**Redox Controls on Arsenic Enrichment and Release from Aquifer Sediments in Central
Yangtze River Basin**

Michael V. Schaefer^a, Xinxin Guo^b, Yiqun Gan^b, Shawn G. Benner^c, Aron M. Griffin^d, Christopher
A. Gorski^d, Yanxin Wang^{b*}, Scott Fendorf^{a*}

^aEarth System Science Dept., Stanford University, Stanford, CA, USA

^bState Key Laboratory of Biogeology and Environmental Geology, China University of
Geosciences, Wuhan, Hubei, P. R. China

^cDepartment of Geosciences, Boise State University, Boise, ID, USA

^dCivil and Environmental Engineering, Pennsylvania State University, University Park, PA, USA

*Corresponding Authors

Email: fendorf@stanford.edu; yx.wang@cug.edu.cn

ABSTRACT

More than 100 million people in Asia are presently exposed to groundwater with arsenic (As) concentrations exceeding the World Health Organization standard of $10 \mu\text{g L}^{-1}$. Arsenic contaminated groundwater within basins of the central portion of the Yangtze River has recently been reported, but the processes controlling arsenic concentrations have yet to be resolved. We examined the hydrologic and geochemical factors controlling arsenic within the Jiangnan Plain, an inland sedimentary basin of the Yangtze River, where arsenic concentrations exhibit strong seasonal variability driven by surface and groundwater mixing (Schaefer et al., 2016). Hydrologic fluctuations alter redox conditions in the aquifer, leading to oscillations between arsenic/iron reduction and oxidation. Here we investigate the depth-distribution of solid and aqueous phase iron and arsenic species and, through a series of laboratory manipulations, constrain the biogeochemical processes controlling seasonal changes in groundwater arsenic concentrations. In sediment incubations from ~20 m below the surface, where solid-phase arsenic concentrations exceed 100 mg kg^{-1} , both unamended and glucose-amended sediment samples result in arsenic release to the aqueous phase. *In-situ* carbon was capable of promoting As release in the sediment. In contrast, sediment batch incubations from other depths resulted in limited As release. Solid phase arsenic in the enriched zone was relatively oxidized but may become reduced over short time periods. In sediments below the As-enriched zone, glucose amendment resulted in arsenic reduction, but arsenic release to the aqueous phase was restricted by the subsequent formation of arsenic sulfide minerals. Buried sedimentary arsenic coupled with anaerobic microbial respiration of subsurface organic carbon within the Jiangnan Plain aquifer leads to rapid release of As to groundwater. Arsenic release

40 from sediments at ~20 m depth is sufficient to explain arsenic concentrations throughout the
41 aquifer, and provides a mechanism to explain how shifts in hydrology result in seasonally
42 variable arsenic concentrations in groundwater.

43

1. INTRODUCTION

Deposition of arsenic-bearing sediments across floodplains leads to widespread geogenic arsenic (As) contamination of South and Southeast Asian aquifers including the Brahmaputra/Ganges, Mekong, and Red Rivers, encompassing Bangladesh and West Bengal, India, Vietnam, and Cambodia where over 100 million people are at risk of As exposure (Fendorf et al., 2010). Chronic exposure to As concentrations above the World Health Organization (WHO) drinking water limit of $>10 \mu\text{g L}^{-1}$ increases the risk of a variety of ailments including dermal lesions (Das et al., 2008), cancers (Steinmaus et al., 2000; Naujokas et al., 2013), and neurological impairment (Wasserman et al., 2004; Wasserman et al., 2007). Current estimates are that up to 19.6 million individuals are at risk of As exposure through drinking water in China (Rodríguez-Lado et al., 2013).

Recent advances in statistical predictive models show promise in identifying As-affected areas with sparse data (Rodríguez-Lado et al., 2013), but the regional scale of surface-feature based statistical models is larger than the spatial variation of As concentrations, which can vary over tens of meters (Michael, 2013). Although similarities exist between aquifer systems in Asia, no comprehensive model exists that captures the complexity of when and where high As concentrations occur across Asian aquifers. Reductive dissolution of As-containing iron oxides is the predominant mechanism leading to elevated As concentrations in low-lying areas across Asia (Nickson et al., 1998; Smedley and Kinniburgh, 2002), but As concentrations vary significantly over small geographic regions (van Geen et al., 2003). Previous studies have focused on identifying the relevant source of reactive organic carbon with reports of co-deposited sedimentary carbon (Nickson et al., 2000; McArthur et al., 2004; Meharg et al., 2006)

and surface-derived dissolved organic carbon (DOC) (Harvey et al., 2002; Mailloux et al., 2013) serving as the relevant electron donor. However, reactions releasing As are limited by the reactivity of Fe-oxide phases hosting As with respect to available reactive organic carbon for microbial metabolism (Stuckey et al., 2016); it is now clear that the reactivity of both the electron donor and acceptor must be considered to accurately model As release. Identifying where within the sediment profile reactions mobilizing As occur and what limits these reactions is important to predict the distribution of arsenic contamination and understand changes induced by land-use change, groundwater extraction, and other perturbations on groundwater As concentrations.

Seasonal variation in As concentrations makes avoiding As difficult, and although large variations have not been widely observed, it is unclear whether this is due to lack of temporal resolution in testing (i.e., a lack of retesting a single well in multiple seasons) or because As concentrations do not generally vary with season (Cheng et al., 2005; Ayotte et al., 2015). Within the Jiangnan Plain of the Yangtze River Basin, As concentrations do vary seasonally (Duan et al., 2015) resulting from changes in surface and groundwater interactions (Schaefer et al., 2016). Increases and decreases in dissolved sulfide, Fe(II), and As concentrations occur over periods of weeks to months as soluble, reduced species are oxidized following mixing of oxic surface water with reduced groundwater; as oxidant supply diminishes the aquifer again becomes reducing and concentrations increase (Schaefer et al., 2016).

We utilized a $\sim 10 \text{ km}^2$ field area in the Jiangnan Plain with seasonally variable chemistry to assess whether Fe/As reduction is coupled to detrital (*in situ*) carbon or surface-derived carbon,

or a combination of these sources. The carbon source may determine the time required to observe changes in As concentrations linked to anthropogenic disturbances such as large-scale groundwater extraction (Winkel et al., 2011) and pond excavation (Neumann et al., 2010). If the relevant source of reduced carbon is surface-derived, the lag time to observe changes is expected to be on the order of 100-1000 years assuming flow rates in pristine groundwater systems (Benner et al., 2008) or on the order of decades with irrigation pumping (Harvey et al., 2006). Conversely, if the relevant reduced carbon source is located at or near the depth of water extraction, the lag time for changes in water chemistry to occur may be similar to chemical reaction rates, which are on the order of hours to days, not dependent on advection rates. We hypothesized that a buried source of As must exist at a depth near highly variable groundwater As concentrations. Further, a carbon source reactive toward As and Fe in the sediments must co-occur or be replenished seasonally in order for seasonal changes in As concentrations to persist.

In the present study, we used a combination of field measurements, spectroscopic examination of sediments, and an expanded set of laboratory incubations and extractions to determine the reactions responsible for seasonal variation in aqueous As concentrations. Solid phase chemistry in the sediment profile coupled with hydrologic changes explain the observed seasonality in aqueous As concentrations. We also assess whether As in the sediment poses a threat to groundwater quality under scenarios of changing aquifer conditions and place our results from the Jiangnan Plain in context with other arsenic-affected basins in China and South and Southeast Asia.

2. METHODS

2.1 Field Setting and Sampling Procedures

2.1.1 The Jiangnan Plain

The Jiangnan Plain is an inland river basin supplied with alluvial sediment from the Yangtze River and Han River (a major tributary to the Yangtze). The >55,000 km² basin is located downstream of the Three Gorges Dam and has a subtropical monsoon climate with hot, wet summers and cold, dry winters. The field area for this study is a ~10 km² site within the Jiangnan Plain where land-use is mainly agricultural consisting of aquaculture ponds and upland and flooded crops. Surface water levels at the site vary by 5-8 m annually while groundwater levels fluctuate by ~1 m. These shifts lead to an annual switch between groundwater discharge and recharge that drives seasonal As, Fe(II), and sulfide concentrations in the aquifer (Schaefer et al., 2016). Hydrology in the field area is likely under the influence of human activity through substantial construction of aquaculture ponds, diversion of surface water for irrigation canals, and groundwater extraction for industrial and agricultural use. Further details of the field area (30.15° N, 113.66° E) are provided in previous publications (Gan et al., 2014; Duan et al., 2015; Schaefer et al., 2016).

2.1.2 Well Installation

Drilling occurred in November 2011 and sediment cores were collected during well installation using a Geoprobe 6620DT direct push drill rig (0-20 m depth) or every 3 m using a rotary drill method (20-50 m depth). Immediately after cores were brought to the surface, they were sectioned into 20 cm lengths, capped, and placed into anaerobic boxes with oxygen scavenging

packs (AnaeroPack, Mitsubishi, Japan). Samples were then frozen and shipped to Stanford University, where they remained frozen until further analysis. Subsamples used for bulk analysis and acid extractions were thawed and dried in an anoxic chamber (95%:5% N₂:H₂, < 1 ppm O₂) and homogenized by manual grinding. Sediments used for incubations were thawed and added to reaction vessels without drying. Dry mass was calculated by determining the water content of samples by weighing samples before and after drying, and all reported values are referenced to dry sample mass.

2.2 Sediment Analysis

2.2.1 Bulk Characterization

The bulk elemental composition of samples was determined using energy dispersive x-ray fluorescence (ED-XRF) spectroscopy (Spectro Xepos). Between 1.5 and 2 g of ground sediment was placed in a plastic cup fitted with a thin layer of polypropylene Prolene film (Chemplex). X-rays were generated with a 50-watt x-ray tube and fluorescent x-rays were detected on five energy targets to cover the elemental range from sodium to uranium. Measurements were performed in a He atmosphere to minimize x-ray attenuation. Bulk elemental abundance was calculated based on the intensity of the characteristic fluorescent x-rays of each element. Carbon and nitrogen contents were determined by placing 19 to 20 mg of dry, finely ground sediment in a small tin and combusting at 1060°C. N₂ and CO₂ gas were measured post-combustion on a Carlo Erba Elemental Analyzer. Carbon and nitrogen analyses were performed in duplicate.

2.2.2 Iron and Arsenic X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) was used to probe the local chemical environment of As and Fe in sediments recovered from the field area. Arsenic K-edge x-ray absorption near-edge structure (XANES) spectroscopy was used to differentiate arsenate, arsenite, and arsenic sulfide species. Iron K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy was used to apportion the Fe pool into mineralogical classes. Both As XANES and Fe EXAFS spectra were collected at beamline 11-2 at the Stanford Synchrotron Radiation Lightsource (SSRL).

Dried subsamples of selected cores were suspended in deoxygenated deionized (DDI) water, and the suspension was filtered onto cellulose filter paper (Whatman). Samples from batch incubations (details in section 2.3) were filtered directly from incubation suspensions but otherwise treated the same. Reference standards were prepared by diluting and homogenizing powdered reference material with boron nitride to minimize self-absorption. Three to seven scans were collected for each sample and averaged. Background subtraction, normalization, and fitting were performed with the IFEFFIT routine in Athena (Ravel and Newville, 2005).

Energy was tuned with a double crystal Si(220) monochromator and fluorescent x-rays were detected with either a 30- or 100-element solid-state Ge detector. Incident X-ray intensity (I_0) was measured via an in-line ionization detector and all reported intensities are relative to I_0 . Higher-order harmonics were minimized with harmonic rejection mirrors, and the monochromator was typically detuned ~30%.

Arsenic K-edge XANES spectra were collected by scanning from 11635 to 12290 eV in 6 eV steps except from 11840-11900 eV, where the step size was reduced to 0.3 eV. Energy was calibrated to the top of the white line of sodium arsenate (11874 eV). Linear combination fitting was

performed in the range 11842-11922 eV on both normalized absorbance spectra and the first-derivative of As XANES data using standards of arsenian pyrite (Stanford Mineral Collection), $\text{H}_x\text{AsO}_3^{3-x}$ adsorbed on ferrihydrite, and $\text{H}_x\text{AsO}_4^{3-x}$ adsorbed on ferrihydrite.

Iron K-edge EXAFS spectra were collected by scanning from 6880 to 8012 eV to generate k-space data in the range 0-15.3 $\text{\AA}^{-1}$. Energy was calibrated to the K-edge of Fe foil and set to 7111 eV. Iron spectra were fit using the Fe EXAFS (χ) function over a k range 3-12 $\text{\AA}^{-1}$ using linear combination fitting to minimize the least squares function. Fitting was restricted to the use of four components per spectrum. Standards used for Fe EXAFS fits included ferruginous smectite (SWa-1, Source Clay Mineral Repository); glaucophane, hornblende, and biotite (Stanford Mineral Collection); and ferrihydrite-, goethite-, and hematite-coated sands.

2.2.3 Carbon NEXAFS Spectroscopy

Carbon near-edge X-ray absorption fine structure (NEXAFS) spectroscopy was performed at the Canadian Light Source (CLS) on the spherical grating monochromator (SGM) beamline to determine the chemical speciation of C within native sediments. Samples were affixed to a copper holder using carbon tape and transferred into the beam line vacuum chamber ($\sim 10^{-7}$ torr). Fluorescent X-rays were detected using silicon drift detectors (SDD, Amptek). Samples were scanned from 270-320 eV in continuous (fast) scan mode. Each scan lasted 60 s and 25-40 scans were collected per sample. The beam was moved to a fresh area of the sample between each scan to minimize beam damage. Individual scans were summed to provide a single spectrum for each sample, and energy was calibrated using citric acid. Each calibrated spectrum was normalized by dividing by the scattering spectrum of blank

gold foil (average of >300 scans) in aXis software (Hitchcock et al., 2012). Normalized, calibrated spectra were then imported to Athena (Ravel and Newville, 2005) where pre- and post-edge normalization was performed prior to peak fitting with Gaussian and arctangent functions.

2.2.4 Mössbauer Spectroscopy

Mössbauer transmission spectra were collected to determine the relative ratios of Fe(II) and Fe(III) species in sediment samples, as well as to differentiate Fe(III) oxides and Fe(III) bound in silicate minerals. Samples were prepared by mounting anoxic sample between two pieces of 5 mil Kapton tape inside an anaerobic glovebox. Measurements were performed using a SVT-400 Mössbauer system (SEE Co., USA). Spectra were collected at 20 K to ensure Fe-oxides achieve magnetic ordering (so they manifest as a sextet feature) but to also avoid magnetic ordering of Fe in silicate minerals, allowing unambiguous differentiation of each component. Although we cannot rule out the possibility of Fe-oxides ordering below 20K or silicates ordering above 20K, our fitting represents the most likely scenario. Spectra were calibrated relative to α -Fe(0) foil and fit with Recoil software using a Voigt-based model (Rancourt and Ping, 1991). We assume consistent recoilless fractions in each sample so that relative areas of fitted components are proportional to the relative abundance of each component.

2.3 Aqueous Analyses

2.3.1 Field Samples

Prior to sampling, wells in the field area were purged and temperature (± 0.1 °C), conductivity (± 1 $\mu\text{S cm}^{-1}$), pH (± 0.01) and oxidation-reduction potential (ORP, ± 0.1 mV) were measured in

the field using a Hach HQ40D multimeter. ORP was converted to Eh by adding +240-251 mV depending on the water temperature. Samples were acidified in the field, and arsenic concentrations were measured using a Titan 930 hydride generation atomic fluorescence spectrophotometer (HG-AFS) with a detection limit of $0.05 \mu\text{g L}^{-1}$. Manganese concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Intrepid II XSP) with a detection limit of 0.1 mg L^{-1} . Aqueous Fe(II) and sulfide concentrations were measured in the field using a Hach 2800 portable spectrophotometer and Hach reagent kits.

2.3.2 Laboratory Samples

Major elements from acid extractions were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo ICAP 6300). Aqueous Fe(II) speciation was performed using an adapted version of the 1,10 phenanthroline method (Tamura et al., 1974). Briefly, samples were diluted (if necessary) until the final Fe concentration was $<100 \mu\text{M}$. Each sample was split for Fe(II) and total Fe analysis. The total Fe sample was reduced with hydroxylamine-HCl prior to chromophore addition; 1,10 phenanthroline was then added in excess to both samples, and the pH was buffered at ~ 3 with ammonium acetate prior to measurement at 510 nm on a spectrophotometer. Good agreement ($< 5\%$ difference in 7 of 11 samples, all samples $<30\%$ difference) was observed for total Fe measured by 1,10-phenanthroline and ICP-OES (Electronic Annex, Figure EA-1).

2.4 Batch Experiments

2.4.1 Sediment Incubations

Sediment microcosms were performed in duplicate to track arsenic release under unamended and glucose amended conditions. 20 g of anoxic sediment was suspended in 100 mL of an anoxic solution containing 2 mM glucose or DDI water. Aliquots (5 mL) of homogenized sediment-water slurry were sampled daily for 4 d and filtered with a 0.2 μ m pore membrane after which major elements were measured with ICP-OES. Following the aqueous sampling period, the incubations were left in the anoxic chamber undisturbed for 30 d until solids were removed for XAS analysis as described in Section 2.2.2.

2.4.2 Chemical Extractions

Chemical extractions of sediments were performed to evaluate the reactivity of As in sediment from various depths. HCl extractions were performed in triplicate on anoxic sediment samples by weighing 100 mg of sediment into a 15 mL centrifuge tube and adding 12 mL of 2 M HCl (trace metal grade). Reactors were shaken for ~20 h, then filtered (0.2 μ m) and diluted with DI water. Major elements were measured by ICP-OES, and Fe(II) and total Fe were measured on a spectrophotometer using the 1,10 phenanthroline method (Tamura et al., 1974).

3. RESULTS

3.1 Aqueous Chemistry

Groundwater within the field area (Duan et al., 2015), and throughout the Jiangnan Plain (Gan et al., 2014), is contaminated with As; within the field area we examined, wells screened at 10, 25, and 50 m average $65 \mu\text{g L}^{-1}$ As between May 2012 and December 2014 (Table 1) and every well in the field area recorded at least one measurement above $10 \mu\text{g L}^{-1}$ during the sampling period. Arsenic concentrations vary seasonally with periods of groundwater recharge and discharge, reaching $>1000 \mu\text{g L}^{-1}$ and $< 200 \mu\text{g L}^{-1}$ annually at the well where sediment was collected (Figure 1). Iron and Mn concentrations average 5.1 and 1.3 mg L^{-1} , respectively, while sulfide concentrations average $39 \mu\text{g L}^{-1}$. The pH ranges from 6-8, with an average of 7.1. The coupling of increases and decreases in dissolved Fe(II) and As concentrations at the field area (Figure 1) indicates that both reductive dissolution and oxidative (re)precipitation of As-containing Fe-oxides control As concentrations in the aquifer (Schaefer et al., 2016).

3.2 Sediment Characterization

3.2.1 Bulk Sediment Properties and Chemistry

Texture analysis of recovered borehole sediment showed a sedimentary history similar to many large Asian deltas (Smedley and Kinniburgh, 2002), including a clay and silt cap overlying sand deposits with distributed clay lenses/layers (Figure 2). The stratigraphy is similar to other boreholes in the Jiangnan Plain (Zhang et al., 2008), where the top ~20 m is composed of clay and silt deposits, and from 20-50 m (maximum depth of this study) lies a sandy aquifer with

interbedded clay and silt layers. Deeper clay layers (Figure 2) split the sand deposits into locally distinct aquifers in some areas, although similar water level measurements in 25 and 50 m wells are observed in nested wells across the field area indicating a continuous and/or connected aquifer at the regional (km) scale (Schaefer et al., 2016).

Solid-phase As concentrations in the sediment profile average 12.7 mg kg^{-1} but reach $>100 \text{ mg kg}^{-1}$ in a zone of As enrichment between $\sim 18\text{-}20 \text{ m}$ below ground level (Figure 2, Table 2). This zone is coincident with low sediment carbon ($18\text{-}20 \text{ m}$ range $0.4\text{-}2.6 \text{ g kg}^{-1}$, $0\text{-}51 \text{ m}$ average 10.3 g kg^{-1}) and sulfur ($18\text{-}20 \text{ m}$ range $12\text{-}52 \text{ mg kg}^{-1}$, $0\text{-}51 \text{ m}$ average 591 mg kg^{-1}). Bulk Fe concentrations average 37 g kg^{-1} through the profile and range from $9.4\text{-}61.2 \text{ g kg}^{-1}$ (Table 2).

3.2.2 Solid-phase Arsenic Speciation

Arsenic K-edge XANES analysis of sediment samples reveals that As exists predominantly as $\text{H}_x\text{AsO}_4^{3-x}$ near the land surface (85% As(V) at 1.5 m depth), but As speciation is dominated by a combination of $\text{H}_x\text{AsO}_3^{3-x}$ (As(III)) and As-sulfide phases from $3\text{-}18 \text{ m}$ depth (Figure 2, Figure 3, Table 3). At 18.7 m depth, bulk As content increases and As speciation switches to being dominated by $\text{H}_x\text{AsO}_4^{3-x}$ (82% As(V)). Below the $18\text{-}20 \text{ m}$ oxidized zone, reduced As phases again dominate (Figure 2). Arsenic sulfides present in sediments likely result from incorporation of As in authigenic Fe-sulfide minerals (Lowers et al., 2007).

3.2.3 Solid-phase Iron Speciation

3.2.3.1 Mössbauer Spectroscopy

Mössbauer spectroscopic analysis of sediments reveals that Fe exists in a combination of phases at each depth analyzed; they can, however, be represented effectively by three phases: Fe(II), silicate-bound Fe(III), and goethite/Fe-oxide (Figure 4, Table EA-1). Fe(II) spectral parameters are indicative of Fe(II) in primary minerals such as chlorite and talc (Blaauw et al., 1980), in reduced secondary silicates such as smectite (Schaefer et al., 2011), or Fe^{II} sorbed on mineral surfaces such as aluminum oxide or clays (Gehin et al., 2007; Larese-Casanova et al., 2010). Goethite was used as a representative Fe-oxide, and Mössbauer spectral parameters are consistent with goethite in each of the samples. Fe(III)-silicate minerals are assigned on the basis of an unordered Fe(III) doublet at 20 K (Murad and Cashion, 2004). Iron in oxidized sediment near the surface (Figure 4) is a mix of each of these phases, but ~40% of the Fe pool exists as Fe-oxide. In the relatively oxidized As-enriched zone (18-20 m), Fe-oxides are similarly abundant. From 18 m and below, the proportion of Fe-oxides decreases and a concomitant increase in Fe(II) is observed, while <5% change is observed in the Fe(III)-silicate fraction through the sediment profile.

3.2.3.2 Iron EXAFS Spectroscopy

EXAFS spectra were collected to determine the speciation of Fe phases in sediments. Comparison of Fe EXAFS spectra (Figure 5) shows changes in Fe mineral phase through the depth profile, and Fe mineralogy is closely linked to As dynamics in the aquifer (Figure 2). Surface sediments (1.5 m) contain ~30% (EXAFS) to ~40% (Mössbauer) of the Fe within Fe(III) oxides. The reduced zone below this depth (2.5 m and 7.1 m samples) contains Fe in silicate minerals, consistent with the instability of Fe-oxides under strong reducing conditions. Between

18 and 23 m depth, 25-50% of sediment Fe exists as oxides, consistent with more oxidized conditions at these depths. At 31 m depth a small amount of Fe sulfide (7%) improved linear combination fit results and is consistent with higher total sulfur content at this depth. However, Mössbauer results did not indicate the presence of Fe sulfides. Results of Fe EXAFS spectroscopy are generally consistent with results from Mössbauer spectroscopy (Figure 4, Figure 5, Table EA-1, Table EA-2).

3.2.4 Carbon NEXAFS Spectroscopy

Carbon 1s NEXAFS spectroscopy was used to probe the chemical speciation of carbon in aquifer sediments (Figure 6a). Spectra from all depths exhibit features generally observed in NEXAFS spectra of soil/sediment organic matter (SOM) including resonances indicating the presence of aromatic, phenolic, aliphatic, and carboxyl functional groups (Schumacher et al., 2005; Kleber et al., 2011). In all samples, a peak is observed at 285 eV indicative of aromatic C, whereas the shoulder feature at 287.5 eV indicates the presence of aliphatic compounds. The peak at ~288.5 eV indicates amide and carboxylate C. The peak at 290.3 eV, most prominent in the spectrum from 43.5 m, indicates the presence of carbonyl groups. The ratio of the intensity of peaks at 285 and 288.5 eV provides an indication of the relative aromaticity of the carbon in the sample (Kleber et al., 2011). The 285/288.5 peak ratio increases from 0.33 at 1.5 m to 0.47 at 17.9 m before decreasing to 0.28 between 20 to 23 m (Figure 6b). The decrease in peak ratio indicates a decrease in relative aromaticity of the carbon at these depths. In general, spectra throughout the profile are indicative of C in microbial biomass.

3.3 Batch Incubations and Extractions

To determine the potential for As partitioning from solid to aqueous phase over the sediment depth profile, we conducted batch incubations with DDI water or 2 mM glucose, as well as chemical extractions with 2 M HCl. When sediment is suspended in anoxic DDI water, arsenic is released from solids of the As-enriched zone at 20 m depth, but As release is limited at all other depths (Figure 7). The rate of As release in DDI water from sediments of 20 m depth is initially rapid, with 70% of net As release occurring within the first day of incubation (Figure EA-2, Figure EA-3). By day 4 of the incubation, 10% of total solid-phase As (Figure EA-4), or $11.4 \mu\text{g As g}^{-1}$, was released from the 20-m sediments in DDI. Total carbon is low at this depth (Figure 7, Table 2); accordingly, we tested (1) whether desorption is dominantly driven by chemically or biologically mediated processes and (2) whether arsenic release is limited by the reactivity of *in situ* carbon and Fe/As oxides.

Sediment incubations with 2 mM glucose resulted in $24.4 \mu\text{g As g}^{-1}$ (23%) released from 20 m-depth sediment, but similar to DDI incubations, $<1 \mu\text{g As g}^{-1}$ ($< 4\%$) was released from incubation of sediments from all other depths (Figure 7). Over a 4 d incubation, glucose addition enhanced As desorption approximately 2-fold compared to incubations with DDI water (Figure 7). Arsenic release rates in the presence of glucose were more extensive and over an extended time-period compared to DI water (Figure EA-2).

Sediment extractions with 2 M HCl liberate $58 \mu\text{g As g}^{-1}$ from 20 m-depth sediment, approximately half of the $107 \mu\text{g As g}^{-1}$ (Figure 2, Table 2). This amount exceeds As release observed in incubations with glucose by approximately 2-fold. Arsenic release from HCl

extractions has a similar trend over the depth profile to the incubations with glucose and DDI, but HCl extractions released more As, especially in near-surface sediments (Figure 7).

3.4 XAS Analysis of Incubated Sediment

Sediments incubated with glucose were analyzed by As K-edge XANES spectroscopy to evaluate changes in As speciation post-incubation (Figure 3). Glucose addition stimulates net reduction of As at all depths, as indicated by a net decrease in the arsenate fraction in all incubated samples (Figure 8). At depths with limited bulk carbon and sulfur (~18-25 m), solid phase As transitions from $\text{H}_x\text{AsO}_4^{3-x}$ to $\text{H}_x\text{AsO}_3^{3-x}$ after glucose addition, which promotes As desorption (Kocar et al., 2006; Tufano et al., 2008). We also observed transformation of $\text{H}_x\text{AsO}_3^{3-x}$ and $\text{H}_x\text{AsO}_4^{3-x}$ moieties to arsenic sulfide in sediments from 7, 31, and 43 m depth (Figure 8, Table 3). At these depths, glucose addition does not stimulate As release to the aqueous phase (Figure 7), but instead causes a transformation to As-sulfides (Figure 8, Table 3), sequestering As in the solid phase.

Batch incubation of sediment with glucose causes reduction of $\text{H}_x\text{AsO}_4^{3-x}$ to $\text{H}_x\text{AsO}_3^{3-x}$ in sediment retrieved from both 1.5 m and 20 m depths. Both sediments have carbon content <8 g kg⁻¹ and sulfur content <100 mg kg⁻¹; the arsenic content varies by nearly an order of magnitude from 12 mg kg⁻¹ at 1.5 m to 107 mg kg⁻¹ at 20 m. Initially, sediment from 1.5 m-depth has 85% $\text{H}_x\text{AsO}_4^{3-x}$, which decreases to 35% $\text{H}_x\text{AsO}_4^{3-x}$ at the end of incubation; likewise, the 20 m-depth sample decreases from 53% to 22% $\text{H}_x\text{AsO}_4^{3-x}$ after glucose incubation (Table 3). Arsenic sulfides were not detected by XANES analysis of either of these samples before or after glucose amendment (Table 3). Release of arsenic to the aqueous phase differed between

371 sediments from these two depths despite similar net reduction of As. Sediment collected from
372 1.5 m released $0.2 \mu\text{g As g}^{-1}$ sediment (1.4% arsenic released) while the 20 m sample released
373 ~100 times more arsenic, $24.4 \mu\text{g As g}^{-1}$ (23%), during incubation with glucose amendment
374 (Figure 7).

375

4. DISCUSSION

4.1 Controls on Arsenic Dissolution and Mobilization

Seasonal incursions of oxic surface water to the subsurface decrease groundwater As concentrations for 1-3 months annually. Rapid cycles in As concentrations are plausible in the presence of a deep source of As and a reaction pathway that can rapidly transfer As between solid and aqueous phases. The combination of a deep (20 m) sedimentary source of Fe-oxides and As with a C source that is reactive toward Fe and As reduction provides such a pathway. Arsenic release occurred from sediments approximately 20 m below the ground surface (Figure 7), coincident with peak dissolved As concentrations measured in the aquifer (Schaefer et al., 2016). Periods of surface water recharge coincide with low groundwater As concentrations via introduction of an oxidant during recharge; upon gradient reversal to groundwater discharge, and the cessation of oxidant delivery to the subsurface, anoxic conditions dominate along with elevated As concentrations (Schaefer et al., 2016). The rapid changes in As concentration within the Jiangnan plain suggest that As cycling is occurring at depths proximal to the screened wells at 25 m. Sediment at well-depths with the highest dissolved As concentrations (~20 m depth) in the Jiangnan plain contains $>100 \text{ mg As kg}^{-1}$ and provides a potential source of As. Sediments at ~20 m depth contained oxidized Fe(III) and As(V) (Figure 2) and ~0.2% carbon (Figure 7, Table 2) at the time of sediment coring. Iron(III) oxides account for 25-40% of the Fe pool between 18-23 m (Figure 4, Figure 5, Table EA-1, Table EA-2) and likely concentrate arsenic at this depth through the formation of arsenate/arsenite surface complexes (Waychunas et al., 1993; Fendorf et al., 1997; Dixit and Hering, 2003). Water in contact with oxidized sediments

containing Fe(III) oxides generally exhibits low dissolved arsenic concentrations due to the high affinity of arsenic oxoanions for Fe(III) mineral surfaces (Fendorf et al., 1997; Dixit and Hering, 2003). However, under Fe reducing conditions, As-bearing Fe(III) oxides undergo reductive dissolution, releasing As to the aqueous phase (Nickson et al., 2000; Islam et al., 2004; Pedersen et al., 2006; Tufano and Fendorf, 2008). A seasonal change to anoxic groundwater appears to induce reductive dissolution of arsenic from the Fe(III) oxide hosts.

The extent of As release from sediment is controlled by reduction of Fe(III) and As(V) (Nickson et al., 1998; Islam et al., 2004; Fendorf et al., 2010), but whether As-mobilizing reactions occur is dependent on both the Fe/As phase and organic matter available (Stuckey et al., 2016). Batch incubations of Jiangnan Plain sediment show that at ~20 m depth, As is transferred to the aqueous phase upon onset of anaerobic conditions without the need for an exogenous electron donor (Figure 7). Arsenic release occurs on the timescale of hours to days (Figure EA-2, Figure EA-3), which supports field data showing arsenic concentrations changing over weeks to months (Figure 1). Detrital carbon is reactive toward As host minerals at these depths. Carbon NEXAFS analysis indicates that organic matter co-located with As-enriched sediments (20-23 m) is more oxidized than adjacent sediments as indicated by a higher 288/285 eV peak ratio (Figure 6). LaRowe and Van Cappellen illustrated through a thermodynamic analysis that oxidized C is more easily metabolized in anaerobic environments than relatively reduced C compounds (LaRowe and Van Cappellen, 2011). The relatively oxidized C co-located with abundant sediment As could more effectively fuel Fe(III) reduction and As release compared to relatively reduced C compounds in adjacent sediments. Addition of electron donor (glucose) doubles the amount of As released to solution through (further) microbial reduction of As(V)

and Fe(III)-oxides (Figure 7); these reductive processes are known to be key drivers of As transfer from the solid to aqueous phase (Kocar et al., 2006; Tufano and Fendorf, 2008; Tufano et al., 2008). These results show that As release from sediment (of 20-m depth) is possible on the order of hours to days under simulated field conditions with or without addition of an exogenous carbon source for microbial respiration.

Although $\sim 10 \mu\text{g g}^{-1}$ As is released from 20 m sediment without the addition of a reduced carbon source, glucose addition doubles the amount of As released (Figure 7). Sediments from all depths that were amended with glucose undergo net reduction (Figure 7), but As release is limited to the near-surface and ~ 20 m sediments (Figure 7). Arsenic release in near-surface sediments may provide a sustained source of As to the aquifer while As (along with Fe) in the subsurface may be cycled between oxidized (insoluble) and reduced (soluble) phases. Increased As release with glucose addition implies that while carbon addition is not a prerequisite for As release (at the 1.5 and 20 m depths), the sediments could respond to inputs of DOC to the subsurface by releasing additional As through stimulated microbial reduction.

The depth of maximum bulk As concentration (~ 20 m) also results in the largest As release, but even on a mass-normalized basis the sediments at 20-23 m release 3-5 times more As than any other depth measured (Figure EA-4). In contrast, arsenic release from deep sediments does not occur in sediment incubations from the Mekong Delta (Stuckey et al., 2016). Similarly, a lack of As release without carbon amendment has also been observed in Bangladesh sediment incubations from 13 m (Islam et al., 2004) and 43 m depths (Dhar et al., 2011). In West Bengal, organic leaching from peat layers has been postulated to supply C utilized in Fe-oxide

reduction, releasing As to the aqueous phase (McArthur et al., 2004). However, we did not observe peat deposits in the shallow aquifer of the Jiangnan Plain and sediment C content is less than 3% throughout the sediment profile (Table 2).

4.2 Impacts on Seasonally Variable Arsenic Concentrations

Seasonal variation in groundwater As concentrations have not been reported for Bangladesh (Cheng et al., 2005) or West Bengal, India (McArthur et al., 2010), and seasonal variations are restricted to wells proximal to the Mekong River in Cambodia (Polizzotto et al., 2008). Within the noted systems of Bangladesh/West Bengal and Cambodia, recharge through fine-grained surface sediments means that transport of As and/or DOC from the surface to the aquifer is on the order of 10-100 years under natural conditions (Benner et al., 2008; Richards et al., 2016; Lawson et al., 2016) or on the order of decades with irrigation or other large-scale pumping (Harvey et al., 2006). Fracture flow has also been implicated in increasing infiltration rates through impermeable clay layers by two orders of magnitude in Bangladesh (Stahl et al., 2014). These previously measured flow rates are incompatible with the seasonal changes in groundwater arsenic concentrations observed in the Jiangnan Plain (Schaefer et al., 2016).

A deep sediment zone with high solid-phase As and a carbon source capable of providing electrons for As and Fe reduction would yield conditions suitable for rapid seasonal shifts in As concentrations in the aquifer—provided an oxidant is also seasonally supplied to the aquifer. During periods of groundwater discharge, reducing conditions prevail and As is released from buried sediments causing an increase in dissolved As concentrations (Figure 9B). When water

levels change and groundwater recharge occurs, an oxidant (O_2 , NO_3) is delivered to the reduced water causing a drop in As concentrations (Figure 9A).

Although surface recharge provides an oxidant that temporarily decreases As concentrations, it also may promote As reduction and release at depth during anoxic periods. Modest DOC influx from the surface can stimulate enhanced reactivity of buried carbon at depth (Fontaine et al., 2007), and influx of an oxidant such as O_2 has been shown to increase the reactivity of *in situ* carbon compounds via direct (self-priming) oxidation (Aller, 1994) or indirect (Hall and Silver, 2013) mechanisms that include production or activation of oxidative hydrolytic enzymes that initiate organic matter decomposition/alteration. Because a seasonal switch to aerobic conditions may make more C compounds subject to oxidation compared to anaerobic conditions (LaRowe and Van Cappellen, 2011; Keiluweit et al., 2016), seasonal incursions of O_2 could further oxidize C compounds that were thermodynamically unavailable under anaerobic conditions and provide a renewed source of oxidized C compounds seasonally. This annually renewed source of relatively oxidized C compounds would make Fe(III) reduction reactions thermodynamically viable after O_2 is consumed. Further, Fe(II) and As(III) are oxidized during this period, potentially forming a phase that is more reactive toward microbial reductive dissolution upon transition to anaerobic conditions. The decrease in $Fe(II)_{(aq)}$ also serves to make the energetics of Fe(III) reduction more viable following the aerobic period. Thus, dissolved oxygen, and possibly nitrate, that leads to a temporary decrease in As concentrations likely also regenerates the reactivity of the *in-situ* carbon source with As(V)-Fe(III) oxides, leading to season shifts in groundwater As concentrations of up to $1000 \mu g L^{-1}$.

4.3 Relevance to Other Major River Basins of Asia

Arsenic is mobilized through reductive dissolution of Fe/As oxides throughout Asia, but differences in the source of organic carbon and the reactivity of the Fe/As oxides varies. In the Red River Delta, sediment burial age and reactivity of sedimentary carbon have been used to explain spatial variation in As concentrations (Postma et al., 2012). In the Mekong Delta, the dominant process leading to As contaminated aquifers results from reduction of surficial fine-grained sediments combined with vertical transport of solutes to the aquifer (Polizzotto et al., 2008; Kocar et al., 2008); thus the spatial distribution of As depends on land surface features and hydrology. In the Ganges-Brahmaputra-Meghna delta system, a variety of carbon sources have been proposed to explain As concentrations in the subsurface. A process of surficial As release similar to the Mekong has been posited (Polizzotto et al., 2005) as well as Fe(III) reduction sustained by transport of surface-derived carbon to the subsurface (Harvey et al., 2002; Mailloux et al., 2013) or by detrital organic carbon (Meharg et al., 2006). In contrast, the processes controlling As concentrations in the Jiangnan Plain differ from As contaminated aquifers in South and Southeast Asia despite the similarities in sediment origin. Throughout the sediment profile in the Jiangnan Plain, arsenic exists as a combination of $H_xAsO_4^{3-x}$, $H_xAsO_3^{3-x}$, and arsenic sulfides (Figure 3, Table 3). However, unlike As-contaminated systems in South and Southeast Asia, sediment in the Jiangnan Plain is arsenic-enriched in an oxidized layer ~20 m below the surface (Figure 2), and As is readily released from aquifer sediments. Seasonal changes in As concentrations at the field site (Schaefer et al., 2016) are consistent with rapid As release in laboratory incubations (Figure EA-2, EA-3). Sediments with low carbon content would not release significant amounts of As without addition of an exogenous source of reactive

carbon such as inflow of DOC (Harvey et al., 2002; Neumann et al., 2010; Mailloux et al., 2013). However, we have previously shown that at this field area, groundwater recharge results in decreased As concentrations due to aquifer oxidation (Schaefer et al., 2016). In the Jiangnan plain, we find that detrital carbon is sufficiently reactive with *in-situ* Fe(III) minerals to cause reduction and transfer of As from the solid to aqueous phase.

4.4 Potential for Future Arsenic Release

Depth integration of bulk solid phase As concentrations (Figure 2, Table 2) shows that 390-728 g As per m² resides in the As-enriched zone alone. This implies that each m² of the field area containing similar stratigraphy has the potential to contaminate 39-73 x 10⁶ L (39,000-73,000 m³) of water to the 10 µg L⁻¹ level, or 390-730 m³ of water to 1000 µg L⁻¹. Guided by our batch incubations, we estimate that 10-20% of the sediment-associated As is easily mobilized and thus each square meter with similar stratigraphy has the potential to contaminate 39-73 m³ (10% release) or 78-146 m³ (20% release) of water to 1000 µg L⁻¹. Assuming a vertical column of water beneath this zone and a porosity of 0.4, the As-enriched zone could supply As sufficient to contaminate the entire aquifer to 1000 µg L⁻¹ to a depth of 100-360 m (using various assumptions and calculations of depth integration and 10-20% release). Finally, using conservative estimates (390 g As m⁻², 10% of As available for release, As-enriched zone as the sole source of As) the As-enriched zone needs to extend under only 5% of the land area to explain As concentrations throughout the aquifer in July 2013, the month of peak As concentrations observed at the site (Duan et al., 2015; Schaefer et al., 2016).

5. CONCLUSIONS

Annual variations in As, Fe(II), and S^{2-} concentrations in the Jiangnan Plain arise from seasonally shifting surface and groundwater flow gradients and an associated oscillation of reductive and oxidative processes (Schaefer et al., 2016). Arsenic-enriched sediment at ~20 m depth provides a source of As to the aquifer. Batch sediment incubations showed that the arsenic in this zone undergoes reductive dissolution, especially when stimulated by glucose addition (Figure 7), although an exogenous carbon source was not necessary for substantial As release. The oxidative formation and reductive dissolution of Fe(III)-oxides under seasonal redox changes explains the observed seasonal variability in As concentrations at the field area. These results support deep sediment reductive release of arsenic. Our observations suggest that within the Jiangnan plain sediments, under current conditions, organic carbon in the sediments is capable of promoting As release. However, we cannot discount the potential of surface derived DOC as an additional driver of As mobilization. Seasonal changes in groundwater flow likely drive redox cycling; the specific role of hydrological change in supplying or modifying organic carbon remains unknown but likely promotes the reactivity of both organic matter and As-bearing Fe(III) oxides.

From the Jiangnan plain, we surmise that As concentrations are altered by human activities changing subsurface hydrology and chemistry; land use changes that may alter arsenic include pond excavation (Neumann et al., 2010), groundwater extraction, and infiltration of organic compounds (Ziegler et al., 2015). Likewise, continued monitoring of As concentrations used for drinking and irrigation is necessary across Asia as we continue to understand the complex mechanisms leading to As contamination in Asian groundwater.

ACKNOWLEDGEMENTS

This work was funded by the National Natural Science Foundation of China (No. 41521001 and No. 41120124003) and the Chinese Ministry of Science and Technology (2014DFA20720). Portions of this work were also supported by the US National Science Foundation (grant number EAR-0952019), a US National Science Foundation Graduate Research Fellowship Program Grant No. DGE-114747 awarded to M.V. Schaefer, and the EVP program of Stanford's Woods Institute. We would like to thank Jay Dynes, Juan Salvador Lezama Pacheco, Marco Keiluweit, and Tom Regier for help with measurements and interpretation of XAS data and Yanhua Duan, Guangchao Li, Jason Stuckey, Doug Turner, Samantha Ying, and many staff and students at China University of Geoscience – Wuhan for help in the field and laboratory. Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource, a Directorate of SLAC National Accelerator Laboratory and an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University. Research described in this paper was performed at the Canadian Light Source, which is supported by the Canada Foundation for Innovation, Natural Sciences and Engineering Research Council of Canada, the University of Saskatchewan, the Government of Saskatchewan, Western Economic Diversification Canada, the National Research Council Canada, and the Canadian Institutes of Health Research.

REFERENCES

- Aller R. C. (1994) Bioturbation and remineralization of sedimentary organic matter: effects of redox oscillation. *Chem. Geol.* **114**, 331–345.
- Ayotte J. D., Belaval M., Olson S. A., Burow K. R., Flanagan S. M., Hinkle S. R. and Lindsey B. D. (2015) Factors affecting temporal variability of arsenic in groundwater used for drinking water supply in the United States. *Sci. Total Environ.* **505**, 1370–1379.
- Benner S. G., Polizzotto M. L., Kocar B. D., Ganguly S., Phan K., Ouch K., Sampson M. and Fendorf S. (2008) Groundwater flow in an arsenic-contaminated aquifer, Mekong Delta, Cambodia. *Appl. Geochem.* **23**, 3072–3087.
- Blaauw C., Stroink G. and Leiper W. (1980) Mössbauer analysis of talc and chlorite. *J Phys Colloq.* **41**, C1–411–C1–412.
- Cheng Z., van Geen A., Seddique A. A. and Ahmed K. M. (2005) Limited Temporal Variability of Arsenic Concentrations in 20 Wells Monitored for 3 Years in Araihaaz, Bangladesh. *Environ. Sci. Technol.* **39**, 4759–4766.
- Das N. K., Sengupta S. R. and others (2008) Arsenicosis: diagnosis and treatment. *Indian J. Dermatol. Venereol. Leprol.* **74**, 571.
- Dhar R. K., Zheng Y., Saltikov C. W., Radloff K. A., Mailloux B. J., Ahmed K. M. and van Geen A. (2011) Microbes Enhance Mobility of Arsenic in Pleistocene Aquifer Sand from Bangladesh. *Environ. Sci. Technol.* **45**, 2648–2654.
- Dixit S. and Hering J. G. (2003) Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environ. Sci. Technol.* **37**, 4182–4189.
- Duan Y., Gan Y., Wang Y., Deng Y., Guo X. and Dong C. (2015) Temporal variation of groundwater level and arsenic concentration at Jiangnan Plain, central China. *J. Geochem. Explor.* **149**, 106–119.
- Fendorf S., Eick M. J., Grossl P. and Sparks D. L. (1997) Arsenate and chromate retention mechanisms on goethite. 1. Surface structure. *Environ. Sci. Technol.* **31**, 315–320.
- Fendorf S., Michael H. A. and van Geen A. (2010) Spatial and Temporal Variations of Groundwater Arsenic in South and Southeast Asia. *Science* **328**, 1123–1127.
- Fontaine S., Barot S., Barré P., Bdioui N., Mary B. and Rumpel C. (2007) Stability of organic carbon in deep soil layers controlled by fresh carbon supply. *Nature* **450**, 277–280.
- Gan Y., Wang Y., Duan Y., Deng Y., Guo X. and Ding X. (2014) Hydrogeochemistry and arsenic contamination of groundwater in the Jiangnan Plain, central China. *J. Geochem. Explor.* **138**, 81–93.
- van Geen A., Zheng Y., Versteeg R., Stute M., Horneman A., Dhar R., Steckler M., Gelman A., Small C., Ahsan H., Graziano J. H., Hussain I. and Ahmed K. M. (2003) Spatial

- 600 variability of arsenic in 6000 tube wells in a 25 km² area of Bangladesh. *Water Resour.*
601 *Res.* **39**, 1140.
- 602 Gehin A., Greneche J. M., Tournassat C., Brendle J., Rancourt D. G. and Charlet L. (2007)
603 Reversible surface-sorption-induced electron-transfer oxidation of Fe(II) at reactive sites
604 on a synthetic clay mineral. *Geochim. Cosmochim. Acta* **71**, 863–876.
- 605 Hall S. J. and Silver W. L. (2013) Iron oxidation stimulates organic matter decomposition in
606 humid tropical forest soils. *Glob. Change Biol.* **19**, 2804–2813.
- 607 Harvey C. F., Ashfaq K. N., Yu W., Badruzzaman A. B. M., Ali M. A., Oates P. M., Michael
608 H. A., Neumann R. B., Beckie R., Islam S. and Ahmed M. F. (2006) Groundwater
609 dynamics and arsenic contamination in Bangladesh. *Chem. Geol.* **228**, 112–136.
- 610 Harvey C. F., Swartz C. H., Badruzzaman A. B. M., Keon-Blute N., Yu W., Ali M. A., Jay J.,
611 Beckie R., Niedan V., Brabander D., Oates P. M., Ashfaq K. N., Islam S., Hemond H.
612 F. and Ahmed M. F. (2002) Arsenic mobility and groundwater extraction in Bangladesh.
613 *Science* **298**, 1602–1606.
- 614 Hitchcock A. P., Hitchcock P., Jacobsen C., Zimba C., Loo B., Rotenberg E., Denlinger J. and
615 Kneedler R. (2012) aXis 2000—Analysis of X-ray Images and Spectra. *McMaster Univ.*
616 *Hamilt.*
- 617 Islam F. S., Gault A. G., Boothman C., Polya D. A., Charnock J. M., Chatterjee D. and Lloyd J.
618 R. (2004) Role of metal-reducing bacteria in arsenic release from Bengal delta sediments.
619 *Nature* **430**, 68–71.
- 620 Keiluweit M., Nico P. S., Kleber M. and Fendorf S. (2016) Are oxygen limitations under
621 recognized regulators of organic carbon turnover in upland soils? *Biogeochemistry*, 1–15.
- 622 Kleber M., Nico P. S., Plante A., Filley T., Kramer M., Swanston C. and Sollins P. (2011) Old
623 and stable soil organic matter is not necessarily chemically recalcitrant: implications for
624 modeling concepts and temperature sensitivity. *Glob. Change Biol.* **17**, 1097–1107.
- 625 Kocar B. D., Herbel M. J., Tufano K. J. and Fendorf S. (2006) Contrasting effects of
626 dissimilatory iron(III) and arsenic(V) reduction on arsenic retention and transport.
627 *Environ. Sci. Technol.* **40**, 6715–6721.
- 628 Kocar B. D., Polizzotto M. L., Benner S. G., Ying S. C., Ung M., Ouch K., Samreth S., Suy B.,
629 Phan K., Sampson M. and Fendorf S. (2008) Integrated biogeochemical and hydrologic
630 processes driving arsenic release from shallow sediments to groundwaters of the Mekong
631 delta. *Appl. Geochem.* **23**, 3059–3071.
- 632 Larese-Casanova P., Cwiertny D. M. and Scherer M. M. (2010) Nanogoethite Formation from
633 Oxidation of Fe(II) Sorbed on Aluminum Oxide: Implications for Contaminant
634 Reduction. *Environ. Sci. Technol.* **44**, 3765–3771.

- 635 LaRowe D. E. and Van Cappellen P. (2011) Degradation of natural organic matter: A
636 thermodynamic analysis. *Geochim. Cosmochim. Acta* **75**, 2030–2042.
- 637 Lawson M., Polya D. A., Boyce A. J., Bryant C. and Ballentine C. J. (2016) Tracing organic
638 matter composition and distribution and its role on arsenic release in shallow Cambodian
639 groundwaters. *Geochim. Cosmochim. Acta* **178**, 160–177.
- 640 Lowers H. A., Breit G. N., Foster A. L., Whitney J., Yount J., Uddin M. N. and Muneem A. A.
641 (2007) Arsenic incorporation into authigenic pyrite, Bengal Basin sediment, Bangladesh.
642 *Geochim. Cosmochim. Acta* **71**, 2699–2717.
- 643 Mailloux B. J., Trembath-Reichert E., Cheung J., Watson M., Stute M., Freyer G. A., Ferguson
644 A. S., Ahmed K. M., Alam M. J., Buchholz B. A., Thomas J., Layton A. C., Zheng Y.,
645 Bostick B. C. and Geen A. van (2013) Advection of surface-derived organic carbon fuels
646 microbial reduction in Bangladesh groundwater. *Proc. Natl. Acad. Sci.* **110**, 5331–5335.
- 647 McArthur J. M., Banerjee D. M., Hudson-Edwards K. A., Mishra R., Purohit R., Ravenscroft P.,
648 Cronin A., Howarth R. J., Chatterjee A., Talukder T., Lowry D., Houghton S. and
649 Chadha D. K. (2004) Natural organic matter in sedimentary basins and its relation to
650 arsenic in anoxic ground water: the example of West Bengal and its worldwide
651 implications. *Appl. Geochem.* **19**, 1255–1293.
- 652 McArthur J. M., Banerjee D. M., Sengupta S., Ravenscroft P., Klump S., Sarkar A., Disch B. and
653 Kipfer R. (2010) Migration of As, and $3\text{H}/3\text{He}$ ages, in groundwater from West Bengal:
654 Implications for monitoring. *Water Res.* **44**, 4171–4185.
- 655 Meharg A. A., Scrimgeour C., Hossain S. A., Fuller K., Cruickshank K., Williams P. N. and
656 Kinniburgh D. G. (2006) Codeposition of Organic Carbon and Arsenic in Bengal Delta
657 Aquifers. *Environ. Sci. Technol.* **40**, 4928–4935.
- 658 Michael H. A. (2013) An Arsenic Forecast for China. *Science* **341**, 852–853.
- 659 Murad E. and Cashion J. (2004) *Mossbauer Spectroscopy of Environmental Materials and their*
660 *Industrial Utilization.*, Kluwer Academic Publishers.
- 661 Naujokas M. F., Anderson B., Ahsan H., Aposhian H. V., Graziano J. H., Thompson C. and Suk
662 W. A. (2013) The Broad Scope of Health Effects from Chronic Arsenic Exposure:
663 Update on a Worldwide Public Health Problem. *Environ. Health Perspect.* **121**, 295–302.
- 664 Neumann R. B., Ashfaq K. N., Badruzzaman A. B. M., Ali M. A., Shoemaker J. K. and
665 Harvey C. F. (2010) Anthropogenic influences on groundwater arsenic concentrations in
666 Bangladesh. *Nat. Geosci.* **3**, 46–52.
- 667 Nickson R., McArthur J., Burgess W., Ahmed K. M., Ravenscroft P. and Rahman M. (1998)
668 Arsenic poisoning of Bangladesh groundwater. *Nature* **395**, 338–338.

- 669 Nickson R. T., McArthur J. M., Ravenscroft P., Burgess W. G. and Ahmed K. M. (2000)
 670 Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Appl.*
 671 *Geochem.* **15**, 403–413.
- 672 Pedersen H. D., Postma D. and Jakobsen R. (2006) Release of arsenic associated with the
 673 reduction and transformation of iron oxides. *Geochim. Cosmochim. Acta* **70**, 4116–4129.
- 674 Polizzotto M. L., Harvey C. F., Sutton S. R. and Fendorf S. (2005) Processes conducive to the
 675 release and transport of arsenic into aquifers of Bangladesh. *Proc. Natl. Acad. Sci. U. S.*
 676 *A.* **102**, 18819–18823.
- 677 Polizzotto M. L., Kocar B. D., Benner S. G., Sampson M. and Fendorf S. (2008) Near-surface
 678 wetland sediments as a source of arsenic release to ground water in Asia. *Nature* **454**,
 679 505–U5.
- 680 Postma D., Larsen F., Thai N. T., Trang P. T. K., Jakobsen R., Nhan P. Q., Long T. V., Viet P.
 681 H. and Murray A. S. (2012) Groundwater arsenic concentrations in Vietnam controlled
 682 by sediment age. *Nat. Geosci.* **5**, 656–661.
- 683 Rancourt D. G. and Ping J. Y. (1991) Voight-based methods for arbitrary-shape static hyperfine
 684 parameter distributions in Mössbauer spectroscopy. *Nucl. Instrum. Methods Phys. Res.*
 685 **B58**, 85–97.
- 686 Ravel B. and Newville M. (2005) ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-
 687 ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* **12**, 537–541.
- 688 Richards L. A., Sültenfuß J., Magnone D., Boyce A., Sovann C., Casanueva-Marengo M. J.,
 689 Ballentine C. J., van Dongen B. E. and Polya D. A. (2016) Age and provenance of
 690 groundwater in a shallow arsenic-affected aquifer in the lower Mekong Basin, Kandal
 691 Province, Cambodia. In *Arsenic Research and Global Sustainability: Proceedings of the*
 692 *Sixth International Congress on Arsenic in the Environment (As2016), June 19-23, 2016,*
 693 *Stockholm, Sweden* CRC Press. p. 74. Available at:
 694 [https://books.google.com/books?hl=en&lr=&id=XwBPDAAAQBAJ&oi=fnd&pg=PA74](https://books.google.com/books?hl=en&lr=&id=XwBPDAAAQBAJ&oi=fnd&pg=PA74&ots=Nf1qE1RnUT&sig=1RhAhMPe0x0XVKpFgwT-D1QeLtM)
 695 [&ots=Nf1qE1RnUT&sig=1RhAhMPe0x0XVKpFgwT-D1QeLtM](https://books.google.com/books?hl=en&lr=&id=XwBPDAAAQBAJ&oi=fnd&pg=PA74&ots=Nf1qE1RnUT&sig=1RhAhMPe0x0XVKpFgwT-D1QeLtM) [Accessed July 22,
 696 2016].
- 697 Rodríguez-Lado L., Sun G., Berg M., Zhang Q., Xue H., Zheng Q. and Johnson C. A. (2013)
 698 Groundwater Arsenic Contamination Throughout China. *Science* **341**, 866–868.
- 699 Schaefer M. V., Gorski C. A. and Scherer M. M. (2011) Spectroscopic Evidence for Interfacial
 700 Fe(II)–Fe(III) Electron Transfer in a Clay Mineral. *Environ. Sci. Technol.* **45**, 540–545.
- 701 Schaefer M. V., Ying S. C., Benner S. G., Duan Y., Wang Y. and Fendorf S. (2016) Aquifer
 702 Arsenic Cycling Induced by Seasonal Hydrologic Changes within the Yangtze River
 703 Basin. *Environ. Sci. Technol.* **50**, 3521–3529.
- 704 Schumacher M., Christl I., Scheinost A. C., Jacobsen C. and Kretzschmar R. (2005) Chemical
 705 Heterogeneity of Organic Soil Colloids Investigated by Scanning Transmission X-ray

- 706 Microscopy and C-1s NEXAFS Microspectroscopy. *Environ. Sci. Technol.* **39**, 9094–
707 9100.
- 708 Smedley P. L. and Kinniburgh D. G. (2002) A review of the source, behaviour and distribution
709 of arsenic in natural waters. *Appl. Geochem.* **17**, 517–568.
- 710 Stahl M. O., Tarek M. H., Yeo D. C. J., Badruzzaman A. B. M. and Harvey C. F. (2014) Crab
711 burrows as conduits for groundwater-surface water exchange in Bangladesh. *Geophys.*
712 *Res. Lett.* **41**, 2014GL061626.
- 713 Steinmaus C., Moore L., Hopenhayn-Rich C., Biggs M. L. and Smith A. H. (2000) Arsenic in
714 Drinking Water and Bladder Cancer: Environmental Carcinogenesis. *Cancer Invest.* **18**,
715 174–182.
- 716 Stuckey J. W., Schaefer M. V., Kocar B. D., Benner S. G. and Fendorf S. (2016) Arsenic release
717 metabolically limited to permanently water-saturated soil in Mekong Delta. *Nat. Geosci.*
718 **9**, 70–76.
- 719 Tamura H., Goto K., Yotsuyanagi T. and Nagayama M. (1974) Spectrophotometric
720 determination of iron (II) with 1, 10-phenanthroline in the presence of large amounts of
721 iron (III). *Talanta* **21**, 314–318.
- 722 Tufano K. J. and Fendorf S. (2008) Confounding impacts of iron reduction on arsenic retention.
723 *Environ. Sci. Technol.* **42**, 4777–4783.
- 724 Tufano K. J., Reyes C., Saltikov C. W. and Fendorf S. (2008) Reductive Processes Controlling
725 Arsenic Retention: Revealing the Relative Importance of Iron and Arsenic Reduction.
726 *Environ. Sci. Technol.* **42**, 8283–8289.
- 727 Wasserman G. A., Liu X. H., Parvez F., Ahsan H., Factor-Litvak P., van Geen A., Slavkovich
728 V., Lolacono N. J., Cheng Z. Q., Hussain L., Momotaj H. and Graziano J. H. (2004)
729 Water arsenic exposure and children's intellectual function in Araihaazar, Bangladesh.
730 *Environ. Health Perspect.* **112**, 1329–1333.
- 731 Wasserman G. A., Liu X., Parvez F., Ahsan H., Factor-Litvak P., Kline J., Geen A. van,
732 Slavkovich V., Lolacono N. J., Levy D., Cheng Z. and Graziano J. H. (2007) Water
733 Arsenic Exposure and Intellectual Function in 6-Year-Old Children in Araihaazar,
734 Bangladesh. *Environ. Health Perspect.* **115**, 285–289.
- 735 Waychunas G. A., Rea B. A., Fuller C. C. and Davis J. A. (1993) Surface chemistry of
736 ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed
737 arsenate. *Geochim. Cosmochim. Acta* **57**, 2251–2269.
- 738 Winkel L. H. E., Trang P. T. K., Lan V. M., Stengel C., Amini M., Ha N. T., Viet P. H. and Berg
739 M. (2011) Arsenic pollution of groundwater in Vietnam exacerbated by deep aquifer
740 exploitation for more than a century. *Proc. Natl. Acad. Sci.* **108**, 1246–1251.

- 741 Zhang Y., Li C., Wang Q., Chen L., Ma Y. and Kang C. (2008) Magnetism parameters
742 characteristics of drilling deposits in Jiangnan Plain and indication for forming of the
743 Yangtze River Three Gorges. *Chin. Sci. Bull.* **53**, 584–590.
- 744 Ziegler B. A., McGuire J. T. and Cozzarelli I. M. (2015) Rates of As and Trace-Element
745 Mobilization Caused by Fe Reduction in Mixed BTEX–Ethanol Experimental Plumes.
746 *Environ. Sci. Technol.* **49**, 13179–13189.
- 747

TABLES

Table 1. Groundwater Chemistry for the Jiangnan Plain Site from May 2012 to December 2014

Parameter	min	max	mean	median	n
Arsenic ($\mu\text{g L}^{-1}$)	b.d. ¹	1205	65	35	1240
Sulfide ($\mu\text{g L}^{-1}$)	b.d.	476	39	15	1105
Iron (mg L^{-1})	b.d.	39.8	5.1	4.2	1198
Manganese (mg L^{-1})	b.d.	9.58	1.3	0.68	1185
Conductivity ($\mu\text{S cm}^{-1}$)	233	1585	922	874	1202
Eh (mV)	9.6	471	130	119	1199
pH	5.96	7.89	7.12	7.13	1202
Temperature ($^{\circ}\text{C}$)	12.9	26.4	19.3	19.3	1202

¹below detection

Table 2. Bulk Elemental Concentrations of Sediment Samples

Depth	C	Al	Si	P	S	Ti	Mn	Fe	As
m	g/kg	g/kg	g/kg	mg/kg	mg/kg	g/kg	mg/kg	g/kg	mg/kg
1.5	7.9	117	294	610	96	4.8	931	49.2	12.2
2.5	7.9	132	274	580	121	4.6	855	61.3	19.2
3.7	15.9	96	245	433	315	5.0	539	52.7	11.7
4.7	14.4	114	243	367	1055	4.8	501	50.1	17.2
5.9	13.6	105	315	557	379	4.4	639	38.1	6.4
7.1	11.3	93	261	582	410	5.1	780	46.7	11.3
8.3	18.2	99	246	408	2545	4.8	408	53.9	8.4
9.5	27.1	83	232	580	464	5.3	1083	47.3	3.9
10.3	19.9	69	248	476	871	4.1	636	33.9	1.8
11.9	18.1	62	253	447	890	3.7	523	28.2	0.0
12	18.4	72	247	469	1130	4.2	602	33.8	2.2
14.1	13.7	71	272	506	595	4.4	524	30.3	2.8
14.3	6.6	75	255	503	495	4.7	719	38.7	1.5
15.2	1.6	103	324	392	113	4.2	331	40.1	1.4
16.5	19.6	98	249	463	1665	4.5	514	51.4	9.9
17.9	2.7	96	259	919	12	5.1	870	55.4	20.0
18.7	1.4	107	313	812	20	4.4	690	43.1	88.2
20.1	1.6	86	316	1139	21	4.9	616	35.6	107.5
21.9	0.4	81	353	923	52	3.9	470	26.5	4.4
23.3	1.2	99	318	1239	31	4.4	909	38.0	24.2
25.1	0.5	79	352	1077	46	4.0	510	27.4	6.0
26.8	0.6	91	345	746	165	3.6	321	25.4	0.0
28.9	2.2	81	275	530	255	3.8	441	27.4	3.3
30.1	6.7	67	266	5555	134	4.1	441	27.6	0.0
30.9	22.6	60	235	253	2034	3.1	504	31.1	25.6
31.6	3.9	57	256	499	567	3.7	415	23.1	0.0
35.2	5.8	85	258	533	1111	4.2	701	37.4	7.2
37	2.5	117	311	635	33	4.9	220	53.4	9.9
37.9	12.1	70	239	399	540	3.6	603	29.1	1.0
41.2	5.6	39	259	267	2313	1.7	272	9.5	0.7
42.3	16.6	105	290	689	306	4.6	881	47.5	11.1
43.5	17.9	110	279	731	281	4.4	1064	54.1	15.5
44.7	20.3	109	280	606	301	4.5	948	49.1	13.8
48.5	9.7	44	253	779	566	1.8	1022	17.6	5.5
50.3	16.7	60	240	383	508	3.4	484	27.2	1.4
51.4	6.2	48	286	361	849	2.2	478	16.3	3.7

Table 3. Arsenic Speciation Determined by As K-edge XANES Spectroscopy.

Depth (m)	Native Sediment			Glucose Incubations			Change in Species Abundance		
	Arsenian Pyrite	H ₃ AsO ₃ ³⁻	H ₃ AsO ₄ ³⁻	Arsenian Pyrite	H ₃ AsO ₃ ³⁻	H ₃ AsO ₄ ³⁻	ΔArsenian Pyrite	ΔH ₃ AsO ₃ ³⁻	ΔH ₃ AsO ₄ ³⁻
1.5	0.00	0.15	0.85	0.04	0.61	0.35	+0.04	+0.46	-0.50
2.5	0.03	0.60	0.37	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7.1	0.23	0.51	0.25	0.35	0.56	0.09	+0.12	+0.05	-0.17
17.9	0.00	0.66	0.34	0.00	0.77	0.23	+0.00	+0.11	-0.11
18.7	0.00	0.18	0.82	0.00	0.19	0.81	+0.00	+0.02	-0.02
20.1	0.00	0.47	0.53	0.00	0.78	0.22	+0.00	+0.32	-0.32
23.3	0.00	0.80	0.20	0.00	0.85	0.15	+0.00	+0.05	-0.05
30.9	0.86	0.09	0.06	0.90	0.10	0.00	+0.04	+0.01	-0.06
43.5	0.24	0.73	0.03	0.30	0.70	0.00	+0.06	-0.04	-0.03

FIGURES

Figure 1. Difference in surface water and groundwater level (SW-GW), and aqueous concentrations of Fe(II) and arsenic, from June 2012–November 2014. Data are from 25 m at the site of sediment collection.

Figure 2. Sediment characterization at borehole SY03. Bulk As content (small circles and grey fill) and arsenate fraction (filled blue circles), bulk ferric fraction determined by Mössbauer spectroscopy (filled red squares), and extractable ferric fraction (open red squares) are plotted as a function of sediment collection depth. Bulk As concentrations were measured by X-ray fluorescence (XRF). Ferric-iron fractions were determined from speciation of 2M HCl extracts and represent the Fe(III) fraction of the extracted Fe, not the bulk Fe oxidation state. Arsenate speciation was determined by linear combination fits of bulk As K-edge XANES spectra (complete XANES spectral fits are provided in Figure 2). Sediment texture is shown on the right for reference.

Figure 3. Arsenic K-edge XANES spectra of sediment from borehole SY03. The solid grey line shows normalized absorbance of an average of 3 to 8 spectra. The dotted black line is the best fit determined by linear combination fitting using the three standards shown.

Figure 4. Mössbauer spectra of sediment samples recovered at borehole SY03. All spectra were collected at a temperature of 20 K. Each spectrum was fit as a combination of three Fe phases: an octahedral Fe(II) doublet (solid black), an octahedral Fe(III) doublet that did not magnetically order at 20 K (solid grey), and a goethite sextet that magnetically ordered at 20 K. The solid line shows the overall fit. While the sextet parameters are indicative of goethite, our interpretation is limited to classifying this phase as a Fe(III) oxide. Mössbauer spectral fit parameters and the relative abundance of each phase are provided in Table SI-1.

Figure 5. Fe K-edge EXAFS spectra (solid lines) and least squares fit results (dashed lines) for sediment samples collected between 1.5 and 30.9 m depth.

Figure 6. Carbon near-edge X-ray absorption fine structure (NEXAFS) spectra of sediments collected from 1.5 to 43.5 m below ground level. (a) Normalized fluorescence spectra for sediment at eight depths. Solid black lines are data. Solid blue lines show Gaussian peak positions used to fit all spectra. Peak heights shown are the solution of the least-squares fit for sediment at 1.5 m depth, and the fit is shown overlaid on the 1.5 m spectrum as dashed blue lines. Peak numbers correspond to the following moieties: 1 quinone, 2 aromatic, 3 phenolic, 4 aliphatic, 5 carboxyl/amide, 6 O-alkyl, 7 carbonate. (b) The ratio of peak height of aromatic (285.1 eV) to carboxyl/amide (288.6 eV) peaks describe the aromaticity of sediment samples as a function of sediment depth.

Figure 7. (a) Arsenic release to solution in batch incubations with deionized water, 2 mM glucose, or extraction in 2 M HCl. Arsenic concentrations (DI and 2 mM glucose; average of duplicates) batch reactors were measured after 4 days of incubation at 25 °C. HCl extractions were performed in triplicate. (b) Carbon bulk abundance as a function of sediment collection depth. The grey box highlights the increase in As release where bulk C content is at a minimum.

Figure 8. (a) Change in solid phase arsenic speciation after batch incubation of sediment with 2 mM glucose for 4 days. Differences are determined by comparing the results of As K-edge XANES linear combination fits (LCF) determined on native sediment to LCF of sediment incubated in batch reactors with glucose. (b) Bulk sulfur concentration as a function of sediment collection depth (black circles) and As sulfide fraction of native sediment (blue circles). Red symbols indicate the As sulfide fraction determined by LCF after glucose incubation. The difference between the blue circle and the red x at a given depth result in the data shown in panel A.

A

Figure 9. Schematic diagram of the dominant redox processes occurring during (a) groundwater recharge and (b) groundwater discharge.