1 Reactivity and Speciation of Mineral-Associated Arsenic in
2 Seasonal and Permanent Wetlands of the Mekong Delta

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Abstract

Millions of people in the deltaic regions of S/SE Asia regularly consume As contaminated groundwater. Arsenic persists within these groundwaters despite being flushed by several pore volumes of recharge, indicative of an in-situ solid phase source. Despite the importance of this solid phase source, the identity and reactivity of the minerals hosting and releasing As in the deltaic aquifers remain poorly constrained. Here we seek to define the chemistry and reactivity of As and its host minerals in aquifer sediments recharged by both seasonally saturated and permanent wetlands on the Mekong Delta of Cambodia.

Sediment cores were retrieved to depths of up to 30 m. Selective extractions on near-surface sediments (to depths of 4 – 6 m) indicate that more than a third (27-50%) of the Fe in the profile is “reducible” (citrate-bicarbonate-dithionite-extractable) – nominally consisting of Fe(III) oxides. The Fe(III) oxide fraction was approximately the same under seasonal wetlands (mean = 39%) compared with sediments from beneath permanent wetlands (mean = 37%). Correspondingly, Fe K-edge extended X-ray absorption fine structure (EXAFS) spectra analysis indicates that the Fe mineral phases are predominantly goethite and hematite (30-50%).

Analysis of solid phase As speciation by X-ray absorption near edge structure (XANES) spectroscopy showed arsenate in the shallowest sediments (upper 1 and 4 m of seasonal and permanent wetlands), and arsenite and/or As sulfides as the dominant phases in the deeper sediments. The reducible As fraction ranged from 17 – 42 % of the total As at both sites. The exception was found in a peat layer at 6 m beneath the seasonal wetland, in which only 1% of the total As was reducible.

Arsenian pyrite was the predominant form of As in the peat. Thus, a pool of As hosted by reducible mineral phases persists in sediments below both the seasonal and permanently saturated wetland sites.

1. INTRODUCTION

Humans with exposure to As *in utero* and/or during early childhood through drinking water exhibit increased mortality from cancer and chronic renal disease, as well as greater risk for several chronic respiratory symptoms (Dauphine et al., 2011; Smith et al., 2012; Smith et al., 2013). Further, As exposure through drinking water can be more detrimental to lung function than smoking (von Ehrenstein et al., 2005). Prolonged As exposure from drinking water also increases mortality from cardiovascular disease, especially among smokers (Argos et al., 2010; Chen et al., 2011). The most significant large-scale human exposure to As occurs in the basins of major rivers draining the Himalaya including the Indus (Fatmi et al., 2013), Ganges-Brahmaputra-Meghna (Chakraborti et al., 2013), Mekong (Berg et al., 2007; Buschmann et al., 2008; Phan et al., 2010), Red (Berg et al., 2007), Yangtze (Currell et al., 2011; Gan et al., 2014; He and Charlet, 2013), and Yellow (He and Charlet, 2013; Wang et al., 2012; Zhang et al., 2012), where over 100 million people are estimated to consume drinking water containing $> 10 \mu\text{g As L}^{-1}$ (the World Health Organization standard) (Ravenscroft et al., 2009).

The predominant mechanism by which As from basin sediments transfers to groundwater occurs under anaerobic conditions, in which microorganisms couple the oxidation of organic C to the dissimilatory reductive dissolution of As-bearing Fe

oxides, hydroxides, and oxyhydroxides (hereafter referred collectively as Fe(III) oxides) (Akai et al., 2004; Islam et al., 2004; McArthur et al., 2001; Nickson et al., 1998; Nickson et al., 2000; Van Geen et al., 2004). A mechanistic understanding of As-bearing Fe(III) oxide reductive dissolution impacts on As release to porewater is derived principally from model systems (Campbell et al., 2006; Coker et al., 2006; Cummings et al., 1999; Tufano et al., 2008). Arsenic(V) reduction precedes Fe(III) reduction for ferrihydrite on a thermodynamic basis, while the chemical gradients determine the preference for goethite or hematite (Kocar and Fendorf, 2009); in any case, As and Fe reduction increase the lability of As surface complexes (Herbel and Fendorf, 2006; Kocar et al., 2006; Tufano and Fendorf, 2008; Tufano et al., 2008). Further, Fe(III) oxides will undergo reductive dissolution under anaerobic conditions (Tufano and Fendorf, 2008), leading to As desorption.

Arsenic speciation and Fe/Mn mineralogy are critical factors determining As partitioning and therefore susceptibility to aqueous transport. In oxidizing aquifer sediments, As(V) adsorbs more strongly than As(III), and Mn oxides may oxidize As(III) to As(V), leading to increased As retention (Stollenwerk et al., 2007). Further, competing ligands, such as $\text{H}_x\text{PO}_4^{3-x}$ and HCO_3^- , have differing impacts on As adsorption (Stollenwerk et al., 2007). Under reducing conditions, As can be removed from solution through precipitation or incorporation of As(Fe) sulfides (Bostick et al., 2004; Lowers et al., 2007; O'Day et al., 2004). Arsenic(V) and As(III) both adsorb extensively on Fe(III) oxides under circumneutral pH conditions (Dixit and Hering, 2003); however, As(III) (as H_3AsO_3) complexes are more labile and subject to desorption upon shifting geochemical conditions, inclusive of changes in

equilibrium induced by advective flow (Tufano and Fendorf, 2008). Additionally, As(V) is retained more appreciably than As(III) on silicate minerals, such as chlorite and halloysite (Lin and Puls, 2000). Arsenic(V) can also substitute for SiO_4^{4-} within silicate minerals; biotite has, in fact, been implicated as a host of As in Bengal Basin sediments (Seddique et al., 2008).

Linking As reactivity and speciation to the identity, relative quantity, and reactivity of Fe-bearing minerals in the river basins of South and Southeast Asia is needed to understand the distribution and transport of As. Moreover, efforts to this end have concentrated in the Bengal Basin (Akai et al., 2004; Datta et al., 2009; Ghosh et al., 2006; Hasan et al., 2009; Itai et al., 2010; Polizzotto et al., 2006; Polizzotto et al., 2005; Seddique et al., 2008; Seddique et al., 2011; Swartz et al., 2004; Uddin et al., 2011), and to a lesser extent in the Red River Delta (Vietnam) (Phuong et al., 2012; Postma et al., 2010; Postma et al., 2007) and Datong Basin (China) (Xie et al., 2009a; Xie et al., 2009b; Xie et al., 2011; Xie et al., 2008). Little is known about mineralogical aspects of the Mekong Delta influencing dissolved As concentrations (Kocar et al., 2008; Rowland et al., 2008). In these complex systems, Fe mineralogy may vary with depth and redox conditions (Datta et al., 2009; Polizzotto et al., 2006; Uddin et al., 2011). Further, Fe(III) oxides are commonly recognized as predominant hosts of As in the sediments, although they are rarely identified with certainty (Hasan et al., 2009; Postma et al., 2010; Uddin et al., 2011; Xie et al., 2008), and their importance relative to other potential host minerals for As as a function of depth in sedimentary profiles is unclear (Akai et al., 2004; Polizzotto et al., 2006; Seddique et al., 2008; Seddique et al., 2011; Swartz et al.,

2004). Moreover, extensive groundwater pumping perturbs groundwater flow paths in places like the Bengal Basin, complicating the determination of spatial variations in the controls of As partitioning between solid and aqueous phases. Therefore, the controls of Fe mineralogy on As reactivity in sedimentary profiles of river basins in South and Southeast Asia are confounded and poorly constrained.

Accordingly, here we seek to quantify the mineralogical hosts of As and assess their reactivity – using specific extractants – along groundwater recharge pathways. Our field area in the Mekong Delta is relatively free of groundwater pumping (Lawson et al., 2013), and benefits from a previously defined coupled biogeochemical-hydrologic assessment (Benner et al., 2008; Kocar et al., 2014; Kocar et al., 2008; Polizzotto et al., 2008b), revealing a steady-state system in which the annual mass of As input (via sediment deposition) to interior wetlands is roughly in balance with the mass of As discharged to the Mekong River (through aqueous transport) (Polizzotto et al., 2008a). Arsenic is released in the near-surface clays/silts (Kocar et al., 2008), and is transported downward to the sandy aquifer, where net annual groundwater flow is horizontal toward the river (Benner et al., 2008). The near-surface clays/silts exhibit differential release of As depending on flood duration (Kocar et al., 2008; Polizzotto et al., 2008a). Therefore, the reactivity and speciation of As and the associated host phases are of prime importance in the near surface. Our field area with a defined flow regime and As mass balance provides the ideal system to (1) track As speciation and reactivity as a function depth (along the recharge flow path), (2) define the mineralogy and reactivity of As host phases, and (3) thereby explain As retention and potential for release along the

flow path in both seasonal and permanent wetlands. Moreover, due to similarities in topography, hydraulic gradients, and geologic deposition, our results from the Mekong Delta may be applicable to other major river deltas systems of South and Southeast Asia (Berg et al., 2007; Lawson et al., 2013; Polizzotto et al., 2008a).

2. MATERIALS AND METHODS

2.1. Field area

The field area we examined is *ca.* 50 km² of the upper Mekong Delta in Kandal Province, Cambodia, and is bracketed by the Mekong and Bassac rivers (Lat. 11 31 3.90N, Long. 105 0 41.77E) (Polizzotto et al., 2008b). Elevated levees along the riverbanks give way to native wetlands with a general stratigraphy of approximately 15 m of fine texture material (clays and silts) overlying > 30 m of aquifer-forming sands (Benner et al., 2008). The annual monsoon causes the river stage to breach the levees, resulting in deposition of floodwater and As-bearing sediments into the wetland basin. The fine-over-coarse stratigraphy and fluctuating hydraulic gradient result in a net annual flow velocity of 0.04 – 0.4 m a⁻¹ vertically through the clay-silt aquitard and 1 – 13 m a⁻¹ horizontally through the aquifer sands toward the Mekong River (Benner et al., 2008).

The monsoon-driven flooding of the wetland basin between the Mekong and Bassac rivers is generally seasonal, except in topographically low abandoned river channel (oxbow) wetlands. Permanent flooding in the oxbow wetlands leads to As release (solid to solution transfer) in the surface clay aquitard and subsequent

downward transport to the sandy aquifer where groundwater concentrations reach up to 16 μM (Polizzotto et al., 2008b).

The near-surface clays/silts of the Seasonal Wetland are comprised of alternating brown (natural levee) and gray (floodplain) strata with an organic-rich (5.4 % C) gray-black layer between 5.4 and 5.6 m. A black peat layer (21.5 % C) is present between 6.0 and 6.1 m. The Permanent Wetland, lying in an oxbow of the Mekong river, consists of mottled clays-silts to a depth of 1.3 m overlying gleyed clays-silts, with the exception of a gleyed sandy layer between 2.8 and 3.1 m.

2.2. Well and lysimeter installation and aqueous chemical analysis

Wells were installed by manual rotation of a 3.8 cm diameter pipe with a 10.2 cm cutting auger; water was pumped continuously through the pipe to displace sediment cuttings. Sections of pipe were added to achieve the desired well depth, and 3.2 cm PVC was inserted as well casing. All wells contained 1 m screened intervals. Shallow wells (≤ 8 m) were backfilled with clay, and deep wells (> 12 m) were backfilled with coarse sand and capped with clay. A peristaltic pump (Geotech II, Geotech Environmental Equipment, Inc.) was used to purge each well for 1 h before sampling. Low-yield wells were pumped dry and re-infiltrated water was collected on the following day. Well water was poured into a 60 mL syringe, filtered through a 0.2 μm filter, and collected into a bottle. Alkalinity was determined by titrating the sample with 0.1 M H_2SO_4 to a colorimetric endpoint using a Hach digital titrator and bromocresol green-methyl red indicator (Hach). Samples were acidified

to ~ 2 % v/v with concentrated HNO₃ for elemental analysis by inductively coupled plasma mass spectroscopy (Thermo Scientific XSERIES 2 ICP-MS).

Tension lysimeters (Soilmoisture Equipment Corp., Goleta, CA) were installed in triplicate at depths of 1.1 m and 1.5 m in the Seasonal Wetland. Holes were dug with a hand auger, excavated sediments were saved in a bucket, and lysimeters were installed. Finally, boreholes were backfilled and sealed with the original sediments. Pore-water was drawn by suction (-800 mBar) into bottles and was acidified to ~ 2% v/v with concentrated HNO₃ for elemental analysis by ICP-MS. Alkalinity was measured on unacidified samples as described for well water analysis.

2.3. Sediment collection

An excavator was used to dig to a depth of 6.5 m in the Seasonal Wetland and 4 m in the Permanent Wetland. Aluminum cores (3 cm diameter, 5 cm length) were pounded into a fresh sediment face, immediately sealed with melted wax, vacuum sealed in a bag containing an anaerobic pouch (Mitsubishi Gas Chemical America, Inc.), placed on ice in the field and stored at 4 °C in the dark. At least two sediment cores were retrieved per depth. Deeper sediments (9 – 30 m) were accessed during well installation by manually lowering a stainless steel core sampler (30.5 cm length, 2.2 cm diameter) with a rod inside the 3.8 cm diameter well drilling pipe. Deeper sediments were preserved as described for the shallow sediments. All sediment samples were stored anaerobically at 4 °C in the dark for less than 4 months before being dried under 95%N₂/5%H₂ atmosphere prior to analysis.

2.4. General sediment characterization

Total elemental composition was determined by X-ray fluorescence spectrometry (XRF) (Dittmar et al., 2007). Total C and N was performed using a Carlo-Erba NA 1500 Elemental Analyzer. Synchrotron powder XRD was performed at beam line 11-3 at SSRL with an incident beam energy of 12735 eV. Samples were prepared as described previously (Stuckey et al., 2015). Peak identification was performed using JADE XRD Pattern Processing Ver. 6.5 (Materials Data, Inc., 2002).

2.5. Selective extractions

The sediment cores were extruded, dried under 95%N₂/5%H₂ atmosphere, and homogenized by mortar and pestle. Specific As and Fe pools were quantified in the near-surface sediments (≤ 6 m deep) by parallel (rather than sequential) selective extractions (Kocar et al., 2008): “ligand displaceable” (1 M PO₄²⁻, pH 5.0), “acid reactive” (nominally from dissolution of amorphous Fe/Mn oxides, acid volatile sulfides, and carbonates [1 M HCl]), and “reducible” (nominally from Fe and Mn oxides [citrate-bicarbonate-dithionite – CBD]) (Keon et al., 2001; Loeppert and Inskeep, 1996). Total As was determined by X-ray fluorescence spectrometry.

2.6. Bulk x-ray absorption spectroscopy

Similar to analyses described in Stuckey et al. (2015), bulk As X-ray absorption spectroscopy (XAS) was performed at beam line 11-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). Briefly, energy selection was maintained by a Si (220) monochromator calibrated to 11874.0 eV for the As K-edge of Na₃AsO₄.

Fluorescent X-rays were measured with a multi-element Ge detector. For As K-edge extended X-ray absorption fine structure (EXAFS) spectroscopic analysis, a He-purged cryostat at 25 K was utilized. Arsenic standards were sufficiently diluted in boron nitride to achieve a unit change in absorption across the K-edge. For bulk Fe EXAFS spectroscopy, also performed at beam line 11-2 at SSRL, energy calibration was achieved by assigning a K-edge position of 7111.0 to an Fe foil. Least squares fitting of the Fe EXAFS (χ) function was performed over a k range of 3 to 12 Å⁻¹. The specific Fe standards used for fitting were defined using a combination of electron microprobe analysis coupled with energy dispersive spectroscopy and XRD (Figs. A.1 – A.9).

Iron EXAFS spectra were obtained for the post-CBD extracted sediments, theoretically containing only non-reducible Fe. Least squares fitting of the bulk (pre-CBD extracted) sediments was performed a second time with the inclusion of the post-CBD extracted spectra as a standard component along with the Fe(III) oxide standards. We evaluated percentages of Fe(III) oxides obtained by EXAFS fitting of soil/sediment, EXAFS fitting including the post-CBD “standard,” and CBD. The predominant Fe standards used for least squares fitting of the Fe EXAFS spectra are kaolinite (KGa-2, Source Clay Mineral Repository), ferruginous smectite (SWa-1, Source Clay Mineral Repository), clinocllore (Stanford Mineral Collection), goethite-coated sand (Hansel et al., 2004), and hematite-coated sand (Hansel et al., 2004).

3. RESULTS

3.1 Groundwater pH and alkalinity

Mean pH levels for surface water and groundwater down to 40 m range from 7.0 to 7.5 in the Seasonal Wetland and 6.8 to 7.3 in the Permanent Wetland (Fig. A.10). Mean alkalinity levels generally increase with depth in the near-surface clay/silt layer (4 – 6 m) of both sites, ranging from 124 – 761 mg CaCO₃ L⁻¹ (Fig. A.11).

3.2. Near-surface (≤ 6.1 m) sediment profile characterization

As described previously (Stuckey et al., 2015), the top 3.0 m of the Seasonal Wetland has a brown hue. Gray layers spanning 3.0 m to 4.0 m and 4.8 m to 5.4 m deep sandwich another brown layer between 4.0 and 4.8 m deep. A thin gray-black sediment layer spans 5.4 m to 5.6 m overlying a gray layer extending to 6.0 m. Finally, a black peat layer is present between 6.0 m and 6.1 m. The total C content is elevated in the blue-gray and black sediments relative to the layers with a brown hue. Total C generally decreases with depth in the brown layers from 0.54 % (0.26 m) to ~ 0.28 % (4.2 m – 4.6 m) (Table 1). Total C ranges from 0.49 % to 0.85 % in the gray layers and from 1.7 % to 21.5 % in the black layers (Table 1).

The Permanent Wetland sediment profile is mottled (reddish brown and gray) in the top 1.3 m and transitions to a gleyed (gray hue) layer spanning 1.3 m to 4.0 m deep. Total C of the Permanent Wetland is 1.2 % in the top 0.26 cm, and ranges between 0.2 and 1.0 % down to 3 m, before returning to 1.2 % at 4 m depth (Table 2).

3.3. Solid-phase arsenic speciation

In the Seasonal Wetland, As speciation consists entirely of arsenate ($\text{H}_x\text{AsO}_4^{x-3}$) down to 3.7 m (Figs. 1 and A.12). Arsenate exists in relatively equal proportion to arsenite (H_3AsO_3) at 5 m before diminishing to a negligible contribution between 6.1 and 9.3 m. Arsenate appears at 12 m and 30 m depths, comprising 42 % and 59 % of the As speciation, respectively. Reduced As species, namely arsenite and As-bearing sulfides predominate in the clay/silt aquitard below 5 m. The As-bearing sulfide phase is arsenian pyrite in the peat layers (Fig. A.13) (Stuckey et al., 2015).

In the Permanent Wetland, we observe a more rapid transition from arsenate to arsenite predominance with depth (Fig. 1). Arsenate is present at 21 % in the deeper clays (9 m and 12 m) and at 64 % in the aquifer sands (27 m). Arsenite comprises the entire remainder of the As species except at 3 m and 12 m, where As-bearing sulfides constitute 33 % and 9 %, respectively.

3.4. Arsenic extractability in the near-surface (≤ 6.1 m) sediments

The mean solid-phase As concentration in the top 6 m of the Seasonal Wetland is 15.8 ± 4.7 mg As/kg – similar to newly deposited sediment in Bangladesh (16 ± 7 mg As/kg) (Datta et al., 2009) – and increases 10-fold in the peat layer between 6.0 and 6.1 m (Table 1, Fig. 2). The ligand-displaceable (1 M PO_4^{2-} , pH 5.0) As represents 12 – 26 % of the total As in the mineral sediments of the top 6 m and 2 % of the total As in the peat layer. The acid-reactive (1 M HCl) As comprises 6 – 15 % of the total As in the mineral sediments of the top 6 m, and 0.9 % of the total As in the peat layer. The reducible (CBD) As constitutes 22 – 42 %, 5 %, and 1 % of the total As in the low C (< 0.8 % C) sediments of the top 5 m, the intermediate C

(5.4 % C) sediment at 5.5 m, and the peat layer (21.5 % C), respectively. Therefore, we observe a decrease in ligand-displaceable, acid-reactive, and reducible As as the proportion of As-bearing sulfides increases (Figs. 1 – 2).

The mean solid-phase As concentration in the top 4 m of the Permanent Wetland is 15.7 ± 2.4 mg As/kg – equivalent to that of the Seasonal Wetland (Table 2, Fig. 2). The ligand-displaceable, acid-reactive, and reducible As comprise 18 – 32 %, 10 – 31 %, and 17 – 29 % of the total As, respectively. The three extractable As pools show no discernible trend with depth as the As speciation transitions from arsenate to arsenite. The ligand-exchangeable As for both sites ranges from 0.8 – 3.0 mg As kg⁻¹ – similar to average values found in the shallow sediments of two sites in Bangladesh (1.7 ± 1.2 and 1.4 ± 2.0 mg As kg⁻¹) (Zheng et al., 2005).

3.5. Sediment mineralogy and iron speciation

In both the Seasonal and Permanent Wetlands, the predominant minerals include quartz, feldspars, micas (especially muscovite), chlorite/hydroxyl-interlayered smectite, kaolinite, and Fe(III) oxides (i.e., goethite and hematite) on the basis of XRD analysis (Figs. A.1 – A.9) and electron microprobe analysis coupled with energy-dispersive spectroscopy (data not shown). In addition, siderite and pyrite (associated with peat layers) are detected at particular depths in both site profiles (Figs. A.2 and A.4). Similar sediment mineralogy was found previously in the upper Mekong Delta floodplain (Rowland et al., 2008; Rowland et al., 2007) and in the Bengal Basin (Datta et al., 2009; Hasan et al., 2009; Itai et al., 2010; Seddique et al., 2011; Swartz et al., 2004; Uddin et al., 2011).

In the Seasonal Wetland, Fe(III) oxides (goethite and/or hematite) comprise 36 – 50 % of the Fe speciation (mol-basis) in the near-surface (≤ 6 m) clays-silts and 17 % in the peat (6.1 m) as determined by Fe EXAFS spectroscopy (Fig. 3 and A.14). Iron oxides are below detection at 9.0 – 9.3 m before increasing to 12 % at 12 m and 14 % in the aquifer sands (30 m). Pyrite is present as 27 % and 52 % of the Fe species in the peat layers (6.1 m and 9.3 m, respectively). Siderite is present in the deeper clays/silts (9 m and 12 m) and aquifer sands (30 m) from 7 – 38 %. Siderite precipitation may vary spatially within sediment profiles due to localized differences in pH, HCO_3^- , and especially Fe(II) activities (Jakobsen and Postma, 1999; Postma et al., 2007). Silicates constitute the remaining 50 – 81 % of the least squares fit of the Fe EXAFS spectra for sediment throughout the profile.

In the Permanent Wetland, goethite and hematite together comprise 24 – 38 % of the Fe speciation (mol-basis) in the clay-silt aquitard to a depth of 12 m, and decrease to 14 % in the aquifer sands (27 m) (Fig. 3). Siderite is present at 2.6 m and 12 m as 28 % and 9 % of the Fe species, respectively. Silicates range from 48 – 73 % of the Fe speciation in the clay-silt aquitard to a depth of 12 m, and increase to 86 % in the aquifer sands (27 m).

3.6. Iron extractability in the near-surface (≤ 6.1 m) sediments

The ligand-displaceable Fe represents 1.4 – 2.8 % of the total Fe in the near surface of the Seasonal Wetland inclusive of the peat layer (Fig. 4). The acid-reactive Fe represents 3 – 10 % and 19 % of the total Fe, respectively, in the mineral sediments of the top 6 m and in the underlying peat layer. The reducible Fe

constitutes 35 – 50 % of the total Fe in the low C (< 0.8 % C) sediments of top 5 m and decreases to an 8 – 9 % contribution in the underlying C-rich layers (5.4 – 21.5 % C).

In the Permanent Wetland, the ligand-displaceable and acid-reactive Fe represent 2 – 16 % and 8 – 41 % of the total Fe, respectively (Fig. 4). The reducible Fe ranges from 1.3×10^4 – 1.9×10^4 mg Fe/kg – similar to levels found in Red River delta sediments (Phuong et al., 2012) – constituting 27 – 44 % of the total Fe.

3.7. Iron oxide fraction in the near-surface (≤ 6.1 m) sediments

The fraction of Fe(III) oxides in the sediments determined by three different means – Fe EXAFS least squares fitting of soils/sediments, Fe EXAFS fitting including the post-CBD “standard,” and CBD extraction – yielded estimates that vary by less than 15 % (of the total Fe [w/w]) for each measurement (Fig. 5). Collectively, the three approaches suggest that 36 – 53 % in the Seasonal and 24 – 44 % in the Permanent Wetlands of the total Fe is present as Fe(III) oxides in the near-surface sediments (Fig. 5). The exception is in the peat layer of the Seasonal Wetland in which the Fe(III) oxide fraction decreases to 4 – 17 % (Fig. 5).

4. DISCUSSION

4.1. Flooding and stratigraphic controls on arsenic speciation and mobility

In the Seasonal Wetland, the water table ranges from ~ 4 m below to > 1 m above the land surface (Benner et al., 2008), corroborating the observed transition from oxidized to reduced As speciation below 4 m (Fig. 1). Arsenic is especially

reduced in the peat layers – present as arsenian pyrite (Fig. 1 and A.13). In the Permanent Wetland, the annual variation in the water table ranges from near-surface (< 0.5 m) to > 1 m above the land surface (Benner et al., 2008; Kocar et al., 2008). The higher water table in the Permanent Wetland aligns with the more rapid transition from oxidized to reduced As speciation as compared to that observed in the Seasonal Wetland (Fig. 1). Thus, we constrain the potential release mechanism of dissimilatory As(V) reduction in the near surface to the top ~ 4 m in the Seasonal Wetland and to < 1 m deep in the Permanent Wetland.

An increased duration and vertical extent of saturated conditions correspond to a predominance of reduced As species in the near-surface clays – leading to greater As mobility when present as arsenite (Herbel and Fendorf, 2006; Kocar et al., 2006; Tufano et al., 2008). However, the enrichment of As and partitioning to arsenian pyrite in the peat layers leads to increased levels of ‘unreactive’ (with respect to the extract used here) As (Fig. 2) – with presumably restricted mobility provided anaerobic conditions are maintained. Thus, flood duration and stratigraphy appear to control As speciation in both the Seasonal and Permanent Wetland. More specifically, the increased saturation and lack of peat layers (and concomitant relative scarcity of As sulfides) in the Permanent Wetland imply increased As release and transport to the underlying aquifer – facilitating the observed As plume emanating from the oxbows (Kocar et al., 2008). Accordingly, in the Permanent Wetland, lysimeter-collected pore-water As concentrations are $0.7 - 0.9 \mu\text{M}$ at 1 and 2 m deep (Kocar et al., 2008), and well-water As concentrations increase to $4.1 \mu\text{M}$ at 16 m (Fig. A.15), though they may reach as high as $8 \mu\text{M}$ in the

near-surface clay-silt layer (Kocar et al., 2008). The Seasonal Wetland, however, has lysimeter-collected pore-water As concentrations of $< 0.1 \mu\text{M}$ at depths of 1.1 and 1.5 m (data not shown), and well-water As concentrations of $< 0.57 \mu\text{M}$ in the top 12 m (Fig. A.15). Hence, aqueous As concentrations increase with depth within the near-surface clays-silts in both depositional environments, although to a much lower degree in the Seasonal Wetland. Thus, As appears to be preferentially released in near-surface sediments under permanent flooding conditions over seasonally saturated conditions.

4.2. Reactivity and mineralogy of arsenic-bearing sediments

The magnitude and proportion of each of the three respective reactive groups of As (ligand-displaceable, acid-reactive, and reducible) is similar for the near-surface sediments of both sites (Fig. 2), with the exception of the peat layer in the Seasonal Wetland in which the proportions of the three As reactive groups are diminished due to the presence of arsenian pyrite. As the three extractions were performed in parallel, the extracted fractions may overlap. For example, the similar magnitude of ligand-displaceable and reducible As as a function of depth suggests that most of the As (arsenate and arsenite) extracted by 1 M PO_4^{2-} (pH 5.0) and CBD is adsorbed onto Fe(III) oxides. If the reducible pool were greater than the ligand-exchangeable pool, then we would expect a substantial fraction of reducible As co-precipitated with Fe(III) oxides (Postma et al., 2007). On the other hand, if the ligand-displaceable pool were greater than the reducible, we would expect non-Fe(III) oxide mineral surface to be contributing substantially to As adsorption. The

only depth locations were ligand-displaceable As supersedes the reducible As is in the C-rich layers of the Seasonal Wetland where arsenian pyrite and arsenite predominate.

The 1 M HCl and CBD extracted fractions overlap as well. Citrate-bicarbonate-dithionite should reduce acid-extractable Fe(III) oxides (e.g., ferrihydrite) as well as Fe(III) oxides more resistant to 1 M HCl (e.g., goethite and hematite). As expected, the reducible As pool was greater than or equal to the acid-reactive pool as a function of depth in both sites (Fig. 2). Likewise, the reducible Fe pool was greater than or equal to the acid-reactive Fe pool (with the exception of the peat layer in the Seasonal Wetland) (Fig. 4). In general, a greater difference between reducible and acid-reactive As and Fe occurred in the top 4 m of the Seasonal Wetland relative to that observed in the Permanent Wetland (Figs. 2 and 4), reflecting an increased proportion of non-acid extractable Fe. Annual wet-dry cycling due to the fluctuating water table in the Seasonal Wetland may lead to a decrease in acid-reactive Fe (Thompson et al., 2006).

Thus, goethite and hematite, rather than ferrihydrite, are the dominant Fe(III) oxides present at both sites similar to findings in Red River floodplain sediments (Postma et al., 2010; Postma et al., 2007). Detection of ferrihydrite in our field sites is limited to the top 0.1 m of the Permanent Wetland (Kocar et al., 2014). Goethite and hematite within the sediments are evidently at least partially extracted with 1 M HCl (Fig. 4). The reactivity of synthetic pure Fe(III) oxides may poorly predict the reactivity of their natural Fe(III) oxide counterparts (Postma et al.,

2010); however, by coupling a CBD extraction with Fe EXAFS, we have quantified a reducible Fe fraction accounted for by goethite and hematite (Fig. 5).

A substantial fraction of the As (~ 25 % of average) in the low C (≤ 1.2 % C) near-surface sediments is associated with the reducible fraction (~ 38 % of the total Fe on average) – correlating with the Fe(III) oxide fraction (goethite and hematite) (Fig. 5). The average total Fe content of our two sites is 4.3 %, over twice as high as the ~ 2 % Fe found at sites in the Bengal Basin (Swartz et al., 2004) and Red River Delta (Postma et al., 2007). Though not directly comparable due to differences in extraction methods, the mean reducible Fe fraction of 38 % observed in our sites falls in between the > 50 % and 19 – 38 % values observed at sites in the Red River Delta (Postma et al., 2007) and Datong Basin (China) (Xie et al., 2008), respectively, and is well above the 5 – 10 % values observed in the Bengal Basin (Swartz et al., 2004). Thus, the Fe reactivity of the Mekong Delta sediments studied is within the typical range observed in sedimentary basins of South and Southeast Asia.

Furthermore, the identification of reactive As hosted by Fe(III) oxides in Mekong Delta sediments corroborates findings in the Bengal Basin (Hasan et al., 2009), Red River Delta (Postma et al., 2010), and Datong Basin (Xie et al., 2008). The presence of As-bearing Fe(III) oxides throughout the near-surface sediments indicates that dissimilatory Fe(III) reduction can serve as the primary release mechanism, a well recognized pathway for S/SE Asia (Fendorf et al., 2010). Our quantification of As-bearing Fe(III) oxide content and reactivity can provide improved inputs for reactive transport models predicting groundwater As distribution (Kocar et al., 2014).

A large fraction of the total As (37 – 63 %) is not ligand-displaceable nor reducible in the top 4 m of both sites (Fig. 1); the form of this phase (or phases) remains unresolved. Arsenic phases requiring more aggressive extraction techniques may include As oxides, sulfides (generally low in our mineral sediments), organo-As compounds, and/or As co-precipitated with silicate minerals (Keon et al., 2001). For instance, > 80 % of As in near-surface sediments of Bangladesh is associated with “insoluble” or organic phases (Seddique et al., 2011). Arsenic incorporation into micas and chlorites, both present in our sediments, has been noted for Himalaya-derived deltaic sediments (Masuda et al., 2012; Seddique et al., 2008).

5. CONCLUSIONS

We have defined the solid-phase As speciation along defined recharge pathways for two sediment profiles of contrasting surface hydrology in the Mekong Delta, as well as identified and quantified the As-bearing Fe (III) oxide phases within these systems. Together, these results help to spatially define and quantify the solid-phases hosting arsenic, which ultimately contribute to near-surface As release to groundwater. The annual replenishment of As-bearing Fe(III) oxides with an average sediment deposition rate of $\sim 1 - 3 \text{ mm y}^{-1}$ (Polizzotto et al., 2008a) likely provides a continuous source of As to the sediments and aquifers of the Mekong Delta. The results presented here indicate that appreciable As-bearing ‘reducible’ Fe(III) oxides (goethite and hematite) exist in the near-surface sediments under seasonally and permanently saturated wetlands. The persistence of these As-

bearing Fe(III) oxide phases, as evidenced by their presence in sediments at depth that are hundreds to thousands of years old indicate that sediments underlying both continuously and seasonally saturated wetlands have the potential to release As indefinitely, provide an appropriate reductant is introduced. Despite similar As-bearing Fe(III) oxide phases – the oxidants in dissimilatory As(V)/Fe(III) reduction – As release is limited where wetlands experience seasonal saturation; by contrast, permanent wetlands promote As release as evidenced by groundwater As profiles. Further, the persistence of goethite and hematite in the sedimentary profile suggests the system is limited by organic carbon suitable for dissimilatory Fe(III) reduction (of goethite or hematite).

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Tables

Table 1. Elemental composition of the sediment profile of the Seasonal Wetland to a depth of 30 m.

Depth	N		C		C/N		Si	Al	Fe	Ti	Mn	Cu	Zn	As	S	P
(m)	Mean (g/kg)	SD (g/kg)	Mean (g/kg)	SD (g/kg)	Mean	SD	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
0.26	0.52	0.02	5.37	0.08	10.3	0.4	228	77	48	5.0	426	34	103	16	140	447
0.46	0.43	0.02	5.05	0.03	11.8	0.6	221	79	47	5.1	712	37	102	17	96	454
0.66	0.41	0.01	4.38	0.01	10.6	0.3	227	79	49	5.2	563	35	99	18	119	520
0.86	0.34	0.00	4.02	0.01	11.8	0.1	229	77	44	5.3	395	37	99	14	103	477
1.06	0.38	0.03	4.49	0.03	11.7	0.9	222	80	50	5.3	761	39	101	20	247	508
1.26	0.37	0.01	3.85	0.03	10.4	0.3	222	80	50	5.2	811	38	104	19	145	493
1.46	0.37	0.04	3.93	0.02	10.6	1.0	228	76	50	5.3	716	36	101	24	149	554
1.66	0.33	0.01	3.87	0.01	11.8	0.5	223	78	51	5.3	594	38	102	21	135	534
1.80	0.34	0.03	3.70	0.04	10.9	1.1	221	80	48	5.2	559	42	102	18	114	484
2.20	0.41	0.00	3.00	0.00	7.2	0.1	211	85	43	4.8	271	36	110	12	121	266
2.63	0.29	0.02	2.45	0.03	8.3	0.7	232	80	40	5.0	423	35	105	10	89	286
3.70	0.49	0.01	4.92	0.02	10.1	0.3	203	87	39	4.5	312	39	112	12	213	186
4.20	0.28	0.03	2.94	0.06	10.5	1.0	206	76	52	5.2	314	38	101	16	2.35E+03	291
4.60	0.28	0.03	2.76	0.02	9.9	0.9	220	81	43	5.3	349	35	103	12	863	279
5.00	0.92	0.03	7.88	0.06	8.5	0.3	188	94	42	4.1	328	55	114	13	366	105
5.46	1.60	0.03	17.14	0.05	10.7	0.2	187	97	32	3.9	214	74	124	14	555	173
5.55	3.36	0.02	54.44	0.71	16.2	0.2	172	87	29	3.5	328	72	109	25	5.27E+03	170
5.80	0.63	0.02	8.48	1.46	13.4	2.3	231	90	24	5.7	184	40	101	10	432	216
6.10	3.19	0.02	214.6	17.6	67.2	5.5	149	54	50	3.3	754	41	127	153	1.59E+04	477
9.0	1.38	-	37.78	-	27.4	-	230	100	50	4.8	633	37	109	23	3.41E+03	396
9.30	3.90	-	405.7	-	104	-	55	28	24	0.8	82	13	35	79	1.04E+04	112
12	0.70	-	5.49	-	7.8	-	267	102	47	5.3	621	31	111	8	70	407
30	0.38	-	4.51	-	11.9	-	274	77	26	3.2	466	13	232	11	278	621

Table 2. Elemental composition of the sediment profile of the Permanent Wetland to a depth of 27 m.

Depth	N		C		C/N		Si	Al	Fe	Ti	Mn	Cu	Zn	As	S	P
(m)	Mean (g/kg)	SD (g/kg)	Mean (g/kg)	SD (g/kg)	Mean	SD	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
0.26	0.22	0.00	6.07	0.04	28.1	0.5	216	68.7	43.6	4.9	680	35	95	18	90	842
0.46	0.59	0.02	2.78	0.09	4.7	0.2	217	69.8	45.5	5.1	466	33	96	16	40	469
0.66	0.60	0.00	3.05	0.01	5.1	0.0	217	72.9	46.9	5.0	369	40	96	16	< 20	348
0.86	0.30	0.09	7.99	0.07	26.5	8.3	215	74.8	47.3	4.7	335	35	106	14	< 20	330
1.06	0.64	0.01	2.55	0.00	4.0	0.1	217	74.4	47.4	4.8	383	35	98	14	< 20	274
1.26	0.63	0.00	2.72	0.04	4.4	0.1	225	72.2	43.2	4.9	360	34	94	16	< 20	277
1.46	0.41	0.00	2.23	0.03	5.4	0.1	221	71.5	45.1	5.2	484	34	92	19	< 20	356
1.66	0.63	0.02	2.91	0.00	4.6	0.1	221	70.7	49.5	5.0	1.93E+03	34	87	20	< 20	428
1.86	0.65	0.01	4.19	0.04	6.5	0.1	222	72.3	43.0	5.2	617	35	86	17	< 20	405
2.06	0.66	0.00	2.85	0.04	4.3	0.1	221	70.8	39.9	5.0	480	31	80	16	< 20	431
2.26	0.56	0.02	5.08	0.04	9.1	0.4	217	64.6	36.6	4.5	670	26	71	13	< 20	431
2.63	0.66	0.01	8.89	0.05	13.4	0.3	214	63.5	39.8	4.5	979	29	76	20	< 20	466
2.90	0.53	0.00	3.26	0.11	6.2	0.2	225	52.1	25.0	3.3	388	178	46	13	1.61E+03	345
3.03	0.28	0.01	8.39	0.00	30.4	1.4	213	65.8	32.0	4.7	457	124	71	15	727	352
3.53	0.59	0.02	11.69	0.12	19.8	0.7	219	65.6	36.6	4.5	790	31	74	16	600	548
3.93	0.45	0.04	9.05	0.01	20.2	1.9	227	64.7	34.1	4.2	669	28	67	12	130	470
9	1.27	-	13.41	-	10.6	-	269	92.5	43.7	5.06	969	32	95	18	355	733
12	0.96	-	10.46	-	10.9	-	266	85.2	34.9	4.52	786	25	69	13	250	633
27	0.15	-	1.67	-	11.1	-	297	60.8	18.3	2.49	265	8	87	5	125	487

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Figure 1. Arsenic speciation as a function of depth in Seasonal and Permanent Wetlands. Panels to the left of each profile show the basic stratigraphy of a ~ 15 m deep clay/silt layer (solid or mottled colors) overlying aquifer sands (light gray checks). Sediment coloring is indicated by brown, gray, or black hues. Peat is shown in black, and dark gray indicates alternating peat and clay/silt deposits. Mottling is indicated by brown/gray checks. The blue dashed lines approximate the average seasonal variation in the water table. Both sites have an elevation of ~ 6 MASL (Benner et al., 2008; Kocar et al., 2008).

Figure 2. Arsenic extractability as a function of depth in Seasonal and Permanent Wetlands. The peat layer at 6.1 m in the Seasonal Wetland has a total As concentration of 150 mg kg⁻¹ (outside of scale); the X-axes are set to 30 mg kg⁻¹ for both sites to optimize visual comparison of the extractable As pools.

Figure 3. Iron speciation as a function of depth in Seasonal and Permanent Wetlands. Panels to the left of each profile show the basic stratigraphy of a ~ 15 m deep clay/silt layer (solid or mottled colors) overlying aquifer sands (light gray checks). Sediment coloring is indicated by brown, gray, or black hues. Peat is shown in black, and dark gray indicates alternating peat and clay/silt deposits. Mottling is indicated by brown/gray checks.

Figure 4. Iron extractability as a function of depth in Seasonal and Permanent Wetlands.

Figure 5. Comparison of citrate-bicarbonate-dithionite extractable (CBD) iron fraction to the iron oxide fraction determined by least squares fitting of EXAFS spectra (1) with mineral standards (EXAFS) and (2) with a combination of mineral standards and the post-CBD extracted sediment “standard” for near-surface sediments of Seasonal and Permanent Wetlands.

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Permanent Wetland

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