



Bioaccumulation and Translocation of Arsenic in the Ecosystem of the Guandu Wetland, Taiwan

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Abstract High arsenic (As) levels occur naturally in geothermal areas, potentially polluting downstream wetland ecosystems. The study was to determine the distribution of As among aqueous, solid, and plant phases in the Guandu Wetland of Taiwan. Chemical compounds (As, Fe, Mn, TOC, SO_4^{2-} , and FeS_2) and isotopic compositions ($\delta^{34}\text{S}$) in water and soil samples were analyzed to characterize the As distribution. The sequential extraction of As and total As in plant samples was analyzed to estimate the bioconcentration factor (BCF) and translocation factor (TF; defined as the ratio of metal concentration in the shoots to those in the roots) of As in *Kandelia obovata* in aqueous and solid phases. The As concentrations in plants (23.69 mg/kg) were higher than in the surrounding water (0.0018 mg/L) and soils (17.24 mg/kg). *Kandelia obovata* have high As bioavailability and low TF, causing easy adaptation to grow in As-contaminated wetland ecosystems. $\text{BCF}_{\text{plants/water}}$ (13657.92) was higher than $\text{BCF}_{\text{plants/soil}}$ (1.38). The uptake and bioaccumulation of As in *Kandelia obovata* are significant; therefore, *Kandelia obovata* is an As accumulator. The uptake As by the *Kandelia obovata* plant might depend on the oxidation of As-contained FeS_2 in the aerial roots and/or adsorption of As on root surface.

Keywords Arsenic · Wetland ecosystem · *Kandelia obovata* · Bioconcentration factor · Translocation factor

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Introduction

Arsenic (As) is a toxic metalloid and human carcinogen in the natural environment (Smedley and Kinniburgh 2002). High As levels occur naturally in geothermal areas because of volcanic activity, resulting in pollution of groundwater, geothermal spring water, downstream wetlands, and estuary ecosystems (Lièvremon et al. 2009).

The Guandu Wetland is located in the estuary of the Tanshui and Keelung Rivers and is widely affected by tidal conditions (Fig. 1). The tidal estuarine wetland is flooded twice a day; therefore, seawater mixing with fresh water results in variations of salinity, sulfate concentrations, pH, and redox conditions, which may cause As release and retention reactions. Most metal sulfides provide a potential sink for As in anoxic sediments (Dellwig et al. 2002), especially in coastal area where sediment material were easily deposited in the marine formation. The biogeochemical reactions in anaerobic environment may govern sulfate/sulfide cycling in sedimentary marine formations (Thamdrup et al. 1993; Canfield and Thamdrup 1996). Numerous studies have indicated that isotopic techniques are useful for understanding the influence of sulfur cycling on As mobility in the geochemical environment (Lipfert et al. 2007; Mukherjee and Fryar 2008; Kao et al. 2011). However, both the accumulation and impact of As on ecosystems in the wetland are not yet adequately distinguished.

Guandu Wetland is a tidal estuary natural preserve which has *Kandelia obovata*, *Phragmites communis* and *Cyperus malaccensis* mangrove species in the benthic-mud areas. *Kandelia obovata* is the most dominant mangrove species in Guandu Wetland (Hsueh and Lee 2000). *Kandelia obovata* has three physiological mechanisms: (1) Aeration roots transfer oxygen to the roots, thus *Kandelia obovata* can survive in anaerobic wetlands (Kadlec and Knight 1996). (2) Viviparous seedlings help disseminate and reproduce *Kandelia obovata* (Chou et al. 1987). (3) The salt tolerance of *Kandelia obovata* enables

survival in the estuary ecosystem (Mitsch and Gosselink 2000). *Kandelia obovata* has been widely studied and was mainly focused on the accumulation of heavy metals, effect of heavy metals on plant growth, and effects of root exudates on heavy metal toxicity (Lu et al. 2007; Xie et al. 2012). As heavy metal transported to the aerial part in *Kandelia obovat*, the stem acts as a cation exchange column which can effectively reduce the amount of heavy metal accumulation in leaves (Hardiman and Jacoby 1984). The high content of heavy metal in roots is an important tolerance mechanism of *Kandelia obovata*.

Variations of salinity, sulfate concentrations, pH, and redox conditions in wetland system may potentially affect As release and retention reactions. Hence the distribution and mobility of As among aqueous, solid, and plant phases are worth for investigation. The purpose of this study was to discriminate the distribution of As among aqueous, solid, and plant phases in the Guandu Wetland, Taiwan. Chemical parameters, As species, ferrous iron species and sulfur isotopic compositions (i.e., $\delta^{34}\text{S}_{[\text{SO}_4]}$ and $\delta^{18}\text{O}_{[\text{SO}_4]}$), were analyzed. The bioaccumulation and translocation capacity of the major wetland plant, *Kandelia obovata*, was quantitatively assessed to illustrate the uptake of As in the wetland environment. Results of this study will provide valuable information to improve our understanding of the transfer pathways of As in mangrove ecosystem in the region.

Materials and Methods

Study Area

The Guandu Wetland is located in the southwestern part of the Guandu Plain in Taipei, Taiwan, which is downstream of the Beitou geothermal spring (Fig. 1). In 1960s, many geothermal fields at Beitou have been developed to generate energy from the steam and hot water reservoirs of Tatun Volcano Group (Song et al. 2000) which lies between two major thrust faults, the Chinshan Fault and the Kanchiao Fault (Lai et al. 2010, 2011). In geothermal spring water at Beitou, Taipei City, Taiwan, the As concentration is as high as 4.32 mg/L (Chen et al. 2007), exceeding the ground water contamination standard of 0.25 mg/L and potentially resulting in bioaccumulation of As in the downstream wetland ecosystem. The As-rich spring water flows to Huang Gang Creek, discharging a high-As flux to the regional Guandu Plain. Long-term irrigation with high As contents has caused the average As content of surface (0–15 cm) and subsurface (15–30 cm) soil in the Guandu Plain to be 145 and 143 mg/kg, respectively, substantially higher than the soil contamination standard of 60 mg/kg (Chiang et al. 2010). High As contents may accumulate downstream of the Guandu Wetland and may influence aqueous, solid, and plant phases in the Guandu Wetland.

Because the Guandu Wetland is near the mouth of the Kee-lung and Tanshui Rivers, it has a semi-diurnal tidal regime with a

tidal amplitude of approximately 1–2 m; and although it is only 10 km away from the Tanshui River estuary, the wetland area is widely affected by tidal fluctuations. Tidal seawater, which can intrude into the upper estuary approximately 25 km from the river mouth, mixes with the river water during high tide, but mixes only partially during low tide (Liu et al. 2001).

The mangrove ecosystems are particularly abundant in the Guandu Wetland, and the *Kandelia obovata* is one of the most dominant plant species found in this area. Mangroves are capable of absorbing and accumulating pollutant toxins in both roots and aerial parts. As a result, the pollutants are transferred to the detrital food chain in the wetland ecosystems. The pathway of toxins transfer in mangroves via detrital food chain introduces As into the detritus feeding communities and thus resulting in input of As into the detrital and coastal food chains. Similarly, the deposit feeders, such as fiddler crabs, which are exposed to high As sediment may transfer the toxin into the food chains. As may be further transferred and biomagnified at higher trophic levels in the wetland ecosystem. It is thus important to know the As distribution in the aqueous, sediment, and mangrove phases to formulate effective management plan in the Guandu Wetland.

Water, Soil and Plant Sampling

The surface water and soil samples in this study were collected from inland sites and 5 randomly selected sites (S1, S2, S5, S7, and S9). Core samples were collected at the inner (depth of 70 cm, S2) and outer sites (depth of 85 cm, S5) (Fig. 1). Porewater samples with a vertical interval of 5 cm were extracted using a Rhizon sampler (microporous polymer, <0.2 μm pore size). The sediment samples with an interval of 5 cm were air-dried (overnight) to facilitate analyzing the chemical compounds. All water samples were stored in polyethylene containers, maintained at 4 °C, and sent to the laboratory within 24 h. All soil samples were stored in N_2 -purged plastic bags, dried at room temperature, and homogenized using 100-mesh sieves in an anaerobic glove box. A split sample was removed from the glove box in an oven at 50 °C for 72 h.

Plant samples were taken from the same location as the surface water, and the soil samples (S1, S2, S5, S7, and S9) were collected in 3 replicates. Samples of *Kandelia obovata* were roughly washed with tap water and then rinsed with deionized water. The various plant tissues, such as live roots, stems, leaves, and seedlings, were separated and delivered to the laboratory within 24 h. The samples were dried in the oven at 50 °C for 48 h, ground into powders, and passed through 100-mesh sieves (Abedin et al. 2002).

Chemical Compounds of Water, Soil and Plant Analysis

The dissolved oxygen (DO; Thermo Fisher Scientific Star-A 2235), redox potential (Eh; Mettler Toledo Inlab 501 Redox),

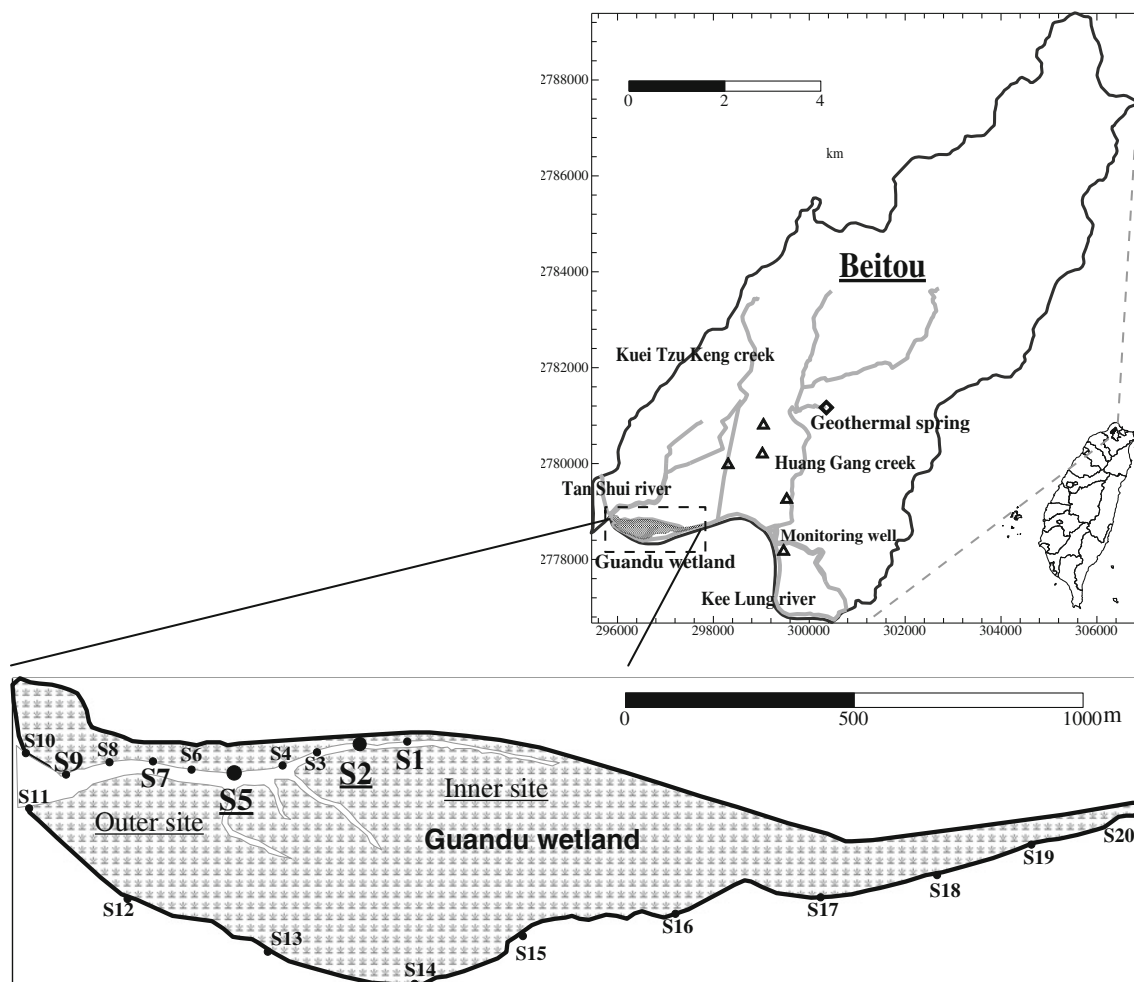


Fig. 1 Study area and sampling sites of the Guandu Wetland. Surface water, surface soil, and plant samples were collected from S1, S2, S5, S7, and S9. Core porewater and sediment samples were collected from S2 and S5

and pH (Mettler InLab Routine; Calibration Buffer Solution 4, 7 and 10) of the water samples were measured in situ. Water samples were filtered through 0.2 μm membrane filters (Advantec; mixed cellulose ester) and acidified with a few drops of 3 M HNO_3 to a pH of about 2 (APHA 1998). The Alkalinity (Alk) and total organic carbon (TOC), and NO_3^- , NH_4^+ , SO_4^{2-} , HS^- , Cl^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , As, Fe, and Mn concentrations were analyzed. Alkalinity and TOC were measured using the titration and high-temperature combustion methods, respectively (APHA 1998). Ions such as SO_4^{2-} , Cl^- , NH_4^+ and HS^- were determined using an ion chromatograph (IC) (DIONEX ICS-900), and Cl^- was determined using AgNO_3 titration. Dissolved metal ions, including Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Fe and Mn, were measured using an inductively coupled plasma-optical emission spectrometer (ICP-OES) (Perkin Elmer Optima 7300DV ICP-OES) (APHA 1998).

The preservative procedure of As and Fe species followed that outlined by Wang et al. (2011). After pumping, all groundwater samples were filtered through a 0.2 μm pore membrane filter to

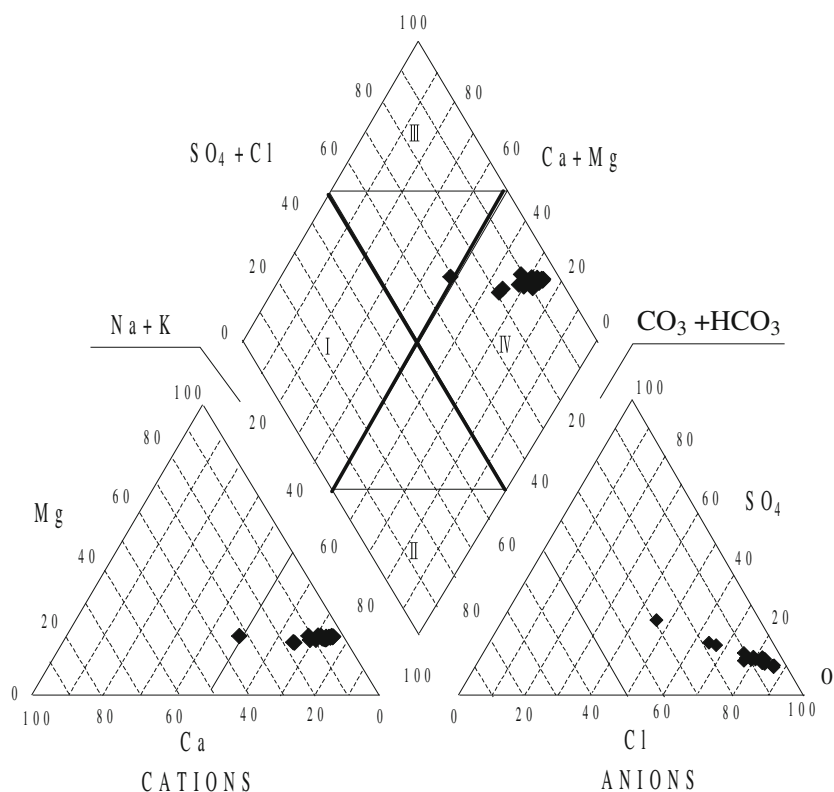
prevent microbial activity and remove suspended particles. In order to pre-treat groundwater samples by the complexation of Fe, acidification of samples had been proposed to prevent the effects of Fe precipitation on As speciation (McCleskey et al. 2004). Ferrous (Fe^{2+}) concentrations of the samples were measured colorimetrically using a ferrozine method (Lovley and Phillips 1987). The difference between the concentrations of total Fe and Fe^{2+} was considered the Fe^{3+} concentration. The arsenic species were separated using an anion column (Phenomenex Nucleosil, 10 μm , 250 mm \times 4.6 mm) connected to a high-performance liquid chromatography (HPLC) (Perkin Elmer Series 200 HPLC Pump), which was interfaced to an electrothermal atomic absorption spectrometer (AAS) (Perkin Elmer AAnalyst 200 AAS) and a hydride generation (HG) system (Perkin Elmer FIAS 100) (Huang et al. 2003). The variances of duplicate measurements were less than 10 %; recoveries of check and spike samples were between 85 % and 115 %, respectively.

The soil samples were air-dried, digested in aqua regia, and filtered to determine the metal ion concentrations such as Fe

Table 1 The physico-chemical parameters in surface water

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17	S18	S19	S20	Mean	Std
Depth (cm)	111	165	102	24	38.5	103	55	58	96	25	25	26	51	50	26	38.4	30	67	54	58		
DO (mg/L)	4.6	7.5	4.6	4.5	7.5	3.6	2.1	6.3	7.2	1.9	6.7	3	6.8	6.7	7.4	3.2	3.8	2.8	3	4	4.9	2.0
EC (μ S/cm)	4700	8910	4420	3930	–	4280	2960	2240	1815	1510	2040	1069	640	464	6260	1937	3890	2510	1243	753	2924.8	2160.4
Eh (mV)	126	46	102	113	114	109	110	99	90	48	80	–37	17	81	53	69	70	55	76	90	75.6	38.5
pH	7.31	7.14	7.19	7.23	7.26	7.14	7.11	7.15	7.17	7.13	7.12	7.1	6.94	6.87	7.13	7.03	7.11	6.99	6.99	6.96	7.1	0.1
As (μ g/L)	1.1	1.8	1.2	1.4	2	1.3	2	2	2.3	2.1	3.3	3.7	2.7	2	2.6	2.6	3.7	3.9	2.9	2.4	2.4	0.8
Fe (μ g/L)	83	67	95	95	63	85	91	62	94	91	58	92	72	86	63	74	115	415	86	177	103.2	77.8
Mn (mg/L)	0.36	0.12	0.3	0.30	0.16	0.34	0.22	0.17	0.16	0.12	0.12	0.11	0.09	0.10	0.13	0.11	0.17	0.16	0.13	0.17	0.2	0.1
TOC (mg/L)	9.4	6.2	7.8	6.9	4.2	6.6	5.2	5.6	6.2	5.4	3.9	4	3.5	3.4	4.6	3.2	4.6	2.7	2.9	2.6	4.9	1.8
Alk (mg/L)	67.7	75.6	66.2	64.8	60.2	71.6	66.2	66.7	74.1	59.7	53.7	50.7	43.2	38.3	64.7	42.8	58.7	50.7	43.8	36.3	57.8	12.1
NO ³⁻ -N(mg/L)	0.32	0.33	0.38	0.5	0.26	0.37	0.5	0.54	0.39	0.64	0.69	0.78	0.86	0.88	0.37	0.74	0.66	0.68	0.74	0.8	0.6	0.2
NH ₄ ⁺ -N(mg/L)	2.7	3.32	2.58	2.58	3.45	2.34	2.7	2.86	4.36	2.49	1.93	1.84	1.61	1.45	2.99	1.62	2.42	1.83	1.47	1.31	2.4	0.8
SO ₄ ²⁻ (mg/L)	238	384	213	166	450	225	154	114	101	69.2	86.8	47.5	37.5	26.6	312	81.6	128	107	57	29.7	151.4	119.5
Cl ⁻ (mg/L)	1340	2810	1180	988	3250	1180	871	572	440	352	479	262	120	38.2	2420	524	851	660	313	87.1	936.9	905.4
Ca (mg/L)	38.3	64.4	35	34.2	60.3	38.8	30.3	22.2	24.1	18.7	19.5	18.8	13.3	13.9	45.2	17.4	21.6	25.1	16.5	15.8	28.7	14.7
Mg (mg/L)	91.1	279	106	98	230	92.4	54.2	46.4	40.6	24.3	37.1	20.1	9	5.34	173	32.8	43	50.8	19.5	10.6	73.2	74.9
Na (mg/L)	678	2130	820	743	1780	713	409	361	285	184	284	149	65	24.2	1300	232	335	394	132	68.8	554.4	576.1
K (mg/L)	34	91.8	34.2	29	72.1	33.3	23.6	21.3	14.7	11.1	15.3	8.94	6.32	4.41	52.1	15.6	16.4	22.2	7.94	18.5	26.6	22.4

Fig. 2 Piper diagram of the chemical parameters in surface water



and Mn, using ICP-MS. Sulfate and total organic carbon contents were analyzed by turbidimetric method and Walkley-Black method, respectively. To determine the total As concentration, 30 % H_2O_2 and 9.6 M HCl were added to the soil samples to remove organic matter; the soil samples were then filtered. The AAS and HG systems (Perkin Elmer FIAS100) were used, in which a mixture of 0.5 % NaBH_4 , 0.25 % NaOH, and 1 M HCl was used to reduce arsenic to arsine (EPA, NIEA S310.62C). All the metal concentrations of solid phases are given on dry matter basis.

The digestion procedure of As in the plant followed that outlined by Tang and Miller (1991). The plant samples, which were various *Kandelia obovata* tissues, required the addition of 25 ml of HNO_3 and were allowed to stand overnight. The plant samples were then supplemented with 30 % H_2O_2 and heated to 120 °C for 3–4 h to remove organic matter. At room temperature the mixtures were filtered (0.2 μm pore membrane filter), and the total As was determined using an electro-thermal atomic absorption spectrometer (AAS) and a hydride generation (HG) system, as described previously. The standard reference material used was tomato leaves (NIST1573a; As=0.112 mg/kg) and the extraction recovered 72 % to 106 % of the total As.

Sulfur Isotope Analysis

Porewater samples were filtered with 0.2 μm membrane filters and acidified with 1 M HCl to maintain the solution $\text{pH}<2$;

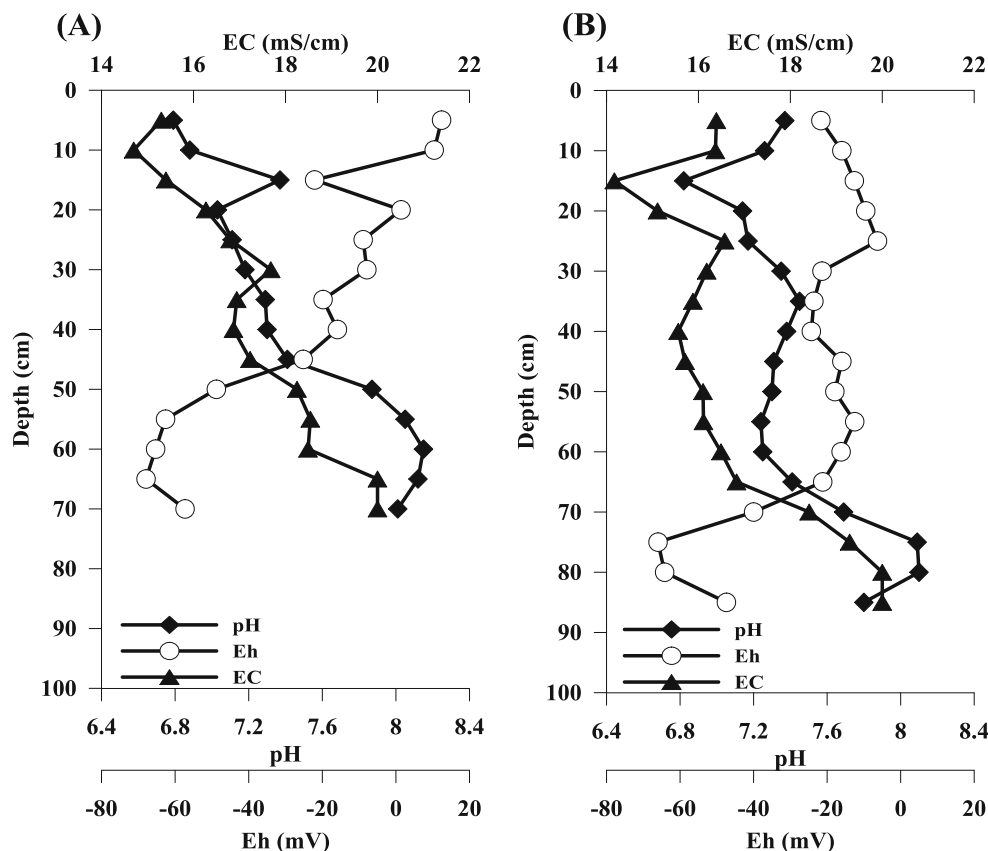
10 % BaCl_2 was then added to the samples to produce BaSO_4 precipitation. The samples were then filtered and dried (Yanagisawa and Sakai 1983). The $\delta^{34}\text{S}_{[\text{SO}_4]}$ was analyzed in the isotope laboratory at the University of Arizona using a continuous-flow gas-ratio mass spectrometer (Thermo Scientific Delta PlusXL) (Supporting material (a)).

Before analyzing the sulfur isotope, chrome-reducible sulfide (CRS; $\text{FeS}_2\text{-S}$) had to be extracted from the sediment samples. Both the sediment samples and a small beaker containing a 15-ml 3 % alkaline zinc (Zn) acetate solution were placed in a bottle. The cap of the bottle was tightened and the solution was flushed with nitrogen for 30 s. After flushing, 15 ml of 6 N HCl (anaerobic acid) and 15 ml of an anaerobic Cr(II) solution were added to the bottle and left to stand for 48 h. An alkaline Zn trap was retrieved to analyze ZnS and measure CRS using iodine titration of ZnS precipitation (Hsieh and Shieh 1997). The

Table 2 The mean and standard deviation (Std) values of 6 chemical parameters (mg/kg) from 20 soil samples

Chemical	Mean	Min	Max	Std
	75.05	43.7	94.5	13.81
TOC	14.51	4.7	25.5	5.06
SO_4^{2-}	1819.9	378.0	3490.0	1002.87
As	16.03	10.1	19.1	2.70
Fe	40725	29000	46900	4754.04
Mn	409	259	625	89.46

Fig. 3 Depth profiles of measured pH, Eh, and EC of **a** core of S2 and **b** core of S5



$\delta^{34}\text{S}_{[\text{FeS}_2]}$ were analyzed using ZnS powder in the isotope laboratory at the University of Arizona by the Thermo Scientific Delta PlusXL (Supporting material (b)).

Calculation of Translocation Factor and Bioconcentration Factor

The translocation factor (TF) is defined as the ratio of metal concentration in the shoots to those in the roots (Cui et al. 2007; Li et al. 2007; Malik et al. 2010)

$$\text{TF} = [\text{As}_{\text{shoots}}]/[\text{As}_{\text{roots}}] \quad (1)$$

where $\text{As}_{\text{shoots}}$ and As_{roots} are the As concentrations (mg/kg) accumulated in the shoots and roots, respectively. $\text{TF} > 1$ indicates that the plant translocates metals effectively from the roots to the shoots (Baker and Brooks 1989).

The bioconcentration factor (BCF) is defined as the ratio of metal concentrations in the roots to those in the soil or water, and is determined using Eq. (2) (Abdul and Thomas 2009)

$$\text{BCF} = [\text{As}_{\text{plants}}]/[\text{As}_{\text{environment}}] \quad (2)$$

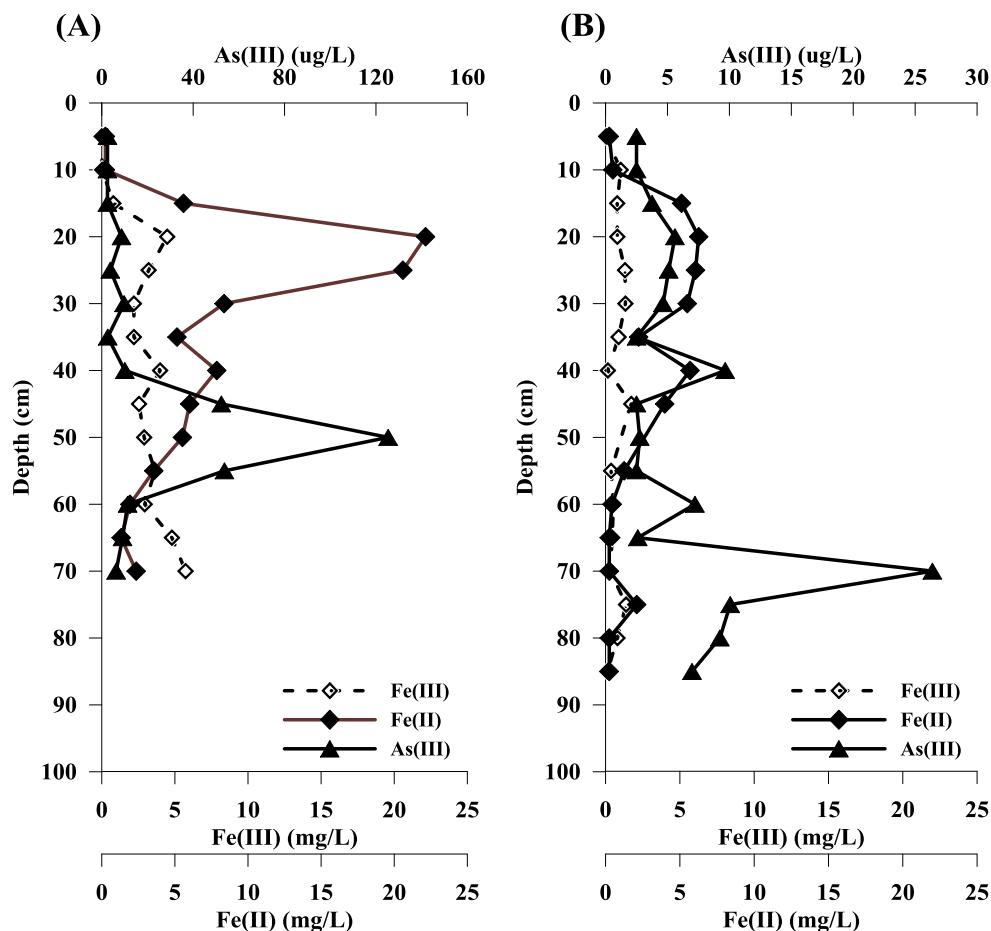
where $\text{As}_{\text{plants}}$ and $\text{As}_{\text{environment}}$ are As concentrations (mg/kg) in the plants and in the environment (soil or water), respectively, $\text{BCF} > 1$ indicates that the plant is a metal accumulator.

Results and Discussion

Aqueous and Solid Phases As in Surface Water and Soil

Table 1 listed 18 analyzed chemical compound concentrations in the surface water samples (S1-S20). The average of DO and Eh in the surface water were 4.86 mg/L and +79.25 mV, respectively, indicating that the oxidative condition in surface water is a major redox state. The significant effect of tidal seawater and infiltration of rainfalls in wetland resulted in high EC, DO, and Eh values in surface water. The range of As, Fe, and Mn concentrations in the surface water were from 0.0039 to 0.0011 (mean: 0.0024 mg/L), 0.06 to 0.42 (mean: 0.10 mg/L), and 0.09 to 0.36 mg/L (mean: 0.18 mg/L), respectively. Notably, As concentrations in the surface water were lower than that outlined in the drinking water standard (0.01 mg/L) of the Environmental Protection Administration (EPA) of Taiwan. According to the classifications of the Piper diagram (Fig. 2) in the Guandu Wetland, Type I represented the carbonate/temporary hardness, Type II represented the alkali carbonate, Type III represented the non-carbonate/permanent hardness, and Type IV represented saline. The Piper diagram indicated that the principal water type in the Guandu Wetland was Type IV ($N=20$). The result showed that the chemical compositions of surface water in the Guandu Wetland were mainly controlled by mixing of seawater. Hence the occurrences of low heavy metal concentration in surface

Fig. 4 Depth profiles of measured As and Fe concentrations of **a** core of S2 and **b** core of S5



water were strongly affected by dilution of tidal seawater. The range of As, Fe, and Mn concentration in the surface soil was from 10.1 to 19.1 (mean: 16.03 mg/kg), 29000 to 46900 (mean: 40725 mg/kg), and 259 to 625 mg/kg (mean: 409 mg/kg). The As concentration in surface soil was higher than general soil content 5–10 mg/kg (mean: 7.2 mg/kg) (Table 2) (Boyle and Jonasson 1973). The As concentration in the surface soil was also lower than the 60 mg/kg soil contamination standard of the Environmental Protection Administration (EPA) of Taiwan. A contents in surface water and topsoil are below the permissible environmental contamination guidelines and possess no environmental risks. However As concentrations in surface water of this study are lower than those in other As contaminated wetland system suggesting that As may be adsorbed on the surface of the Fe/Mn (hydr)oxide in oxidative condition of nature wetland system (Zheng et al. 2004; Gonzalez et al. 2006).

Profiles of Aqueous and Solid Phases in Porewater and Sediment

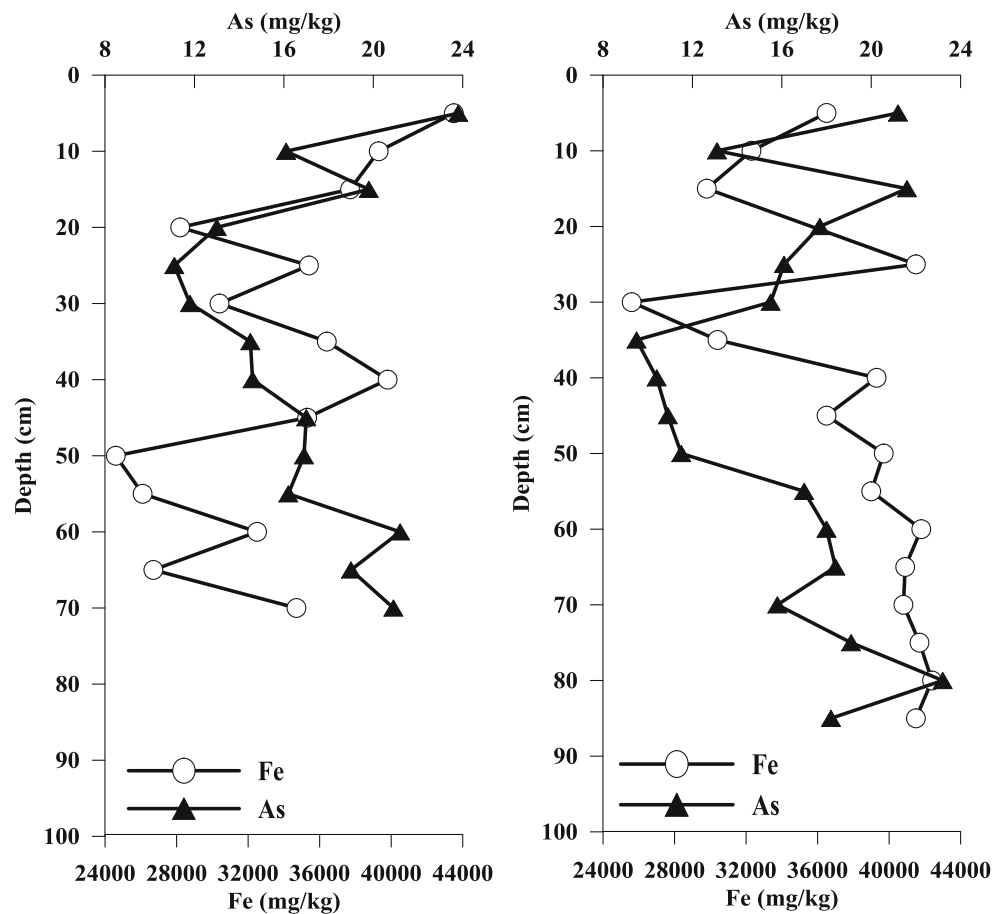
Figure 3 showed the spatial variation of pH, Eh, and EC which were measured in porewaters. The Eh of porewaters decreased from the surface to a deep depth, whereas pH and EC increased.

Infiltration of rainfalls and surface water flows diluted the EC values of pore water in the shallow layer, but had a mild effect in deep layer. Permeated oxidative species (e.g., DO, NO_3^- -N, and SO_4^{2-}) were also increased in the shallow layer (Table 1). The low concentration of aqueous As in the shallow layer may be caused by the adsorption of aqueous As on the amorphous Fe (hydr)oxides (Fig. 4) (McArthur et al. 2001; Nickson et al. 2000), leading to the high solid As concentrations in depth of 5 cm (S2, 23.8 mg/kg) and 15 cm (S5, 21.6 mg/kg) (Fig. 5).

Because aqueous As(V) concentrations were very low or close to zero, we herein only show the As (III) concentration profile. High aqueous As(III) concentrations were found in 45–55 cm deep (up to 125.35 $\mu\text{g/L}$) at S2 and up to 26.39 $\mu\text{g/L}$ in 70 cm deep at S5. Aqueous Fe(II) concentrations in porewater of S2 and S5 ranged from 0.01 to 22.15 mg/L and 0 to 6.27 mg/L, respectively (Fig. 4). The vertical redox gradient of S2 and S5 were moving from the oxidizing to the reducing condition along with depth. Redox-related processes in wetlands were largely controlled by the reduction of FeOOH in the presence of organic matter (OM) during bacteria respiration, serving as electron donors (Bauer et al. 2008; Hossain et al. 2012).

High aqueous As concentrations occurred in the transition zone of the shallow and deep layer and was accompanied with

Fig. 5 Depth profiles of solid-phase As and Fe concentrations of **a** core of S2 and **b** core of S5



the low concentrations of solid-phase As; this may be caused by the reductive dissolution of Fe oxides (Figs. 4 and 5).

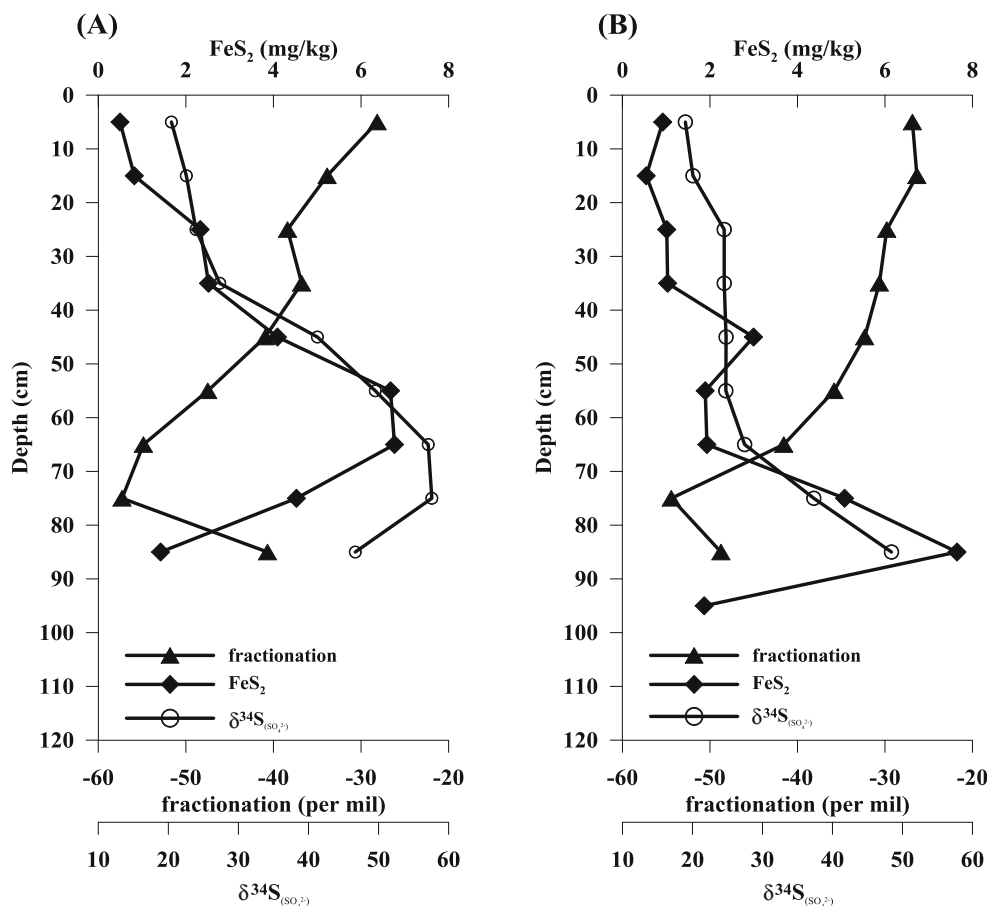
Under the reducing conditions in the deep layer, aqueous As concentrations might be constrained by precipitated sulfide minerals in the sediment (Fig. 6), which are the product derived from sulfate reduction. The sulfur isotopes fractionation factors ($\epsilon = \delta^{34}\text{S}_{[\text{FeS}_2]} - \delta^{34}\text{S}_{[\text{SO}_4]}$) can be used to evaluate the sulfur cycling and microbial processes. Sulfate reducing bacteria (SRB) preferred the lighter sulfur isotopes of sulfate (Kaplan and Rittenberg 1964), and thus, increased in $\delta^{34}\text{S}_{[\text{SO}_4]}$ with depth represents sulfate reduction in deep layer and easy adsorption of As on the pyrite surface. Figure 6 shows that the fractionation factor decreased with depth, but pyrite and $\delta^{34}\text{S}$ increased with depth. Hence in the deep layer, aqueous As can be constrained by the formation of FeS_2 in sediment during bacterial sulfate reduction that is governed by the relative enrichment of the $\delta^{34}\text{S}_{[\text{SO}_4]}$ and S isotope fractionation factor (ϵ) values, in accordance with elevated As and FeS_2 concentrations in sediments (Figs. 5 and 6). In contrast, aqueous As was liberated due to oxidation where solid FeS_2 was dissolved, resulting in the low solid FeS_2 concentrations, low sulfur fractionation factor, and positive Eh values in the shallow oxidizing-layer (Van Stempvoort and Krouse 1994; Lipfert et al. 2007). The sulfide oxidation processes may

liberate As but low aqueous As concentrations were found in shallow oxidizing-layer (Table 1), suggesting other geochemical processes or As transfer pathways such as uptake by plants may be involved.

Arsenic Uptake in *Kandelia Obovata*

The range of As concentrations in the plant (*Kandelia obovata*) was 20.21–28.33 mg/kg (mean: 23.69 mg/kg), and the results indicated that *Kandelia obovata* had a higher As concentration than did the surrounding water (mean: 0.0018 mg/L) and soil (mean: 17.24 mg/kg) (Table 3). *Kandelia obovata* thrives in anaerobic wetlands because its aeration roots transfer oxygen to its roots (Kadlec and Knight 1996), thereby forming iron oxide (iron plaque) around the roots which can adsorb As on the surface. The formed iron plaque on the roots of *Kandelia obovata* can prevent the uptake of As and preserve the root (Kadlec and Knight 1996; Meharg 2004; Fitz and Wenzel 2002; Liu et al. 2004a). The mean As concentration in *Kandelia obovata* decreased from the roots (19.74 mg/kg) to the stems (1.76 mg/kg), leaves (1.71 mg/kg), and seedlings (0.48 mg/kg) (Table 3), suggesting that As accumulated mostly in the roots. These results were also consistent with those of rice and

Fig. 6 Depth profiles of solid-phase FeS₂ concentrations, $\delta^{34}\text{S}_{[\text{FeS}_2]}$, and $\epsilon_{[\text{SO}_4\text{-FeS}_2]}$ of **a** core of S2 and **b** core of S5



fern roots, on which iron plaque was also present (Williams et al. 2007; Casado et al. 2007; Zandsalimi et al. 2011). Therefore, *Kandelia obovata* may still continue to survive in polluted areas, because its tolerance to and adsorption of As are more effective than those of other plants.

In this study, $\text{TF}_{\text{shoots/roots}}=0.199$ indicated that *Kandelia obovata* accumulated As in the roots but did not transfer to the shoots (Table 4). $\text{TF}_{\text{stems/roots}}=0.088$, $\text{TF}_{\text{leaves/roots}}=0.088$, and $\text{TF}_{\text{seedlings/roots}}=0.024$ indicated that the As concentrations in the roots transferring to the stems were similar to those of the leaves but are larger than those of the seedlings (Table 3). As a

result, all translocation factors of *Kandelia obovata* less than 1 indicated that the transformation of As in various plant tissues was extremely low, thereby facilitating adaptation when growing in an As-contaminated wetland ecosystem.

Notably, some previous studies have indicated that the translocation factors of trace metals (such as Al, Cu, Ni, Fe, Pb, and V) in plants (e.g., *Malva parviflora*, *Suaeda aegyptiaca*, *Chrozophora tinctoria*, *Fagonia bruguieri*, *Gynandriris sisyrinchium*, and *Ducrosia anethifolia*) were greater than 1; these plants were also the trace metal accumulators (Abdul and Thomas 2009). In addition, the translocation factors of the Cretan brake fern and Chinese brake fern were 1.00–2.61 and 0.17–3.98, respectively (Wei and Chen 2006).

Table 3 Arsenic concentration in surface water, soil, plant and various plant tissues

Sample	Surface water (mg/L)	Surface soil (mg/kg)	Plant (mg/kg)	Root (mg/kg)	Stem (mg/kg)	Leaf (mg/kg)	Seedling (mg/kg)
S1	0.0011	19.00	22.24	18.14	1.14	2.37	0.59
S2	0.0018	17.60	22.94	19.38	1.20	2.08	0.28
S5	0.0020	16.00	28.33	20.86	4.62	1.91	0.95
S7	0.0020	17.60	24.75	22.04	0.95	1.40	0.36
S9	0.0023	16.00	20.21	18.28	0.90	0.81	0.21
Average	0.0018	17.24	23.69	19.74	1.76	1.71	0.48

Table 4 Translocation factors in various plant tissues

Sample	$\text{TF}_{\text{shoot/root}}$	$\text{TF}_{\text{stem/root}}$	$\text{TF}_{\text{leaf/root}}$	$\text{TF}_{\text{seedling/root}}$
S1	0.226	0.063	0.130	0.033
S2	0.184	0.062	0.107	0.014
S5	0.359	0.221	0.092	0.045
S7	0.123	0.043	0.064	0.016
S9	0.105	0.049	0.045	0.012
Average	0.199	0.088	0.088	0.024

Table 5 Bioconcentration factors of the plant to surface water and soil

Sample	BCF _{plant/water}	BCF _{plant/soil}
S1	20218.18	1.17
S2	12744.44	1.30
S5	14165.00	1.77
S7	12375.00	1.41
S9	8786.96	1.26
Average	13657.92	1.38

Arsenic Bioconcentration Factors in the Plant

In this study, the average BCF_{plant/soil} of *Kandelia obovata* was 1.49; the results show that accumulation and uptake of heavy metals by *Kandelia obovata* was greater than that of other plants. Because BCF_{plants/soil} > 1, *Kandelia obovata* can be considered an As accumulator (Ma et al. 2001). Cao and Ma (2004) applied the BCF_{plants/soil} to evaluate the As bioaccumulation in carrots and lettuce, grown on chromate copper arsenate (CCA)-contaminated soil. The BCF_{plants/soil} is 0.10–1.61. The range of BCF_{plants/soil} in As-polluted mining soils is 0.0001–0.019 according to different tolerant plants (Casado et al. 2007). The BCF_{plants/soil} of *Kandelia candel* on Cu, Zn, Pb, Cd, and Ni is 2.79, 2.77, 3.03, 4.20, and 4.97, respectively (Chiu and Chou 1991).

By contrast, BCF_{plants/water} can reflect the accumulation of As in plants more accurately because only a small portion of the total soil As can easily be uptaken by plant roots. A small fraction (0 %–2 %) of the exchangeable solid phase As appeared to have been adsorbed in the wetland and were extracted by NaNO₃ (Chen 2010), indicating that the uptake of chemical compounds in plants from sediments was difficult. The average BCF_{plant/water} of *Kandelia obovata* was 13657.92, and it was greater than BCF_{plant/soil} in this study (Table 5). The result shows that the uptake of As in *Kandelia obovata* was significant in water because of the low As concentration in the water, which might be removed either by tidal effects or plant uptake. Moreover, approximately 60 %–90 % of the extracted As contents were incorporated in the amorphous and crystalline metal oxides, and the sulfate reduction simultaneously reduced the As mobility (Chen 2012). Only 0.2 % proportions of exchangeable phase were found in shallow layer (Chen 2012), suggesting that the plants uptake of As from soil was mainly from amorphous metal oxides. Under oxidation condition of shallow layer, the aqueous As concentrations with high proportions of sulfides phase were higher than those of in low proportions of sulfides phase. The oxidation of As-bearing sulfide hence may thus mobilize As in the shallow layer. Hence, the uptake mechanism of *Kandelia obovata* might depend on the oxidation of As-contained FeS₂ in the aerial roots and/or adsorption of As in root surface. Notably, the iron plaque forming in the root surface had strong affinity for adsorbing As. (Chen et al.

1980; Liu et al. 2004b). It will be interesting to analyze the roots with and without plaques in future studies.

Conclusions

The study discriminates the distribution and mobility of As among aqueous, solid, and plant phases and assesses bioaccumulation and translocation capacity of As in plant in the Guandu Wetland, Taiwan. The vertical redox profile of core samples S2 and S5 showed two distinct oxidizing and reducing zones. As adsorbed on the surface of Fe oxides and Fe sulfide in the shallow oxidizing layer, and in the deep reducing layer, respectively. High aqueous As occurred in the transition zone of the shallow and deep layer, which may be resulted in the reductive dissolution of Fe oxides. According to results of S isotopic fractionation, As can be constrained by the formation of FeS₂ during bacterial sulfate reduction in deep layer. In contrast, aqueous As was liberated due to FeS₂ oxidation in the shallow layer. Arsenic is mostly accumulated in *Kandelia obovata* roots, and the accumulation and translocation capacity of As are higher than those of in other plants. *Kandelia obovata* is an As accumulator. The uptake mechanism of the plant might depend on the oxidation of As-contained FeS₂ in the aerial roots and/or adsorption of As in root surface. The transfer pathway of As in mangroves among aqueous, solid, and plant phases provides information on As uptake by *Kandelia obovata* in the Guandu Wetland. Furthermore, the results provide the ecological basis for future research in the development of biomonitoring tools and management plan for tidal mangrove plain.

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