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Dynamics of arsenic in salt marsh sediments from Dongtan wetland of the Yangtze River estuary, China

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Abstract

The mobility and transformation of arsenic (As) in salt marsh sediments were investigated in Dongtan wetland of the Yangtze River estuary, China. As in surface water, pore water and the rhizosphere sediments were quantified. The microcosm incubation experiments were conducted during the flooding of the sediments to examine As dynamics that occurred during changing redox conditions. The concentrations of dissolved As in pore water (0.04–0.95 μmol/L) were significantly greater than that in surface water (0.03–0.06 μmol/L). Under anoxic conditions, the reactive As could be initially mobilized by the reductive dissolution of Fe(III) (hydr)oxides. Subsequently, most of the dissolved As was likely to be associated with secondary iron (hydr)oxide phases and remained in solid phases. The seasonal variability of acid volatile sulfide concentrations suggest the anoxic conditions are enhanced during summer by *Spartina alterniflora* compared to *Phragmites australis* and *Scirpus mariqueter*, causing a notable increase in As mobility. Generally, there was a typical variation in redox conditions with season in salt marsh sediments of Dongtan wetland, in which the dynamics of As mobility and transformation possibly were controlled by iron, and all of this could be significantly influenced by the rapid spread of *S. alterniflora*.

Key words: arsenic; iron (hydr)oxides; salt marsh sediment; *Spartina alterniflora*; Yangtze River estuary

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Introduction

Salt marsh is one of the complex coastal ecosystems and is regarded as both a natural sink and a source for contaminants (Williams et al., 1994; Reboreda and Caçador, 2007). Accumulated arsenic (As) in salt marsh sediments could pose a serious threat to ecosystem health (Bostick et al., 2004). There are large areas of salt marsh in the intertidal zone of the Yangtze River estuary, China. It has been reported that the As and heavy metals in estuarine sediments has been significantly impacted by anthropogenic activities such as domestic and industrial waste discharge in recent decades (Chen et al., 2000; Feng et al., 2004; Chetelat et al., 2008; Huang et al., 2008; Yao and Zhang, 2009; Zhang et al., 2009). Periodic desiccation, tidal flooding and seasonal growth cycling of salt marsh plants can lead to the change of redox conditions significantly (Koretsky et al., 2006, 2008a, 2008b), causing potential impacts on the mobility of As in sediments and the accumulation of As in pore water that imposes a potential hazard to aquatic life.

Spartina alterniflora, an invasive halophyte, was intentionally introduced to the coastal region of China in 1979 (Quan et al., 2007) and is now a dominant species in the Yangtze River estuary, with its invasion leading to multiple effects upon the estuarine ecosystems (Li et al., 2009; Nie et al., 2009). Studies showed that the marshland dominated by *S. alterniflora* can potentially facilitate the storage of soil organic carbon (Li et al., 2009; Zhang et al., 2010) and sulfur (Zhou et al., 2009) compared to native species *Phragmites australis* and *Scirpus mariqueter* because of its aboveground biomass were significantly greater (Quan et al., 2007; Zhang et al., 2010). Studies in the literature have pointed out that *S. alterniflora* can significantly influence the redox conditions of the sediment in its rhizosphere (Hines et al., 1999; Kostka et al., 2002; Koretsky et al., 2008a, 2008b). These results mean that the rapid invading exotic species *S. alterniflora* in salt marsh of the Yangtze River estuary may have a potentially significant effect on the patterns of biogeochemical processes of redox-sensitive major and trace elements, inclusive of Fe, S and As. However, few investigations have focused on evaluating the mobility of As and the impacts *S. alterniflora* invasion on As dynamics in salt marsh sediments of the Yangtze River estuary.

The motivation of this study was to: (1) examine the aqueous and solid phases of As in sediment of the different

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rhizospheres, and (2) evaluate the influence of temperature, tide and plants, especially the effects of *S. alterniflora* on the dynamics of As in salt marsh sediments.

1 Materials and methods

1.1 Sample collection and preparation

The study area is located on the eastern coast of Chongming Island and is the largest intertidal zone of the Yangtze River estuary, comprising of three zones from land to sea with the sequence of high marsh, low marsh and bare flat. Surface water was collected in the tidal creeks when ebbing occurred at high marsh (A1, B1), low marsh (A2, B2) and the front of low salt marsh (B3) from the study area (Fig. 1). Using pore water diffusion equilibrators (peepers) as described by Koretsky et al. (2006), pore water was collected at site A2. Peepers were inserted into the sediments from the sediment-water interface to a depth of 40 cm and left to equilibrate with the surrounding sediment pore water for 3 (from 17 October to 27 December 2009) and 8 months (from 28 December 2009 to 5 August 2010).

One core (ca. 40 cm) was sampled with PVC pipe at each of the five sites (Fig. 1) in December 2009 and August 2010, respectively. The sediment profile was logged during the sampling in August 2010. Litter and dark sediment were found at the upper layers (0–5 cm), and few roots were found at deeper layers in the rhizosphere of *P. australis*. Dark or olive-brown sediment and fine roots were apparent at a depth of 18 cm or deeper in the rhizospheres of both *S. alterniflora* and *S. mariquete*. The root network of *S. alterniflora* was denser compared to *S. mariquete*.

All cores were plugged and sealed with tape in the field and taken to the lab on the same day. In the lab, under ambient atmospheric conditions, the intervals of 0–1 cm, 1–2 cm, 2–4 cm, 4–6 cm slices for the first 6 cm and then 3 cm slices for the rest of the core were sectioned in each case at the earliest opportunity after extraction. Each section was immediately placed into a plastic bag, which has as much air squeezed out as possible before sealing and then stored in a bag filled with nitrogen at 4°C until analysis. After the acid volatile sulfate (AVS) analysis, the sediment samples were dried in freeze dryer (Freeze Dryer

Alpha 1–4 Ld Martin Christ Gefriertrocknungsanlagen GmbH, Germany). Prior to analysis, the dried samples were ground to a powder with an agate mortar and sieved through 63-μm nylon mesh to remove sand and roots.

1.2 Microcosm experiments

The redox conditions are changeable with season in salt marsh sediments, causing by periodic desiccation, tidal flooding, seasonal growth cycling of salt marsh plants and the other factors (Koretsky et al., 2006, 2008a, 2008b). To validate our field observations and examine As mobility and transformation that occurred during changing redox conditions, the microcosm experiments were conducted.

For the microcosm experiments, 2 kg of wet sediment was sampled from the sediment-water interface surface. The sediment was air-dried, passed through a 63-μm nylon sieve and mixed to homogeneity. A series of independent microcosm incubation experiments were conducted at (27 ± 2)°C. The sediment was submerged with Milli-Q water and incubated for 1–50 days in the dark. There were two different conditions. In the first batch, unsealed conditions (US), 3.00 g sieved sediment and 20 mL Milli-Q water, which was degassed using N_2 for 3 hr, were put into 30-mL plastic centrifuge tubes and then shaken gently to achieve homogenization. The resulting microcosm was kept in contact with the atmosphere. The second batch, sealed conditions (SO), was similar to the first batch, with the difference being that the external carbon source (0.1 g powder of *S. alterniflora* aboveground tissues) was added to the sediment, and the tubes were sealed to increase anoxic conditions. The blank samples were prepared along with the microcosm samples. Each microcosm sample was performed in triplicate. The incubation samples were harvested at time intervals of 1, 3, 5, 10, 15, 20, 30 and 50 days. The results are given as the mean ± standard deviation.

1.3 Chemical analysis

Surface water temperature, pH and electric conductivity were measured in the field. Pore water samples were extracted by glass syringe at intervals of 3 cm in the field as soon as possible and used for testing pH. Prior to tube centrifuged, the pH and dissolved oxygen in solution of
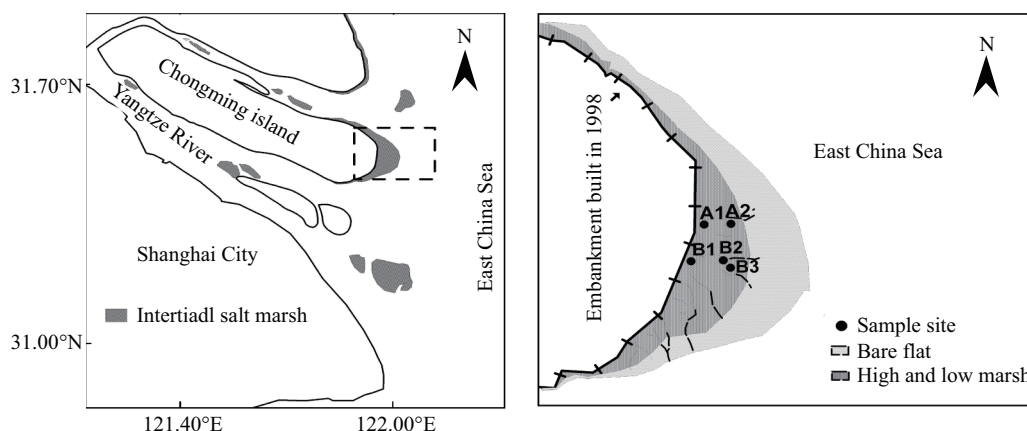
Fig. 1 The Yangtze River estuary and study area. The sampling site A1 and B1 are located in the monocultures of *Phragmites australis* in the high marsh; site A2 and B2 are in the monocultures of *Spartina alterniflora*, and site B3 is in the monocultures of *Scirpus mariqueter* in the low marsh.

incubated sediments were measured by inserting electrode probes into the tubes under N_2 conditions. The tubes were centrifuged at 4200 r/min for 15 min, and the aqueous samples were extracted by glass syringes. Under ambient atmospheric, each aqueous samples was then filtered a 0.45-μm cellulose acetate membrane and preserved (pH < 2) in a glass bottle using nitric acid.

Soluble and exchangeable sulfate in sediments were targeted by Milli-Q water extraction, shaking suspensions for 1 hr, then centrifuged and determined by turbidimetric method (Kolmert et al., 2000). The sodium acetate extraction (1 mol/L) at pH 5 was applied to freeze-dried samples and incubated-sediment paste to target specifically adsorbed cations as well as carbonates and other minerals these are labile at pH 5 (Poulton and Canfield, 2005).

The procedures for AVS analysis, including those conducted on the fresh wet sediments and incubated-sediment paste, were adopted from the method described by Lin et al. (1997) and Lee et al. (2000). Briefly, the sample (ca. 2 g) was added to the reaction flask and sparged for another 2 min with N_2 (100 cm^3/min). The sulfide in sediments was liberated by extraction with 1 mol/L HCl for 40 min at room temperature and then trapped in a 0.2 mol/L $Zn(CH_3COO)_2$ and 0.1 mol/L CH_3COONa solution with a continuous N_2 flow to form ZnS. Each trap was quantified using the Methylene Blue method, with an estimated detection limit of 0.02 μmol/g dry weight. The analytical precision was within 20%. The recovery of S(II) was 97% ± 6% (n = 3), which was validated using $Na_2S\cdot9H_2O$. Total As in sediments was digested by HNO_3: HF: $HClO_4$ ($V/V/V$, 2:3:1) at 180°C for 4 hr. All the suspension solution was centrifuged at 4200 r/min for 15 min and then was filtered through a 0.45-μm cellulose acetate membrane.

The concentrations of the dissolved and the simultaneously extracted Fe and Mn were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian 710-ES, ICP-OES, Agilent, USA). The acetate-extractable Fe were analyzed by atomic absorption spectrometry (AAS, AAnalyst-800, PerkinElmer, USA), due to matrix interferences on the ICP-OES. Total Fe

and Mn in sediments and selected reference materials (GSD-9, China Stream Sediment Reference Material) were analyzed by X-ray fluorescence spectrometry (XRF 1800, Shimadzu, Japan). The metal recoveries ranged from 90% to 110% compared with the certified values and the analytical precision was within 15%. The concentrations of As, which included the dissolved As in pore water and the incubated solution, total As and acetate-extractable As in sediments, were measured by hydride generation atomic fluorescence spectrometry (AFS-9230, Beijing Titan, China), with a detection limit of 0.02 μg/L. The analytical precision of these measurements was always less than 10%. Total organic carbon was determined by titration with $FeSO_4$ after digestion with a $K_2Cr_2O_7$-H_2SO_4 solution at 175°C. Water content was determined by drying the samples at 105°C for 12 hr. The grain size distribution was assessed by laser diffraction particle size analyzer (LS13320, Beckman Coulter, USA) after removal of organic matter and carbonates. Statistical analysis was performed with the SPSS 11.5.

## 2 Results

2.1 Characteristics of samples

The characteristics of samples are provided in Table 1. The surface water pH (7.2–8.2) was slightly alkaline, but the pore water pH was near neutral (Fig. 2). The temperature increased from 9.0 to 29.7°C. Surface water electric conductivity during winter was higher than that during summer. The concentrations of total dissolved As in surface water ranged from 0.03 to 0.06 μmol/L and were less than European Union drinking-water standard 0.13 μmol/L. The grain-size analysis revealed that the predominant size of sediment is 4–63 μm (slit). The fraction of medium slit (< 16 μm) was generally 50% and correlated with total As, Fe and total organic carbon. Total organic carbon concentrations ranged from 0.6% to 1.0%, with a mean value of 0.8% ± 0.2% (n = 123) and varied slightly for different sites. The decreasing order of the mean concentrations of total organic carbon in the rhizosphere sediemts was *S. alterniflora* > *P. australis* > *S.*

Table 1   Characteristics of the surface water and the rhizosphere sediments in salt marsh of Dongtan wetland

Sampling site	Date (mm/yyyy)	Surface water				Sediment			
		Temp. (°C)	EC (μS/cm)	As (μmol/L)		GZ* (< 16 μm) (%)	WC* (%)	TOC* (%)	As* (μmol/g)
P. australis									
A1	12/2009	9.0	16.1	0.06	n = 11	58.5 ± 8.5	31.5 ± 6.1	1.0 ± 0.2	0.17 ± 0.03
A1	08/2010	28.5	15.1	0.03	n = 11	64.7 ± 5.9	34.7 ± 2.9	0.8 ± 0.2	0.20 ± 0.03
B1	12/2009	10.0	21.3	0.05	n = 12	38.2 ± 4.4	27.2 ± 3.1	0.7 ± 0.1	0.15 ± 0.02
B1	08/2010	28.2	8.2	0.03	n = 12	51.1 ± 5.1	30.5 ± 1.1	0.7 ± 0.1	0.18 ± 0.02
S. alterniflora									
A2	12/2009	10.2	29.6	0.03	n = 13	39.5 ± 5.7	51.5 ± 10.4	0.9 ± 0.1	0.17 ± 0.03
A2	08/2010	28.9	17.9	0.03	n = 13	34.3 ± 5.3	46.9 ± 12.8	0.7 ± 0.2	0.16 ± 0.03
B2	12/2009	10.0	28.5	0.04	n = 13	34.4 ± 5.0	52.4 ± 12.2	0.9 ± 0.2	0.18 ± 0.03
B2	08/2010	28.3	8.6	0.06	n = 13	32.0 ± 3.4	51.7 ± 12.0	0.7 ± 0.2	0.16 ± 0.02
S. mariqueter									
B3	12/2009	10.0	28.5	0.04	n = 12	33.3 ± 3.9	50.9 ± 6.6	0.8 ± 0.1	0.16 ± 0.02
B3	08/2010	29.7	11.5	0.03	n = 13	29.9 ± 3.1	46.5 ± 13.3	0.6 ± 0.2	0.15 ± 0.03

EC: electric conductivity, temperature compensated conductivity at 25°C; GZ: grain size; WC: water content.
* Data are expressed as mean ± standard deviation.
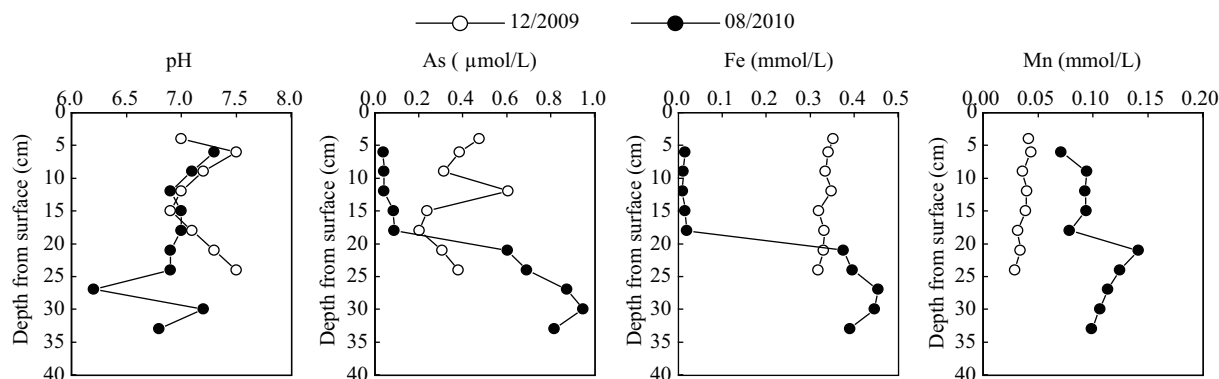
Fig. 2 Depth profiles of the dissolved Fe, Mn and As were obtained by pore water in the rhizosphere sediments of *S. alterniflora* (site A2) in December 2009 and August 2010.

mariqueter. Total As concentrations in sediments ranged from 0.15–0.20 μmol/g, with a mean value of (0.17 ± 0.03) μmol/g ($n = 123$). The concentrations of Fe, Mn and As for incubated sediments were (727 ± 14) μmol/g, (17.8 ± 0.4) μmol/g and (0.20 ± 0.01) μmol/g ($n = 3$), respectively. The concentration of soluble and exchangeable sulfate was (6.6 ± 0.4) μmol/g.

2.2 Depth profiles of pore water

Pore water profiles of dissolved Fe, Mn and As were considerably more variable between August 2010, and December 2009 (Fig. 2). Dissolved Mn concentrations were significantly higher in August, 2010 than in December, 2009, with a peak at a depth of 21 cm. Dissolved As and Fe concentrations ranged from 0.04 to 0.95 μmol/L and 0.01 to 0.46 mmol/L, respectively, and had a similar distribution profile, particularly in August, 2010. Moreover, it is worth noticing that dissolved Fe (< 0.02 mmol/L) and As (< 0.1 μmol/L) were significantly lower from the surface to a depth of 24 cm and then increased sharply in August 2010, demonstrating that an obvious change in redox gradient forming with depth in the rhizosphere of *S. alterniflora*.

2.3 Depth profiles of selective extraction results

2.3.1 Acid volatile sulfide profiles

As a result of oxidation, there was a loss of the AVS in sediment samples when we sectioned the samples and stored them before analysis. Although we obtained a fresh sample from the inside of sediment section when the AVS was analyzed and finished all of the sample analysis were within two weeks, the concentrations of the AVS in sediments were under-estimated; thus, the AVS results must be interpreted semi-quantitatively. As for AVS profiles, there were considerable variations between August, 2010 and December, 2009 at all sites (Fig. 3). In the upper layers of cores (ca. 6 cm) of the *P. australis* rhizosphere, AVS concentrations were significantly higher than those of lower depths, exhibiting a markedly decreasing trend with depth, with the exception of profile B1 in August (Fig. 3a and b). However, in the rhizospheres of both *S. alterniflora* and *S. mariquete*, there was a notable increase in AVS concentrations with depth until a depth of 15 cm or deeper, blow which the AVS decreased (Fig. 3c–e). Note that AVS concentrations in August, 2010 were commonly

higher than that in December, 2009 at all sites, particularly in the rhizosphere of *S. alterniflora* (Fig. 3d).

2.3.2 Arsenic fractions in sediments

The acetate-extractable fraction of Fe and As spanned a larger range with depth, with values ranging from 0.03 to 0.99 μmol/g and 0.02×10^{-2} to 0.42×10^{-2} μmol/g, respectively. There were significantly seasonal and spatial variations for acetate-extractable Fe and As profiles at all sites. Moreover, the profiles were consistent with redox conditions in most of the cores (Fig. 3). For example, an increase trend of the solid fractions of Fe and As clearly coincided with the AVS increase with depth at sites B2 (Fig. 3d) and B3 (Fig. 3e) in August, 2010, suggesting that the acetate-extractable Fe and As concentrations in sediments would increase with anoxic conditions enhanced in the rhizospheres of *S. alterniflora* and *S. mariquete.*

2.4 Dynamics of redox transformations in microcosm incubation experiments

2.4.1 Aqueous dynamics

The changing redox conditions were monitored in aqueous during microcosm incubation. The pH decreased within 3 days and then increased slightly, with the pH remaining constant at 8 and 7 after 20 days in the batch of the US and SO (Fig. 4a). The dissolved oxygen rapidly decreased within 3 days and then gradually increased, particularly a more rapid increase was observed between 3 and 10 days in the batch of the US. However, the dissolved oxygen remained low in the batch of the SO because of isolation and the degradation of the external organic carbon source (Fig. 4b). The increase in dissolved oxygen in the batch of the SO after 30 days indicates that the tube was not fully sealed, which allowed oxygen to permeate into the incubated solution.

In the batch of the SO, the concentrations of dissolved Mn and Fe sharply increased and reached their maximum at the concentrations of 0.24 and 0.49 mmol/L in solution at day 15, respectively, then decreased gradually during incubation (Fig. 4e and g). Following with the initial increase in dissolved Fe and Mn, a rapid increase in dissolved As in solution was observed, with the highest concentration of 0.79 μmol/L occurring at day 10 (Fig. 4i). The sulfate was consumed within 10 days, correlating to
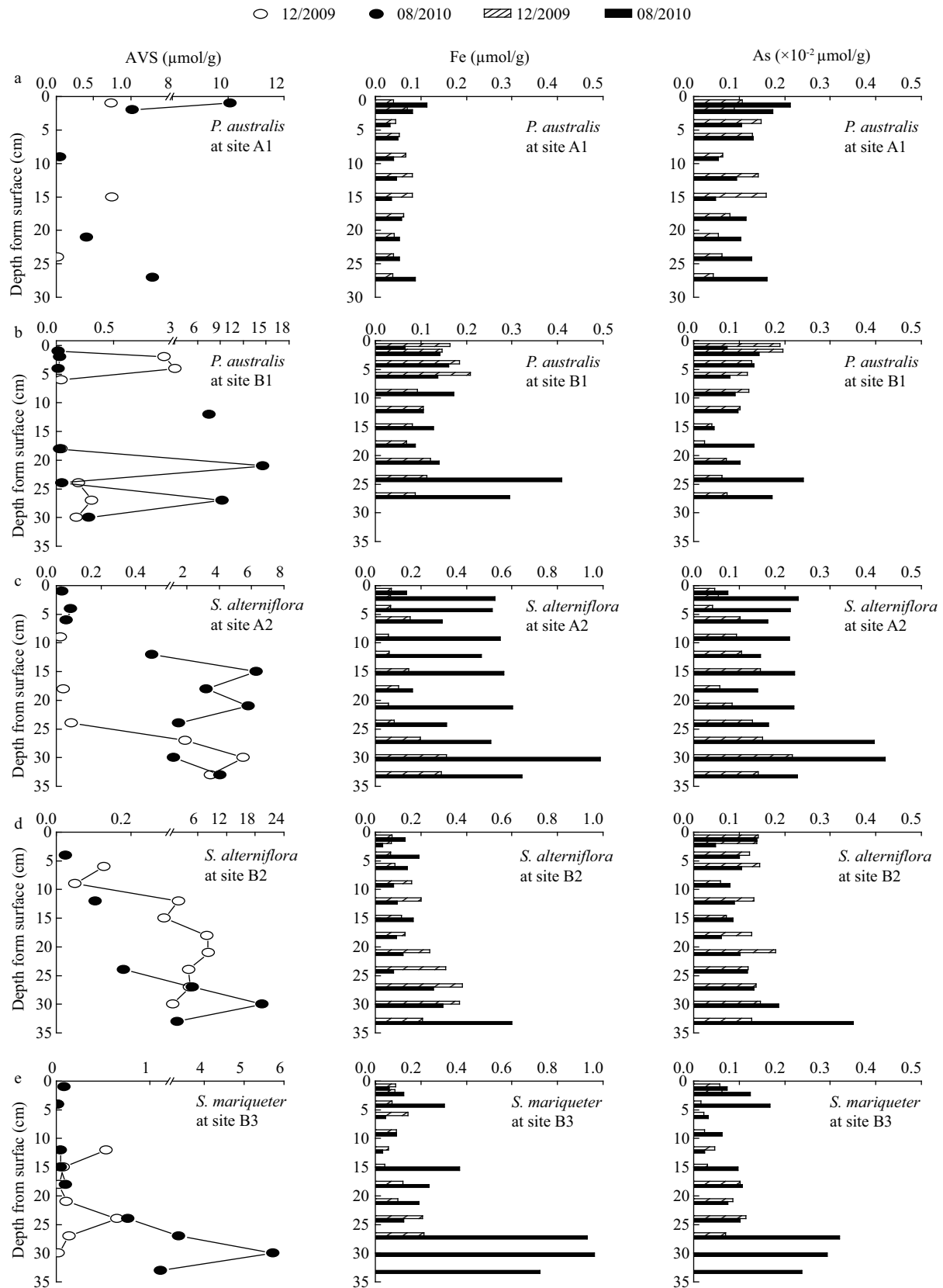
Fig. 3 Distribution profiles of the acid volatile sulfide (AVS) and sodium acetate extractable As and Fe in the different rhizosphere sediments in salt marsh throughout the period of investigation.

the increase of AVS in the incubated sediment (Fig. 4c and d). Similarly, in the batch of the US, dissolved Fe, Mn and As increased within 10 days, but were lower concentration, then were removed from solution gradually.

Sulfate decreased slightly within 10 days, but it slightly increased after 20 days (Fig. 4c), indicating the anoxic condition of the incubated sediment could be significantly impacted by the oxygen.
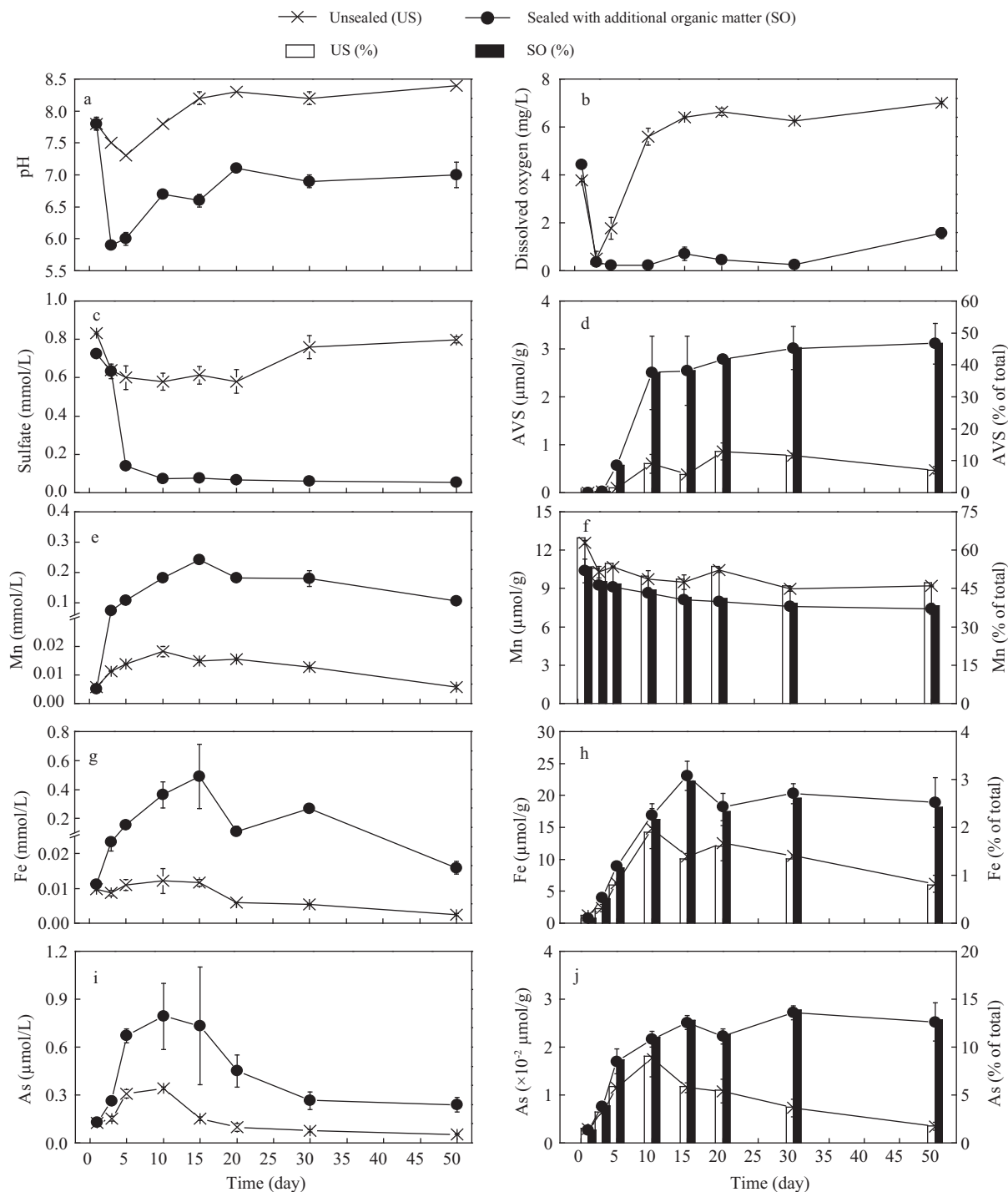
Fig. 4 Aqueous and solid dynamics of Fe, Mn, As and sulfate during sediment incubation in the batch of unsealed (US) and sealed with additional organic matter (SO). (a) aqueous pH; (b) dissolved oxygen; (c) sulfate; (d) sediment AVS; (e) dissolved Mn; (f) acetate-extractable Mn; (g) dissolved Fe; (h) acetate-extractable Fe; (i) dissolved As; (j) acetate-extractable As. Error bars represent one standard deviation of the triplicate samples.

2.4.2 Solid phase dynamics

In the batch of the SO, the concentrations of acetate-extractable Fe and As sharply increased within 15 days, then slightly decreased, and then remained relatively constant at the concentrations of 20 μmol/g and 2.5×10^{-2} μmol/g, respectively (Fig. 4h and j). Following the accumulation of dissolved As and Fe in solution, the acetate-extractable Fe and As in sediment increased from 0.1% to 3.0% of the total Fe and from 1.3% to 13% of the total As within 15 days, suggesting that a large amount of dissolved Fe and As are sequestered into

sediments with the increase of the anoxic conditions. AVS concentrations rapidly increased within 10 days, and then slightly increased, with the concentration increasing by 3 μmol/g during incubation (Fig. 4d). Similarly, in the batch of the US, the AVS and the acetate-extractable Fe and As in sediment increased within 10 days, then gradually decreased, due to the anoxic conditions in the incubated sediment could be significantly impacted by the oxygen during incubation. Acetate-extractable Mn rapidly decreased within 15 days and then remained constant in both two ways of incubation (Fig. 4f), indicating that most

of reductive dissolution Mn was released to solution.

3 Discussion

3.1 Arsenic mobilization during sediment reduction

Differences of the depth-integrated As mean concentrations in different sampling sites were tested using one-way ANOVA ($\alpha = 0.05$). There is no significant difference of As mean concentrations in the different rhizosphere sediments, suggesting that the impacts of plants upon the total As could be limited. However, there is a positive relationship between the fraction of medium slit (< 16 μm) and total As concentrations in sediments, suggesting that the differences of As concentrations in the different rhizosphere sediments could be significantly influenced by the quantity of the fraction of medium slit, which agrees with previous findings that trace elements often partition with fine-grained sediments (Zhang et al., 2009).

The dissolved As in pore water were significantly higher than that in surface water (Table 1, Fig. 2) and the profiles of dissolved As and Fe were of the similar distribution pattern with profiles of AVS (Figs. 2 and 3), indicating that As and Fe become mobilizing during soil reduction, especially when anoxic conditions are enhanced with depth. A positive correlation was found between dissolved Fe and As ($r = 0.68$, in December 2009; $r = 0.99$; in August 2010, $p < 0.05$) in pore water, which agrees with previous findings (Weber et al., 2010).

In the microcosm incubation experiments, the positive correlations can not be found between the dissolved Fe, Mn and As in the batch of the US during initial 10 days. However, between the dissolved Fe and As displayed positive correlation in the batch of the SO during initial 15 days ($r = 0.86$, $p < 0.05$), and the similar relationship were also found between dissolved As and Mn ($r = 0.88$, $p < 0.05$). This also demonstrates that As becomes mobilizing during sediment reduction with the development of anoxic condition.

These results could possibly be explained by the combined effects of (1) increased bulk-soil Fe (hydr)oxides dissolution, (2) the transformation of the amorphous of Fe to more crystalline phases, which potentially leads to a loss of sorption sites and promotes the sorbed As releasing into solution (Smedley and Kinniburgh, 2002; Dixit and Hering, 2003; Tufano, et al., 2008) and (3) the bacterial reduction of As(V) to As(III), which preferentially releases As into pore water because arsenite is less strongly sorbed than arsenate at acidic to near-neutral pH conditions (Dixit and Hering, 2003; Weber et al., 2010). However, we can not determine dissolved As(III) in pore water, and the transformation of As(V) to As(III) requires further investigation.

Sulfate reduction was consistent with the depth-dependent redox conditions in the rhizospheres of both *S. alterniflora* and *S. mariquete*, but not in the rhizospheres of *P. australis* (Fig. 3). This result could possibly be explained by the fact that a significant quantity of the labile organic matter produced by both *S. mariquete* and *S. alterniflora*

exits with the deeper horizon sediments, while much litter produced by *P. australis* exits with the surface sediments of the rhizosphere, and then organic matter decomposition promotes bacterial sulfate reduction. Obviously, the concentrations of AVS in August 2010 were commonly higher than that in December, 2009 (Fig. 3), indicating that anoxic conditions are enhanced during summer, which could be a result of the fact that plants growth can produce much labile and reactive organic material by roots and bacterial activities commonly reach their maximum activity during summer (ca. 25°C). Thus, organic decomposed by soil bacteria in the rhizospheres enhances sediment to become more anoxic, causing the release of more As into pore water in August, 2010 than in December, 2009.

Furthermore, during the warm months, the accumulation of AVS in sediment suggests more sulfate is reduced in the rhizosphere of *S. alterniflora* compared to the native plants *P. australis* and *S. mariquete*, which is likely the result of more labile organic matter being released by roots during the growing seasons, despite O_2 were released from roots simultaneously. Several studies have reported that the increased sulfate reduction rates occurred in the root zone of *S. alterniflora* (Hines et al., 1999; Kostka et al., 2002). Nie et al. (2009) has found that the higher richness and abundance of SRB (sulfate-reducing bacteria) occurred in the rhizosphere of *S. alterniflora* during late growing season. They postulated that this was due to enhanced availability of labile organic carbon during the period of *S. alterniflora* growth. In summary, we suggest that the mobility and transformation of As in the rhizosphere sediments of salt marsh would be enhanced during summer and autumn, particularly in the rhizosphere of *S. alterniflora*.

3.2 Arsenic sequestrated into sediments

In the microcosm experiments, reductive dissolution of Fe(III) and Mn(IV, III) (hydr)oxides resulted in the mobilization of Fe and Mn. Meanwhile, As was released into solution. However, only small fractions of As was released to solution, while most of As remained in sediment. For example, dissolved As increased by 6.1 times in solution within 10 days. However, following the accumulation of dissolved As in aqueous, the acetate-extractable As in the incubated sediment increased by 8.5 times in the batch of the SO (Fig. 4j).

The acetate-extractable Fe and As had a positive correlation during incubation in the batch of the SO ($r = 0.97$, $p < 0.01$) and the US ($r = 0.79$, $p < 0.05$). In our field results, acetate-extractable Fe and As displayed a positive correlation ($r = 0.79$, $p < 0.01$) and were in similar distribution pattern with the AVS in the sediments (Fig. 3). This is possible that the bacterial reductive dissolution of Fe(III) (hydr)oxides produces large quantities of Fe(II) that promotes siderite, green rust and magnetite formation (Kukkadapu et al., 2004; Weber et al., 2010). These secondary mineral phases often immobilize As(III) and As(V) by inner-sphere adsorption (Jönsson et al., 2008; Wang et al., 2010). Note that the acetate-extractable Fe and As in the incubated sediment paste were large higher than that in the freezing-dried sample. Perhaps secondary

iron mineral phases, such as Fe carbonates and green rust, exposed to the air may recrystallize to Fe (hydr)oxides during freeze dried (Hjorth, 2004; Christiansen et al., 2009), resulting in under-estimates the concentrations of the acetate-extractable Fe and As.

In the dissimilatory of iron reduction processes which is simultaneous with sulfate reduction, the sulfide is produced by bacteria, which can reduce As(V) to As(III) (Rochette et al., 2000; Saalfield and Bostick, 2009) and precipitate As(III) in sulfide phases (Bostick et al., 2004; O'Day et al., 2004), thus promoting the dissolved As sequestrated within anoxic environments. However, the result of the HCl-extractable Fe indicates that there is a large amount of reactive Fe (42.3–193.5 μmol/g extracted by 1 mol/L HCl) in the sediments, which may prevent the formation of As-sulfides (Saalfield and Bostick, 2009; Kocar et al., 2010). The remained Fe (hydr)oxides could also increase As retention in the sediments (O'Day et al., 2004; Saalfield and Bostick, 2009).

The lower concentrations of the dissolved As and Fe from surface to a depth of 24 cm in the rhizosphere of *S. alterniflora* (Fig. 2) in August 2010 were observed, which consistents with the brownish-yellow color precipitation on the peepers and low water contents in sediments. This is likely the result of the semi-diurnal tide irregularly floods the low marsh and bare flat twice per day in study area. Although tidal flooding can temporarily limit O_2 diffusion into the sediments, physical disturbances could arise from tidal flow and transport oxygen to sediments, causing oxic conditions in sediment-water interface. Thus, the dissolved Fe(II) and Mn(II) were oxidized by the abiotical or biogeochemical oxidation processes driven by oxygen (Rose and Waite, 2002; Santana-Casiano et al., 2005) and were formed amorphous or crystal Fe and Mn (hydr)oxides. The dissolved As will be captured by the (hydr)oxides of Fe and Mn when it diffuses into oxide layers or the oxygenated surface water permeates to deeper sediment layers.

4 Conclusions

The sulfate reduction showed a significantly seasonal variation, indicating that salt marsh sediments experience periodic semi-diurnal tidal flooding and seasonal changes of plants growth, thus causing sediments to become periodically oxic or anoxic. Under oxic conditions, As in sediments is removed from solution by adsorption to or coprecipitation with Fe(III) (hydr)oxides. When subsurface conditions change from oxidized to progressively more anoxic conditions, the reduction of reactive Fe (hydr)oxides could promote the mobility of As, leading to dissolved As increase drastically in pore water. However, abundant of dissolved As in anoxic conditions could be re-adsorbed onto or incorporated with secondary iron mineral phases. More sulfate was reduced and more dissolved As was released to pore water in depth of the rhizosphere of *S. alterniflora* in August 2010, suggesting that anoxic conditions are enhanced by *S. alterniflora* and more As could be released into surface water. Generally, the

dynamics of As mobility and transformation could be iron-controlled, which could be significantly influenced by the rapid spread of alien invasive plant *S. alterniflora* in salt marsh sediments of Dongtan wetland.

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