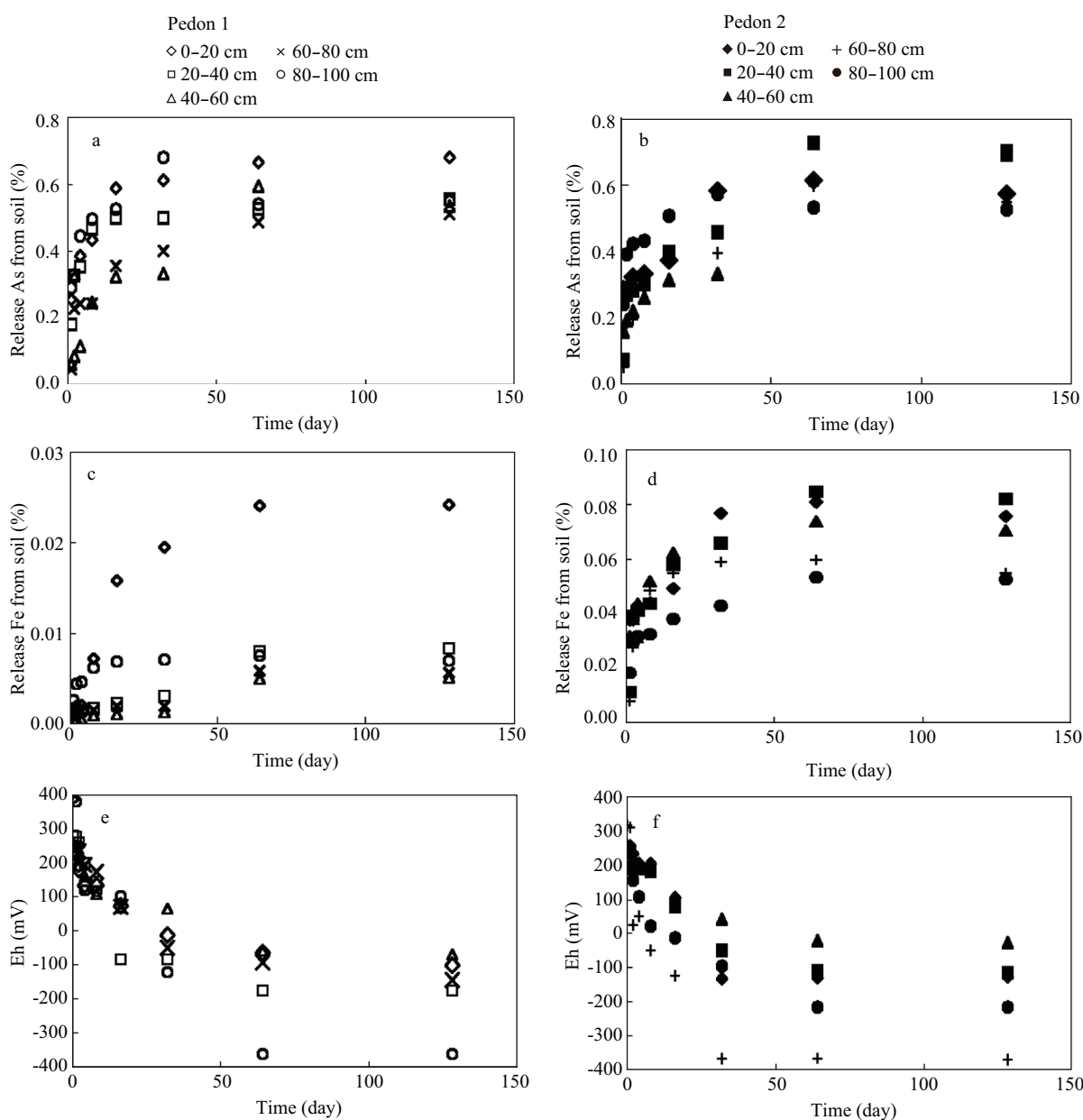


Fig. 2 Long-term measured reductive dissolution/desorption curves of As (a, b) and Fe (c, d) and the reduction potential curves for Pedon 1 (e) and Pedon 2 (f).

Table 2 As(III), As(V) and beudantite compositions in Pedons 1 and 2

Pedon	As species	Depth				
		0–20 cm	20–40 cm	40–60 cm	60–80 cm	80–100 cm
1	As(III)	0	0.1%	52.0%	43.4%	2.0%
	As(V)	32.3%	30.4%	2.1%	0	17.1%
	Beudantite	67.7%	69.5%	45.9%	56.6%	80.9%
2	As(III)	38.1%	38.7%	0	0	0
	As(V)	0	0	30.1%	29.8%	25.3%
	Beudantite	61.9%	61.3%	69.9%	70.2%	74.7%

Table 3 Percentage of As(III) to total As concentration after reduction reaction for 128 days in Pedons 1 and 2

Pedon	Soil depth (cm)				
	0–20	20–40	40–60	60–80	80–100
1	71.0%	76.5%	78.0%	74.7%	72.8%
2	77.3%	75.3%	83.4%	78.0%	76.9%

chemisorptions of ferrihydrite in soil organic matter (SOM) hinders the release of arsenate in an ecosystem. This fact explains As translocation pathways. Throughout the concentration-to-time correlation traces, desorption of arsenate is found to exponentially increase with aging time. Initially (from 0 to 32 days), a dramatic increase in total As concentration is explained by water assisted dissolution. After reaction for another 32 days, the reaction reaches an equilibrium state (i.e., 64 days) (**Fig. 2a, b**). Similarly, Fe desorption exponentially increases with increased reaction time (**Fig. 2c, d**). It is interesting to note that Fe desorption shows a low correlation with that of arsenate in Pedon 1, for soil deeper than 20 cm. Since desorption/dissolution of Pb is almost undetectable, this observation implies that the lower water assisted reduction is a consequence of the greater extent of arsenate-iron minerals (beudantite) in Pedon 1 than in Pedon 2. However, the positive correlation for iron-to-arsenate dissolution concentration suggests a greater extent of arsenate embedded organic-complexes than beudantite compounds in the SOM in Pedon 2 (Chiang et al., 2010). Thus, analysis of As dissolution supports the long-standing hypothesis that there is a significant dependency between As and Fe desorption/dissolutions in a ferrihydrite–organic-complex-rich soil environment (i.e., Pedon 2). In this case, desorption of chemically and physically adsorbed arsenate is substantially affected by changes in redox conditions (i.e., pH, ion constituents, reduction potential (Eh) and adsorbates) and reaction time (**Fig. 2**).

Iron oxyhydroxides are the most important sorbents for As(V) in most soils and aquifer sediments (Voeglin et al., 2007; Frommer et al., 2011; Manning and Goldberg, 1997). Microbial reduction and dissolution of iron (Fe(III)) oxyhydroxides and/or reduction of sorbed arsenate (As(V)) are thought to be the driving factors for As release, which is under such conditions predominantly present in solution as arsenite (As(III)) (Islam et al., 2004; Weber et al., 2010; Harvey et al., 2002). Arsenic adsorbed onto sediment surfaces could be mobilized into water

phase by anaerobic respiration of Fe(III) reducing bacteria (Oremland and Stolz, 2005; Islam et al., 2004). Reductive dissolution or transformation of poorly crystalline Fe(III)-oxyhydroxides into more crystalline solids can lead to a loss of sorption sites for As. Furthermore, under most natural conditions (e.g., dissolved concentrations < 20 $\mu\text{mol/L}$ As), As(III) is less strongly sorbed to oxide and clay mineral surfaces than is As(V) (Stachowicz et al., 2008; Dixit and Hering, 2003; Huang et al., 2011). Under anoxic conditions iron oxides may become reduced either biotically or abiotically while releasing Fe^{2+} (Lovley, 1992). Over the last few decades, many bacteria capable of oxidizing or reducing arsenic and iron hydroxides have been recognized (Lovley, 1991; Oremland and Stolz, 2003). Such microbial activity, in combination with geochemical factors, will control arsenic release mechanisms in natural environments. Microbial processes have a major influence on the fate of arsenic in aquifers (Islam et al., 2004). Microorganisms that use As(V) as a terminal electron acceptor for the degradation of organic matter or oxidation of sulfide have been identified in arsenic-rich aquatic environments and in laboratory investigations (Dowdle et al., 1996; Ahmann et al., 1997; Hoelt et al., 2004). Abiotic reduction of As(V) and Fe(III) by redox-sensitive phenolic compounds (Haury et al., 2000) and sulfide (Rochette et al., 2000) has also been reported.

The presence of glucose in this experiment is to maintain the vitality of the microorganisms. The impact on the release of arsenic proposed mechanisms include: (1) oxidation of pyrite containing arsenic (Das et al., 1996; Mandal et al., 1998), (2) reduction of adsorbed arsenate to arsenite (BGS and DPHE, 2001; Bose and Sharma, 2002), (3) competitive anion exchange of adsorbed arsenic (Acharyya et al., 1999; Appelo et al., 2002) and (4) reductive dissolution of iron oxides containing arsenic (Nickson et al., 2000; McArthur et al., 2001; Swartz et al., 2004). In this research, we focus on the relationship between iron oxides dissolution or Eh value and the release of arsenic.

The change in the valence state of As in solution for the reduction reaction system gives a substantial indication of the translocation pathways in the soil system. The changes in Eh are a dominating factor in the desorption ratios of arsenate-to-arsenite from ferrihydrite (Frommer et al., 2011; Manning and Goldberg, 1997; Masscheleyn et al., 1991; Voegelin et al., 2007). Thus, arsenate (As(V)) is the principal component (95%) when a solution system has an Eh between 200–500 mV. However, for values of Eh between 0 and –200 mV, arsenite (As(III)) is the dominant species. On this basis, the long-term Eh changes in the soil samples for Pedons 1 and 2 (Fig. 2e, f), respectively, which demonstrate an opposite trend with respect to the dissolution curves for As and Fe (Fig. 2a–d), further reveal the dissolution/desorption correlation between As and Fe. Considering that desorption of arsenate from adsorbate or dissolution of arsenate from mineral has extremely slow reaction kinetics for many years (Arai and Sparks, 2002; Grossl and Sparks, 1995; O'Reilly et al., 2001; Takamatsu et al., 1982). Because of the absence of Pb ions in solution, it is speculated that the dissolved or desorbed As (III and V) come mainly from a minor part of the SOM (chemisorptions of ferrihydrite and possibly the organic complexes). As demonstrated, for all soil samples the Eh of

solutions are found to drop exponentially to –300 mV, after reaction proceeds for 128 days (Fig. 2e, f). The variation in Eh values implies that the As dissolution/desorption is mainly triggered by bio-reductive pathways (where As(V) is reduced by charge donation from organic mediates, once the potential barriers for chemisorptions reach the boundary condition) on organic complexes in paddy soil environments.

2.2 X-ray absorption near-edge structure (XANES) analysis

2.2.1 Structural information from As K-edge XANES

Arsenate distribution and transformation was determined as a function of the sampling depth for bulk soils in the two pedons, using XAS. Figure 3 shows a comparison between the As K-edge XANES spectra of bulk soils (Pedon 1 in Fig. 3a and Pedon 2 in Fig. 3b) and that of beudantite, a standard sample of arsenite (As(III) NaAsO_2) and arsenate (As(V) $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) powders (Fig. 3c). The E_0 of As is shown as a function of the valence state in Fig. 3d. It shows a high correlation ($R^2 = 0.9877$). The E_0 of the As anion is linearly proportional to its valence state. The valence state of As in beudantite is determined to be 11,875.4 eV, corresponding to a valence state of five

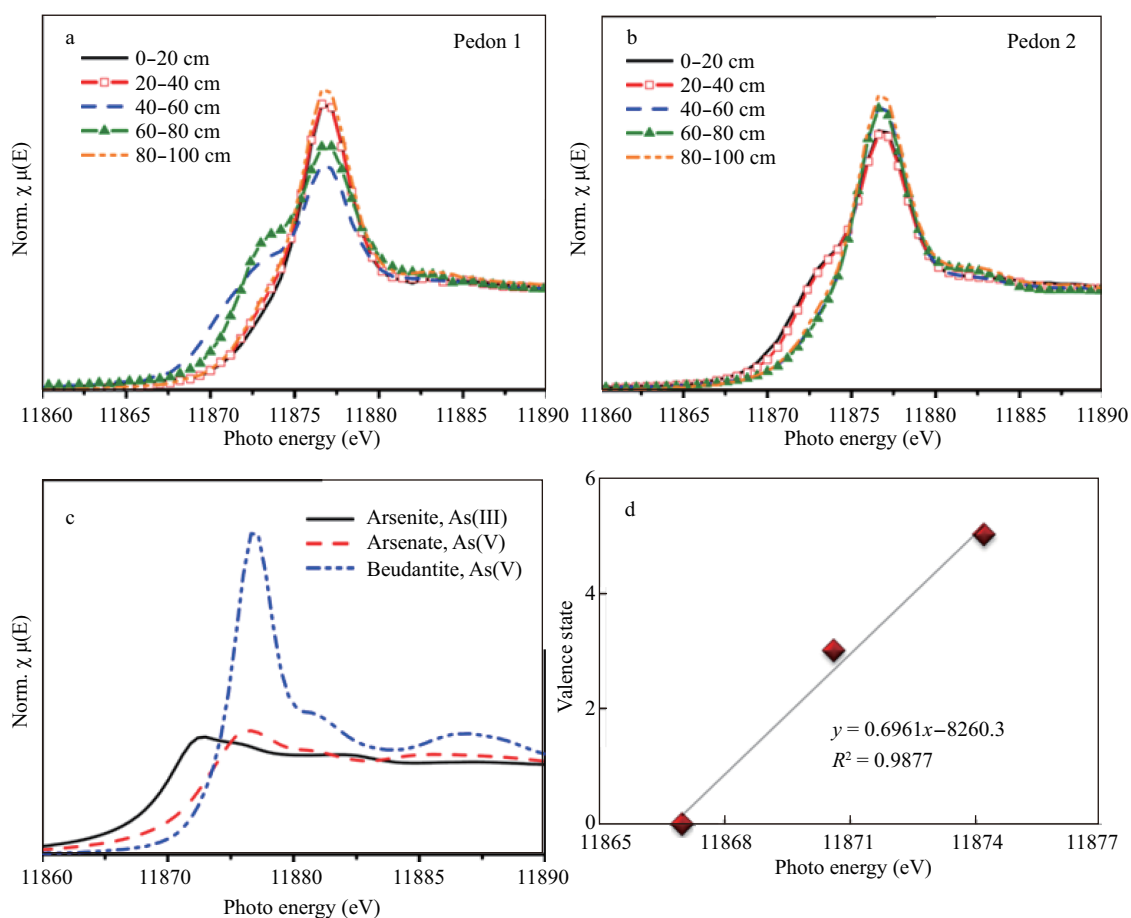


Fig. 3 XANES spectra for bulk soil samples of Pedon 1 (a) and Pedon 2 (b) at different depths, compared with that of arsenate standard As samples (arsenite (As(III) NaAsO_2) and arsenate (As(V) $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$))(c). The E_0 value of As as a function of the valence state in (d).

(As(V)). The positive offset of 1.2 eV from that of As(V) $\text{Na}_2\text{HAsO}_4\cdot 7\text{H}_2\text{O}$ standard powder (11,874.2 eV) can be attributed to its interaction with neighboring atoms that are strongly electro-negative (e.g., oxygen and sulfur) in a well crystallized structure. This phenomenon is further explained by the presence of multiple scattering peaks after the As K edge region (at 11,882 and 11,892 eV), which is a strong indication of the formation of well crystallized AsO_4 tetrahedrons in the beudantite mineral (Szymanski, 1988).

Similarly, such a strong neighbor-induced positive offset is also evidenced in beudantite by its E_0 at the Pb L_3 -edge (Fig. 4). The As in the bulk soil sample of Pedon 1 has a similar E_0 value to that in beudantite at the As K-edge XANES in the regions of 0–40 cm and 80–100 cm depth. This information demonstrates the similarity in As valence states for the bulk soil samples of Pedon 1 and beudantite, in these regions. However, the substantial reduction in E_0 from 11,875.4 eV indicates the presence of trivalent As in Pedon 1 from 40–80 cm depth. Thus, the largest negative E_0 shift reflects the greatest extent of arsenite embedding in the region of 40–60 cm depth for Pedon 1. Similarly, arsenite embedded soil samples are found in Pedon 2, from 0 to 40 cm depth. In addition, the absence of a post-edge multiple scattering peak is a clear indication of the formation of embedded fine particles of mineral type As that may have been released in suspension after the biogeochemical reaction.

The XANES spectra were fitted to those of standard samples (beudantite, arsenite (As(III) NaAsO_2) and arsenate (As(V) $\text{Na}_2\text{HAsO}_4\cdot 7\text{H}_2\text{O}$), using linear combination analysis, in order to further determine the chemical distribution of As species in the soils. This result supports the previous hypothesis that the As anions are preserved

in several conventional methods of soil embedment (i.e., chemisorption of As in amorphous and crystallite alumina-ferrihydrate co-precipitates or organic-complexes) (Shang et al., 1992).

The fitting results are summarized in Table 2, where As(III) are determined to be 52.1%–43.4% in the depth from 40 to 80 cm of Pedon 1 and ca. 38% in the depth from 0 to 40 cm of Pedon 2, respectively. Such consistent results support our previous hypothesis that the As anions were preserved in several conventionally known soil embedment (i.e., chemisorptions of As in amorphous and crystallite alumina-ferrihydrate co-precipitates or organic-complexes) (Chiang et al., 2010). An interesting result is the presence of trivalent As in the air-dried soil sample. This phenomenon confounds the conventional understanding of the thermodynamic equilibrium between As(V) and As(III) in an ecosystem. There are two possible rationales for this dichotomy: (1) the formation of trivalent As minerals; (2) the embedment of trivalent As in certain co-precipitates of Al-Fe hydrates of organic-complexes. Since the trivalent As minerals are absent from the soil sample, it is proposed that As-embedment may be a major pathway for the preservation of trivalent As in soils, due to the presence of underground water at 60–80 cm depth in Pedon 1 and 0–40 cm depth in Pedon 2, respectively. Although two soil samples show different As(III) or As(V) distribution in relation to the depth. However, after statistical analysis, the reduction induced As release is not relate to As(III) or As(V) distribution of soil depth. Therefore, we believe that they were not related in this case.

2.2.2 Structural information from the Pb L_3 -edge XANES

Figure 4 shows a comparison between the Pb L_3 -edge XANES spectra for all bulk soils and that of beudantite and standard samples of PbO and PbO₂. The correlation between E_0 and the valence states of Pb is shown in the inset. Since the E_0 values of most of the transition metals in the 3d orbital is linearly proportional to their valence state (Koningsberger and Prins, 1987), the oxidation states of Pb in the soil samples are determined by using the fitted results in the inset. Therefore, all of the bulk soil samples have similar profiles at the Pb L_3 -edge, indicating their similarities between local Pb chemical environments with respect to valence state, chemical identity and local structural symmetry. However, Pb in all of the bulk soil samples was found to have an E_0 value of 13,037.2 eV, which is similar to that for standard PbO₂ (13,037.1 eV), corresponding to a valence state of four. The E_0 value for Pb in beudantite is determined to be 13,037.7 eV.

These offsets in valence state can be explained by the difference in the heteroatomic chemical bonding of Pb for the different experimental samples (i.e., soil and beudantite) and standard PbO₂. The slightly positive shift in E_0 value implies the presence of anions or cations with strong electro-negativity that attract valence electrons from

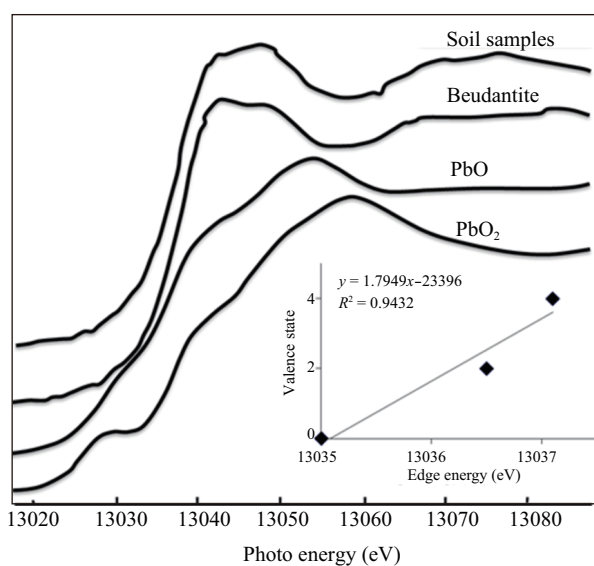


Fig. 4 Comparison between the Pb L_3 -edge XANES spectra of bulk soil samples and beudantite and standard samples of PbO and PbO₂, the correlation between the E_0 value and the valence state of Pb is shown in the inset.

Pb and cause an increase in the value of E_0 . However, the valence state of Pb is predominantly affected by the presence of oxygen-rich ligands that cover the surface of Pb embedded minerals. In this case, the E_0 value for Pb is decreased, because of charge donation from surrounding organic matter (Szymanski, 1988).

The electro-negativity sequences of the existing elements provide important information about the pathways for reductive induced arsenate/arsenite relaxation within soil environments. The electro-negativity of Al, Fe, As, P, Pb, S and O are 1.61, 1.83, 2.18, 2.19, 2.33, 2.58 and 3.44, respectively (Sanderson, 1983, 1988, 1989; Leland and Huheey, 1980; Huheey et al., 1993). For the case of beudantite, the electro-negativity of Pb is found to be smaller than that of its local coordinates (O and S). This heteroatomic interaction triggers a strong electronic repulsive force, which translocates its valence charges to local coordinates, as shown by the positive shift in the E_0 value of Pb from the 4+ state. However in the case of soils, the Pb K-edge spectrum was found slightly downshifted from the position of 4+ Pb (Fig. 4). It implies that a certain extent of soil 4+ Pb would be reduced by the organic matters. The small edge shift indicates the slow/weak kinetics or low ratio of bio-reductive dissolution of Pb, as a result of the low extent of micrometer-scale dissolution

of beudantite. Therefore, it is expected that Pb has a minor effect on the kinetics and chemical stabilization of arsenate/arsenite around the Guandu Plain.

2.2.3 Structural information from the Fe K-edge XANES

Figure 5a shows a comparison between the 1st differential curves of the Fe K-edge X-ray absorption near-edge spectra (1st diff XANES) for freshly collected bulk soils and that of standard tri- and di-valent Fe samples (Fe_2O_3 and FeSO_4). As illustrated, the high degree of similarity between the spectral profiles suggests that Fe atoms perform similar valence hybridizations when locating in soils and FeSO_4 . These spectroscopy features indicate that Fe complexes comprise mainly mineral state beudantite and partially organo-metallic or Fe_2O_3 in local soil environments. This is consistent with the low adsorption and dissolution of soil minerals that is evident in the subsequent kinetic analysis. In addition, the E_0 value of Fe atoms in all bulk soils is determined to be 7113.8 eV, which corresponds to that of trivalent Fe species.

The changes in Fe oxidation states with respect to depth, in Pedons 1 and 2, are illustrated in Fig. 5b, c, respectively. As evidenced by the threshold energy (E_T) and E_0 values for Pedon 1, Fe atoms in all samples remain in an identical

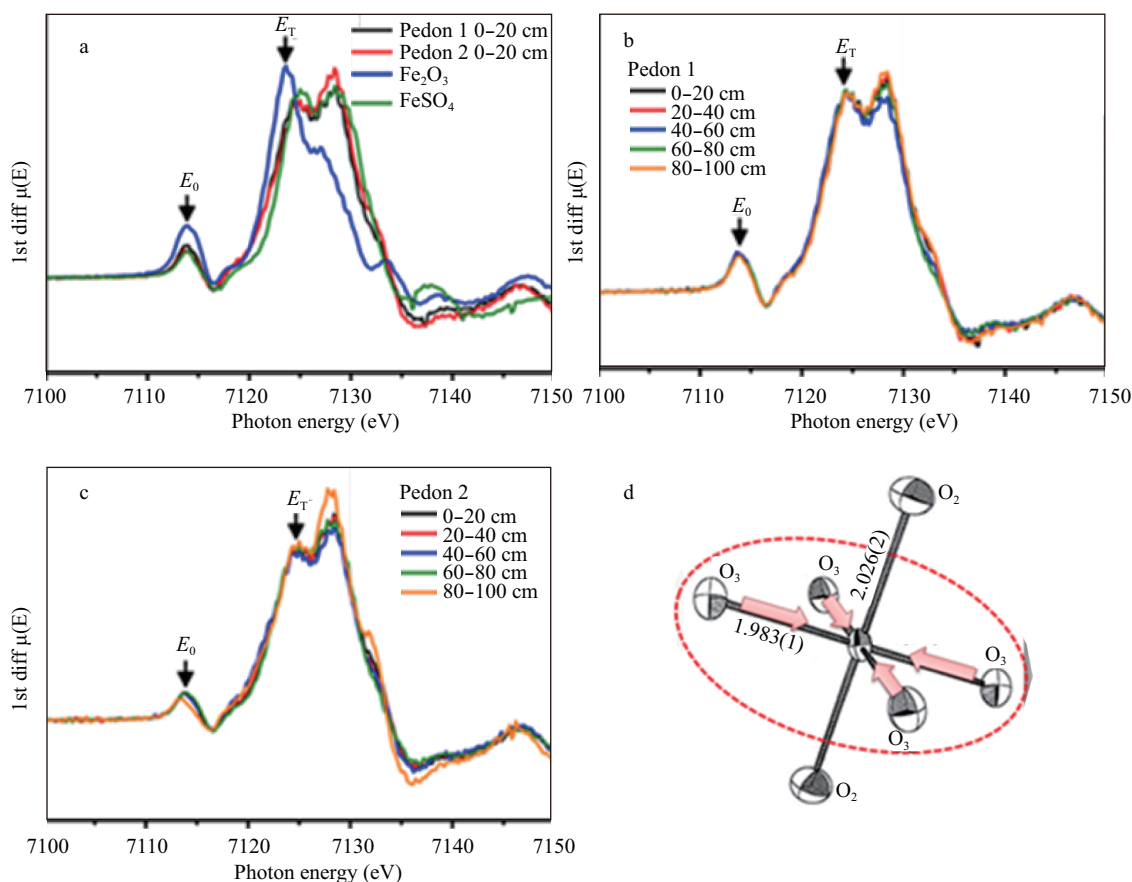


Fig. 5 Comparison between the 1st deviated Fe K-edge X-ray absorption near-edge spectra (1st-dev XANES) of surface soils (0–20 cm in depth) and that of standard Fe_2O_3 and FeSO_4 powders (a); those for different depths of soil in Pedons 1 and 2 are compared in (b) and (c), respectively. (d) Scheme for the local hybridization and charge translocation around Fe in a distorted octahedral site (Szymanski, 1988).

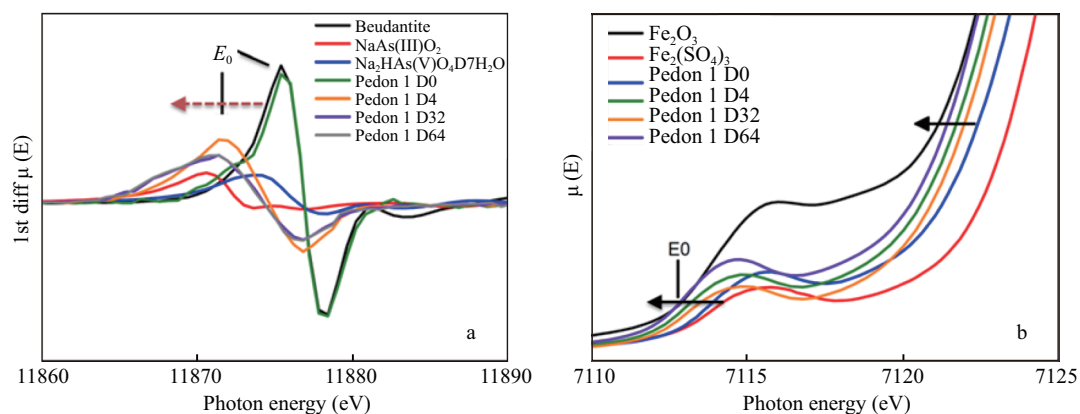


Fig. 6 (a) The 1st diff As K-edge XANES spectra and (b) Fe K-edge XANES spectra of the surface soil of Pedon 1 (in reduction release experiment).

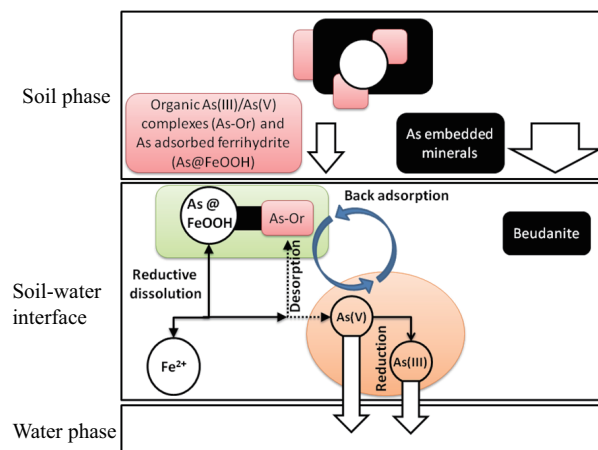
oxidation state and chemical environment, suggesting that there is no reductive dissolution of Fe-embedded minerals. This chemical feature is consistent with the slow reduction kinetics of Fe, as elucidated by the reduction release characterizations. However, in Pedon 2, the reduction in E_0 represents the reduction of Fe from a 3+ to a 2+ valence state. Given the high solubility of iron-hydroxide in natural environments, this small reduction may be explained by the enrichment of surface distorted octahedral iron sites in the beudantite, due to the effect of watering (as consistently evidenced by the highest Pb content for all samples of Pedon 2 being seen at 80–100 cm depth for bulk soil, in **Table 2**. Four oxygen atoms on the equatorial plane donate larger valence charges than that of un-distorted atoms (**Fig. 5d**) (Szymanski, 1988). A slight shift or no shift in E_T indicates that such reduction may be attributable to the effect of surface hydration reduction on Fe-based minerals. Therefore, considering the slow reduction kinetics of Fe-based minerals, low pollution with arsenate is expected during flooding of the highly contaminated paddy soil systems in the Guandu Plain.

The proposed reductive, induced As translocations are further explained by combining the changes to the valence states of As and Fe species in long-term reduction-aged soil samples, using XAS analysis. After reduction release experiments, the Pb L_{3-} edge XANES is similar to that of bulk soils (**Fig. 4**). **Figure 6a** shows a comparison between the 1st order deviated As K-edge XANES spectra of Pedon 1, for different durations of aging (the spectra of the soil samples are denoted as Pedon 1 D0 to Pedon 1 D64, where D0 to D64 denote the time for the reduction reaction from 0 to 64 days). It is clearly shown that the As anions in the freshly collected surface soil of Pedon 1 (Pedon 1 D0) remain at a valence state identical to that of beudantite (which is larger than that of As(V), due to charge donation from As to the neighboring oxygen). After reduction reaction for 4 days, a substantial reduction in valence state, from 5+ to 3.5+, is noted (Pedon 1, D4). The aging was found to slightly decrease the valence state of As to 3.0+ (shown by the dashed arrow). Similarly, the valence state of Fe in the soil samples is progres-

sively reduced by increasing the aging time from 0 to 64 days (**Fig. 6b** arrow). This reductive structural evolution of Fe is consistent with that proposed by Mitsunobu et al. (2008), who observed the desorption of As species from a ferrihydrite surface and from polluted iron-based mineral phases with a dissolution induced grain size in reductive environments, using a combination of Mössbauer spectroscopy and XAS analysis (Mitsunobu et al., 2006).

3 Conclusions

Based on chemical analysis, XAS characterization, reductive desorption experiments and variations in reduction potential, we recognize the following geochemical manners relating to the stabilization of soil organic matters and consequently, clarifying their roles in the relocation of arsenite/arsenate anions in ecosystems around investigating area as proposed in **Scheme 1**. The dissolution and precipitation of As, Fe and Pb in the paddy soils of the Guandu Plain is proposed to proceed as follows: (1) The Pb species comprise mainly mineral oxides (beudantite) and partially organic metal complexes. Both the chemical states are geochemically stable, which contributes slightly to the reductive dissolution of arsenate in Pedon.



Scheme 1 Pathway in SOM in a reductive environment.

(2) The majority of the dissolution/desorption arsenate species are stabilized at the surface of ferrihydrite and organic complexes, through a strong chemisorption bond. These strong chemisorption processes have extremely slow desorption/dissolution kinetics for arsenate, when the reduction reaction is taking place. (3) As and Fe species are highly sensitive to bio-reduction driving forces. However, the stronger chemisorptions bonds in these reduced Fe or organic phases substantially hinder the release of arsenate/arsenite from soil mediates into an ecosystem. (4) The reduction of arsenate into arsenite and the dissolution of sorption-polluted ferrihydrite phases are the essential (or dominating) steps for the subsequent release of As into soil systems. These experiments show that these bio-inspired redox steps cause extremely slow dissolution/desorption of As species in the crater. Detailed studies will be conducted to monitor the long-term geochemical effects on As ingestion in plants and the evolution of local ecosystems.

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