



RESEARCH ARTICLE

10.1002/2016WR018891

Key Points:

- Rates of arsenic release from young riverbed sediments are up to 1000 times the release rates from aquifer sediment
- River recharge induced by groundwater pumping may contaminate previously safe aquifers with arsenic
- Riverbank geomorphology can influence groundwater arsenic concentrations in aquifers adjacent to rivers

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Citation:

Stahl, M. O., C. F. Harvey, A. van Geen, J. Sun, P. Thi Kim Trang, V. Mai Lan, T. Mai Phuong, P. Hung Viet, and B. C. Bostick (2016), River bank geomorphology controls groundwater arsenic concentrations in aquifers adjacent to the Red River, Hanoi Vietnam, *Water Resour. Res.*, 52, 6321–6334, doi:10.1002/2016WR018891.

Received 6 MAR 2016

Accepted 25 JUL 2016

Accepted article online 29 JUL 2016

Published online 18 AUG 2016

River bank geomorphology controls groundwater arsenic concentrations in aquifers adjacent to the Red River, Hanoi Vietnam

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Abstract Many aquifers that are highly contaminated by arsenic in South and Southeast Asia are in the floodplains of large river networks. Under natural conditions, these aquifers would discharge into nearby rivers; however, large-scale groundwater pumping has reversed the flow in some areas so that rivers now recharge aquifers. At a field site near Hanoi Vietnam, we find river water recharging the aquifer becomes high in arsenic, reaching concentrations above 1000 $\mu\text{g/L}$, within the upper meter of recently ($< \sim 10$ years) deposited riverbed sediments as it is drawn into a heavily pumped aquifer along the Red River. Groundwater arsenic concentrations in aquifers adjacent to the river are largely controlled by river geomorphology. High ($> 50 \mu\text{g/L}$) aqueous arsenic concentrations are found in aquifer regions adjacent to zones where the river has recently deposited sediment and low arsenic concentrations are found in aquifer regions adjacent to erosional zones. High arsenic concentrations are even found adjacent to a depositional river reach in a Pleistocene aquifer, a type of aquifer sediment which generally hosts low arsenic water. Using geochemical and isotopic data, we estimate the in situ rate of arsenic release from riverbed sediments to be up to 1000 times the rates calculated on inland aquifer sediments in Vietnam. Geochemical data for riverbed porewater conditions indicate that the reduction of reactive, poorly crystalline iron oxides controls arsenic release. We suggest that aquifers in these regions may be susceptible to further arsenic contamination where riverine recharge drawn into aquifers by extensive groundwater pumping flows through recently deposited river sediments before entering the aquifer.

1. Introduction

Contamination of groundwater with geogenic arsenic is widespread throughout South and Southeast Asia and poses a health risk to millions of individuals who consume this water [Fendorf *et al.*, 2010]. High arsenic groundwater is generally confined to Holocene aquifers [BGS, 2001], whereas Pleistocene aquifer sediments normally host low arsenic groundwater [BGS, 2001; Pal *et al.*, 2002; McArthur *et al.*, 2004; von Brömssen *et al.*, 2007; van Geen *et al.*, 2013]. However, recent work has shown that Pleistocene aquifers may be vulnerable to arsenic contamination as a result of groundwater pumping induced inflow from adjacent contaminated Holocene aquifers [van Geen *et al.*, 2013].

Groundwater pumping can also influence the exchange of water at the river-aquifer interface; drawing river water into aquifers that would have discharged to the river under natural conditions. Several arsenic-affected aquifer systems already appear to be altered (e.g., changes in groundwater geochemistry and groundwater flow patterns) by the capture of river recharge due to groundwater pumping [Berg *et al.*, 2008; Trafford and Lawrence, 1996; Bui *et al.*, 2012; Shamsudduha *et al.*, 2011; Hoqueet *et al.*, 2007; Winkel *et al.*, 2011] and these effects can be expected grow as our reliance on groundwater resources continues to expand [Wada *et al.*, 2012]. Recharging river water flows through sediments at the surface-water groundwater interface which are frequently characterized by steep redox gradients and vigorous metal cycling [Canfield *et al.*, 1993; Polizzotto *et al.*, 2008; Charette *et al.*, 2005; Nagorski and Moore, 1999]. Given that the reductive dissolution of arsenic-bearing iron-oxides is widely accepted as the main cause of arsenic contamination

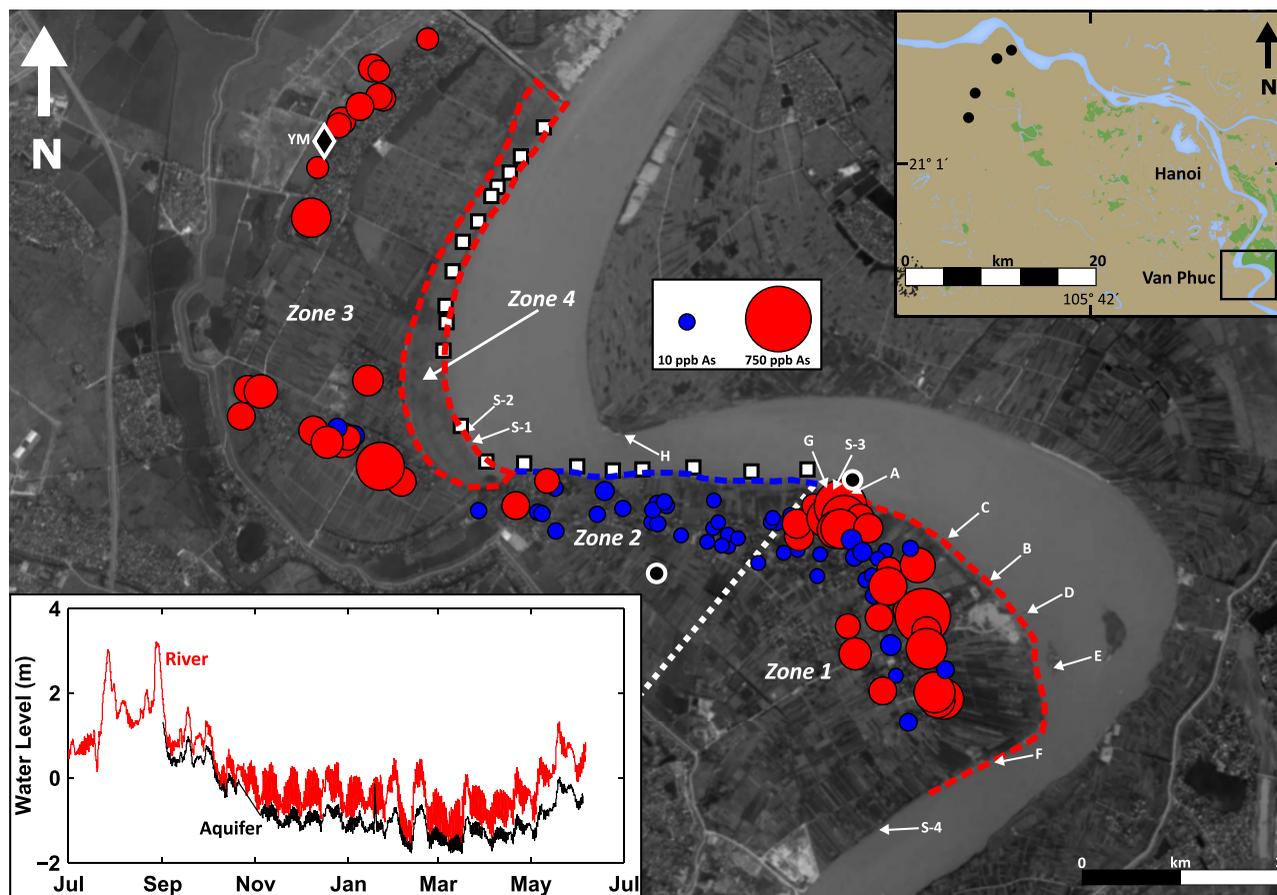


Figure 1. Map of Van Phuc study area showing groundwater arsenic concentrations from local wells represented as circles scaled to their concentrations (red if $\text{As} \geq 50 \mu\text{g/L}$ and blue if $\text{As} < 50 \mu\text{g/L}$). Locations of riverbed porewater sampling are indicated by the letters A–H (locations with porewater depth profiles) and S-1 to S-4 (locations with only one porewater sample). White squares with black borders indicate locations where cores of river sediment were collected for XRF analysis. Red-dashed lines indicate depositional areas and blue-dashed lines indicate areas of erosion. White-dashed line shows the interface between Holocene (east of the line) and Pleistocene (west of the line) sediments that was described by *van Geen et al.* [2013]. Zones 1 through 4 are described in the discussions and conclusions section of the text. Plot in bottom left corner shows water levels in the river and aquifer from July 2010 to June 2011 and the black circles outlined in white show the locations of the river and aquifer water level measurements. The black diamond outlined in white and labeled 'YM' shows the location where drilling for sediment samples was conducted. Inset map shows the location of Van Phuc (bounded by black box) and four study sites (black circles) where *Postma et al.* [2012] measured arsenic release rates.

throughout the region [*McArthur et al.*, 2001; *Swartz et al.*, 2004; *Postma et al.*, 2007; *BGS*, 2001], we hypothesize that riverine recharge can either flush or contaminate adjacent aquifers with arsenic depending on the rate of arsenic mobilization from sediment. Furthermore, we hypothesize that the release of arsenic during riverine recharge will be influenced by river geomorphology which controls the delivery of arsenic bearing sediments to the river-aquifer interface.

Our study focuses on the river-aquifer interface in Van Phuc, Vietnam, a village 10 km southeast of Hanoi, which is located within a meander bend of the Red River (Figure 1). A notable feature of our site is the juxtaposition of Holocene and Pleistocene aquifers abutting both depositional and nondepositional river reaches. Groundwater arsenic concentrations in Van Phuc frequently exceed the World Health Organization (WHO) limit of $0.13 \mu\text{M}$ ($10 \mu\text{g/L}$) by a factor of at least 10, though there is substantial spatial variation in arsenic levels [*van Geen et al.*, 2013]. Located next to the Red River and within the influence of Hanoi's massive groundwater pumping, the aquifer at Van Phuc now receives recharge from the Red River throughout much of the year [*van Geen et al.*, 2013; *Berg et al.*, 2008].

The primary objective of this study is to investigate how surface water recharge impacts groundwater arsenic concentrations in a variety of geomorphic and geologic settings. To investigate how the induced riverine recharge affects arsenic concentrations within the aquifer, we characterize the geochemistry of the river water as it recharges the aquifer (i.e. riverbed pore water) as well as the groundwater further inland. We

perform a geologic/geomorphic characterization of our field site in order to identify how arsenic concentrations in different geologic settings (i.e. Holocene versus Pleistocene) and geomorphic settings (i.e. depositional versus nondepositional river reaches) respond to riverine recharge. In addition we use stable water isotopes to estimate the residence time of riverbed porewater samples and thus estimate the in situ arsenic release rates. We compare our estimates of in situ arsenic release rate to estimates from the literature and we examine the influence of sediment age on the rate of arsenic release.

2. Methods

2.1. Water Sampling and Analysis

To characterize riverine recharge chemistry, we collected porewater samples from the riverbed along the banks of the Red River in Van Phuc at five locations in June 2010, five locations in November 2011, and two locations in May 2012 (Figure 1). At each location, we attempted to collect porewater samples at 0.1, 0.5, and 1 m into the riverbed. Samples were collected by pushing in a 3.2 mm diameter stainless steel sampler (M.H.E Products PushPoint) with a 4 cm long screened interval into the sediment and drawing up a sample with a syringe. After flushing with several syringe volumes, a sample was collected and the temperature, pH, redox potential (Eh), and electrical conductivity were measured using field probes. At the start of each field day, the pH probe was calibrated in pH 4 and 7 buffers and the redox probe was calibrated in ZoBell's solution. Samples for metal analysis were filtered through 0.2 μm Supor (PES) filters into HDPE vials and were acidified to pH < 2 with concentrated nitric acid. Samples for stable water isotopes analysis were filtered through 0.2 μm Supor filters into glass vials. A time series of river water samples was collected from the Red River at Van Phuc and processed in the same fashion.

To determine the influence of riverine recharge and geomorphic effects on groundwater arsenic, we collected water samples from 108 unique (i.e., samples represent different wells) domestic drinking water wells (50 wells sampled in May 2011, 18 wells sampled in November 2011, 23 wells sampled in May 2012, and 17 wells sampled in January 2015) that were all located < 1000 m from the Red River. Well depths were reported by the owner and ranged from 25 to 50 m depth with an average depth of 37 m. The domestic wells had installed pumps and we collected samples directly from the well during active pumping. At each household, information on the well depth and date of construction was collected and a location measurement was taken using a handheld GPS. Prior to collecting samples, the pump was turned on and the well was purged for several minutes. Measurements of the temperature, pH, redox potential (Eh), and electrical conductivity were measured using a field probe. Samples for stable water isotopes and samples for metal analysis were collected as described earlier.

The porewater, groundwater, and river water samples were analyzed for As, Fe, and Mn by ICP-MS with a dynamic reaction cell and Fe and Mn were measured by ICP-OES for some samples. The detection limits (3X standard deviation of blank) for As, Fe, and Mn by were 4, 50, and 5 $\mu\text{g/L}$, respectively (maximum of ICP-OES and ICP-MS detection limits for Fe and Mn reported). Relative standard deviations of triplicate analysis were always < 4%. Seven point calibration curves were generated at the start of analysis and all calibration curves had $R^2 > 0.999$. A blank and three standards were run after 10–12 sample analyses. Reference water TMDA-64.2 (Environment Canada) was run several times during each day's analysis to ensure analytical accuracy. Analysis of reference water agreed within $\pm 5\%$ for As and Mn and $\pm 15\%$ for Fe (absolute difference for Fe was always < 50 $\mu\text{g/L}$).

Stable isotopes of hydrogen were measured by isotope ratio infrared spectroscopy (IRIS) on a wavelength-scanned cavity ring-down spectrometer (model L1102-i, Picarro) with at precision of 1.6‰. Reported $\delta^2\text{H}$ values are the average of two replicate injections of a sample. The isotopic composition is reported in per mil relative to VSMOW water on a scale such that VSMOW (Vienna Standard Mean Ocean Water) and SLAP (Standard Light Antarctic Precipitation) water are 0‰ and -428‰ respectively.

2.2. Sediment Sample Collection and Analysis

Aquifer sediment samples for visual and chemical characterization were collected by drilling a hole with a hollow-stem drill bit while flushing the hole with water through the rotating drill bit and collecting drill cuttings at 1 m intervals. Riverbed sediment samples for chemical characterization were collected at 20 locations along the riverbank by pushing a 30 cm long coring device into the riverbed. Each riverbed core was

Table 1. Estimated Recharge Rates for the Porewater Samples With Unique Recharge Date Estimates^a

Location ID	Depth (m)	As (μM)	Sample $\delta^2\text{H}$	Sample $\delta^2\text{H} - 1.6\text{‰}$	Sample $\delta^2\text{H} + 1.6\text{‰}$
			Estimated Residence Time (As Release Rate) (days ($\mu\text{M}/\text{d}$))	Estimated Residence Time (As Release Rate) (days ($\mu\text{M}/\text{d}$))	Estimated Residence Time (As Release Rate) (days ($\mu\text{M}/\text{d}$))
S2	1	8.64	118 (7.3×10^{-2})	121 (7.1×10^{-2})	115 (7.5×10^{-2})
A	0.5	17.34	122 (1.4×10^{-1})	125 (1.4×10^{-1})	119 (1.5×10^{-1})
A	1	19.08	124 (1.5×10^{-1})	127 (1.5×10^{-1})	120 (1.6×10^{-1})
C	0.1	0.05 ^b	122 ($< 4.1 \times 10^{-4}$)	125 ($< 4.0 \times 10^{-4}$)	119 ($< 4.2 \times 10^{-4}$)
C	1	6.23	120 (5.2×10^{-2})	123 (5.1×10^{-2})	117 (5.3×10^{-2})
S3	0.5	8.1	305 (2.7×10^{-2})	309 (2.6×10^{-2})	302 (2.7×10^{-2})
D	0.1	0.18	317 (5.7×10^{-4})	321 (5.6×10^{-4})	314 (5.7×10^{-4})
D	0.5	0.05*	34 ($< 1.5 \times 10^{-3}$)	297 ($< 1.7 \times 10^{-3}$)	127 ($< 3.9 \times 10^{-3}$)
D	1	0.05*	18 ($< 2.8 \times 10^{-3}$)	295 ($< 1.7 \times 10^{-3}$)	108 ($< 4.6 \times 10^{-3}$)

^aUncertainty in the residence time estimates (and thus As release rate estimates) is presented in the last two columns of the table (see section 2.5.1 for description of uncertainty analysis).

^bIndicates arsenic was below the detection limit. The rates for these samples are therefore upper bounds.

subsampled to obtain a silt/clay layer which was analyzed for elemental composition. Aquifer and riverbed sediment elemental concentrations were measured by X-ray fluorescence using an Innov-X handheld XRF, which was run in triple-beam mode with a limit of detection of 1 mg kg^{-1} for total As. NIST standards (NIST Standard Reference Materials 2709, 2711, and 2710) were measured in the field and were accurate within 10% of reference values.

2.3. Water Level Measurements

Water levels were measured and recorded at 5 min intervals using pressure transducers (Solinst Levellogger) deployed in the river and a well screened at 25 m depth below the land surface (see Figure 1 for site locations). All water level data were corrected for changes in barometric pressure and reported relative to a local surveyed datum.

2.4. Characterization of River Geomorphology

The geomorphic setting of the river reaches along the village of Van Phuc was characterized by field observations. Distinct differences in land surface slope allowed for differentiation between erosional and depositional zones. Erosional zones were characterized by a steeply sloping bank that often formed a near-vertical cliff like face. Depositional zones were characterized by a bank that gently sloped into the river.

2.5. Determination of Arsenic Release Rates

2.5.1. Rates Determined in Present Study

To calculate the rate of arsenic release on our riverbed porewater samples, we first estimated a residence time (i.e., the time duration from the estimated date the sample recharged to the date the sample was collected) for each sample. Within the shallow groundwater, the amount of time since recharge can be estimated based on its isotopic composition ($\delta^2\text{H}$). Recharge is derived from the river (see section 3.1), which has seasonal variation in $\delta^2\text{H}$. Comparing the $\delta^2\text{H}$ of the porewater to the record of river $\delta^2\text{H}$ prior to sampling allowed us to identify when the sample likely recharged (Figure 4). Figure 4 shows the measured $\delta^2\text{H}$ of the porewater samples versus the sample's estimated date of recharge, where the estimated date of recharge for a particular sample was determined by finding the date on which the $\delta^2\text{H}$ of the river water most closely matched the $\delta^2\text{H}$ of the porewater sample. Recharge date estimates and subsequently arsenic release rates were only calculated on porewater samples for which the $\delta^2\text{H}$ led to a unique estimate of the recharge date (i.e. $\delta^2\text{H} > -60\text{‰}$ or $\delta^2\text{H} < -65\text{‰}$ for samples collected in November 2011 and $\delta^2\text{H} > -55\text{‰}$ for samples collected in May 2012). Mean arsenic release rates were calculated by dividing a sample's arsenic concentration by its estimated residence time for the 9 of our 25 porewater samples that had both arsenic and $\delta^2\text{H}$ measurements and a unique recharge date estimate. For these samples, we computed the uncertainty in our estimated residence times, and thus uncertainty in our estimated arsenic release rates, due to uncertainty in the $\delta^2\text{H}$ measurements of the porewater samples (Table 1). This was done by estimating a recharge date for the porewater sample's measured $\delta^2\text{H} + 1.6\text{‰}$ and the porewater sample's measured $\delta^2\text{H} - 1.6\text{‰}$ (1.6‰ is the analytical precision).

2.5.2. Rates Derived From Previously Published Data

To provide a comparison to the rates determined in this study, we derived or compiled rates of arsenic release for Vietnamese groundwaters from previously published research. We used experimental data from *Postma et al.* [2010] to estimate arsenic release rates for river sands and for river muds. *Postma et al.* [2010] performed laboratory incubation experiments on Red River sediments and measured the quantity of arsenic mobilized over time. They found that the rate of arsenic release was nearly constant over the 28 days of the incubation experiments on both river sand (amended with acetate to provide a source of organic carbon) and river muds (not amended with acetate). The arsenic release rate from the river muds was relatively unaffected by amendment with acetate since the muds have ample reactive organic carbon associated with the sediments [*Postma et al.*, 2010] and we used the data from their unamended mud experiments to calculate the arsenic release rate from muds. In the absence of acetate additions, the river sands exhibited minimal arsenic release during the incubation experiments. To calculate an arsenic release rate from the river sands, we used the data from the acetate-amended sand experiments. This gives us a likely upperbound for the arsenic release rate from the river sand. We performed an ordinary least squares fit to the experimental data (i.e., arsenic released per gram of sediment versus time) reported by *Postma et al.* [2010]. The slope of the linear fits gives arsenic release rates per gram sediment for the river muds and sands. We then converted these rates to rates of arsenic accumulation in the aqueous phase by assuming a sediment grain density of 2.65 g/cm^3 and a porosity of 50 percent.

We used data from *Weinman* [2010] to calculate an arsenic release rate for inland aquifer sediments in Van Phuc. *Weinman* [2010] reports measured changes in arsenic concentrations, and flow velocities measured by $\text{He}/^3\text{H}$ age dating of groundwater, between wells along a flow path in an aquifer. In the center of Van Phuc, flow velocities are currently estimated to be 75–100 m/yr, and arsenic concentrations increase between 10 and 50 (median ~ 36) ppb/km in the Holocene aquifer [*Weinman*, 2010].

2.6. Sediment Age Dating

To characterize the relationship between sediment age and the rate of arsenic release, sediment age was estimated or compiled for each location where a rate of arsenic release was measured.

The rate of sediment deposition in the river at Van Phuc was estimated from the thickness of sediment layers in the cores we collected at locations B and C (Figure 1). The riverbed exhibits alternating bands of fine and coarse sediments. The fine sediment indicates deposition in a lower energy environment relative to the coarse sediments. The stage of the Red River annually varies by up to 6 m. From May to June, the river stage increases rapidly and peak flood stage is reached in July–August. The river stage falls between August and November and then remains relatively constant until the following May [*Larsen et al.*, 2008]. In depositional reaches, silt and clay are likely deposited during the falling river stage and low river stage periods and form what is known as a silt drape layer [*Bernard and Major*, 1956]. Sandy sediments are likely deposited during the high river stage periods. Thus a band of fine sediments and a band of coarse sediments are likely deposited on an annual basis. We estimate approximately 0.1 m of deposition annually and used this to calculate the riverbed sediment age range over 0.1–1 m depths. Our finding is broadly consistent with rates of 0.01–0.05 m/yr measured on active rivers in Southeast Asia [*Funabiki et al.*, 2007; *Goodbred and Kuehl*, 1998].

We applied our age estimate for the riverbed sediments Red River at Van Phuc to the Red River sediments used in the incubations by *Postma et al.* [2010]. This is a reasonable approach given that the sediments collected by *Postma et al.* [2010] are from a very similar setting approximately 40 km upstream of our Van Phuc site.

Postma et al. [2012] report aquifer sediment ages for four locations in Vietnam and these data are shown in Figure 6. Sediment ages for the aquifer data from *Postma et al.* [2012] were measured by optically stimulated luminescence (OSL) on quartz grains collected from aquifer sediments. The youngest sediment age from *Postma et al.* [2012] plotted in Figure 6 is the average of two OSL measurements from the same core location with ages of 460 ± 30 years and 600 ± 70 years. The second youngest age plotted has an age of 670 ± 60 years. The second oldest age is the average of two OSL measurements from the same core location with ages of 3500 ± 130 years and 3560 ± 120 years. The oldest sediment age plotted in Figure 6 is 5900 ± 400 years.

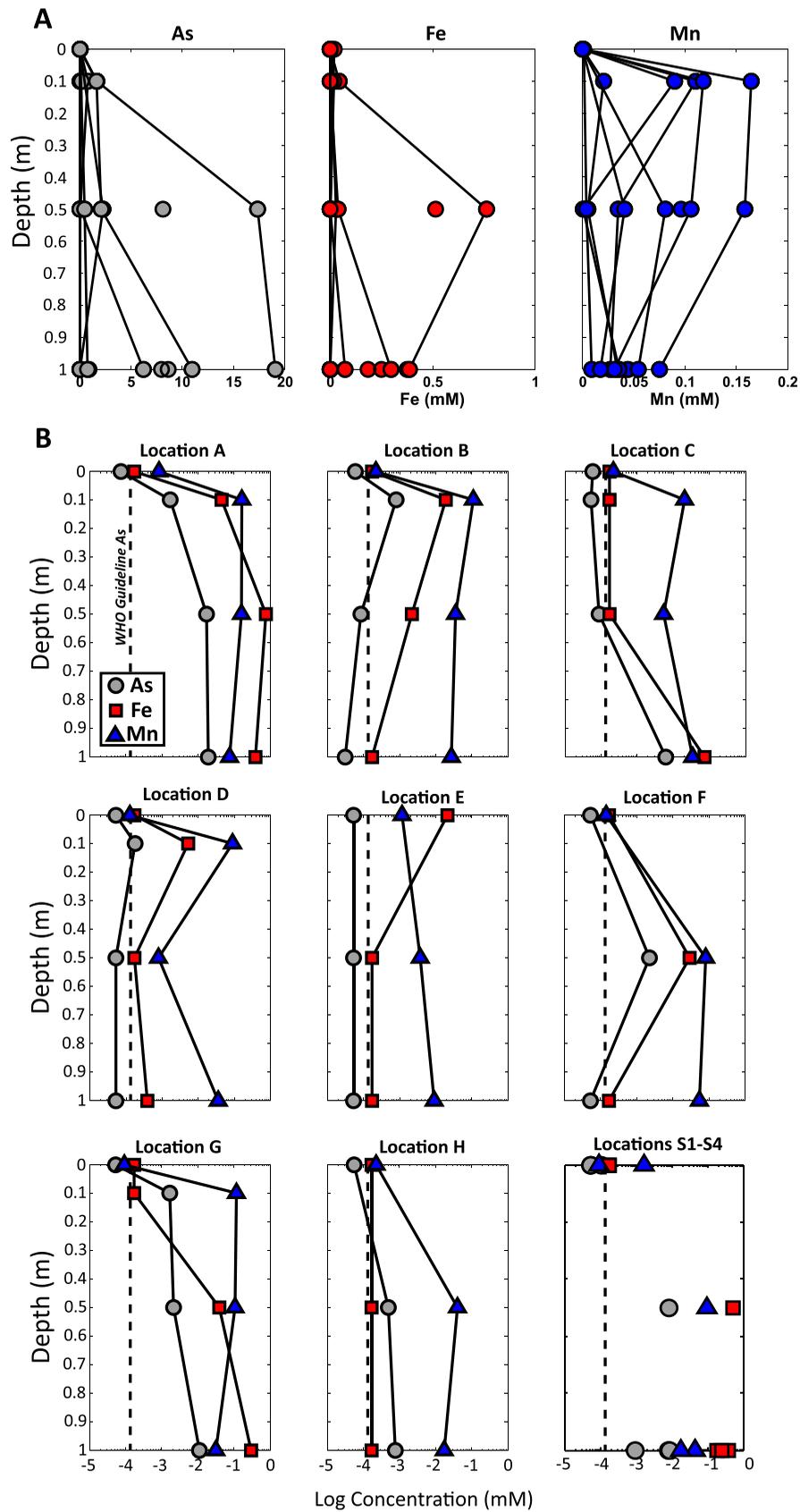


Figure 2. (a) Plots of As, Fe, and Mn versus depth for all porewater samples. Samples from locations where depth profiles were collected are connected by solid black lines. (b) Depth profiles of As, Fe, and Mn for porewater sampling locations. The dashed line indicates the WHO guideline for arsenic in drinking water.

Sediment ages for the aquifer at Van Phuc measured by OSL on quartz grains collected from the aquifer sediments were obtained from *Weinman* [2010]. We also measured the age of aquifer sediment at Van Phuc by carbon dating the sediment organic matter on an accelerator mass spectrometer (AMS). We report the minimum and maximum ages obtained for sediments along the flow-path on which the rate of arsenic release was calculated. The sediment age was determined on the upstream portion of the flow-path by OSL and yielded an age of 800 ± 200 years [*Weinman*, 2010]. We determined a sediment age of 3800 years on the downstream portion of the flow-path by dating of the sediment organic carbon.

3. Results

3.1. River and Aquifer Water Levels

The water level in the Red River varies by over 4 m in the course of a year and exhibits daily fluctuations that frequently exceed 0.3 m (Figure 1). The water level in the aquifer closely tracks that of the river, but is nearly always lower than the river (Figure 1) indicating that the river is recharging the aquifer throughout the year. Groundwater levels logged in three additional wells are consistent with these observations and provide additional confirmation that the river was recharging the aquifer. Our water level data indicating that the river is recharging the aquifer at Van Phuc is consistent with the findings of *Berg et al.* [2008] and *Eiche et al.* [2008], both of whom used geochemical evidence to demonstrate that the Red River recharges the aquifer at Van Phuc.

3.2. Riverbed Porewater and Sediment Chemistry

Porewater samples collected from the uppermost meter of the riverbed show significant arsenic mobilization occurring as river water recharges the aquifer (Figure 2). These samples show arsenic concentrations increasing from $< 0.1 \mu\text{M}$ ($< 7.5 \mu\text{g/L}$) in the river water to a maximum measured concentration of $19 \mu\text{M}$ ($1400 \mu\text{g/L}$) at 1 m depth into the riverbed sediments (Figure 2). Concentrations of iron also increase substantially from the river water to 1 m depth in the riverbed, consistent with the reductive dissolution of iron-oxide minerals. In the porewater samples where high arsenic concentrations ($> 0.67 \mu\text{M} = 50 \mu\text{g/L}$) were measured, we always observed high manganese concentrations ($> 18 \mu\text{M} = 1 \text{mg/L}$) indicative of the onset of reducing conditions, relative to the low manganese concentrations in the river water ($< 1.8 \mu\text{M} = 0.1 \text{mg/L}$). To identify the potential mineral source of arsenic to the shallow porewater, we compared the measured redox potential (pe) and pH of the samples to the pe and pH stability zones of common iron oxides (Figure 3). Stability ranges for iron oxides (Figure 3). Stability ranges for iron oxide minerals were plotted using equilibrium constants for 25°C obtained from LLNL and Minteq thermodynamic database and an Fe^{2+} activity of 2×10^{-6} (0.1mg/L Fe).

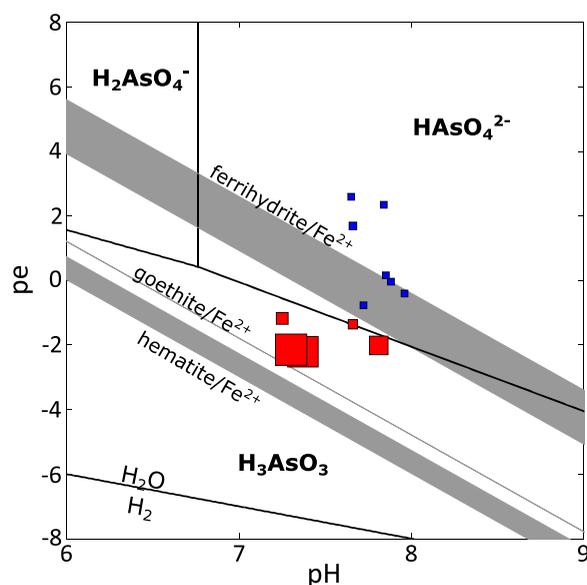


Figure 3. pe/pH diagram showing porewater samples (squares) relative to stability zones (gray bands) of common iron oxide minerals and predominance zones of aqueous arsenic species. Porewater samples are scaled and color-coded (red $\geq 50 \mu\text{g/L As}$, blue $< 50 \mu\text{g/L As}$) relative to their total dissolved arsenic concentrations. Mineral stability zones are plotted for an Fe^{2+} activity 2×10^{-6} .

whereas the low arsenic samples all fall within or above the ferrihydrite stability zone, indicating that ferrihydrite is likely a significant source of arsenic to these shallow pore waters (Figure 3). The samples within or above the ferrihydrite stability zone were uniformly low in iron ($< 6 \mu\text{M}$) while the samples below the stability zone were uniformly high in iron (ranging from 19 to $760 \mu\text{M}$), providing further evidence that ferrihydrite dissolution is releasing both arsenic and iron into solution. It is worth noting that redox disequilibrium is generally the case for groundwater [*Linberg and Runnels*, 1984] and thus pe/pH diagrams often provide only a qualitative view of a systems redox status. However our results, which suggest that

The porewater samples with elevated arsenic fall below the ferrihydrite stability zone whereas the low arsenic samples all fall within or above the ferrihydrite stability zone, indicating that ferrihydrite is likely a significant source of arsenic to these shallow pore waters (Figure 3). The samples within or above the ferrihydrite stability zone were uniformly low in iron ($< 6 \mu\text{M}$) while the samples below the stability zone were uniformly high in iron (ranging from 19 to $760 \mu\text{M}$), providing further evidence that ferrihydrite dissolution is releasing both arsenic and iron into solution. It is worth noting that redox disequilibrium is generally the case for groundwater [*Linberg and Runnels*, 1984] and thus pe/pH diagrams often provide only a qualitative view of a systems redox status. However our results, which suggest that

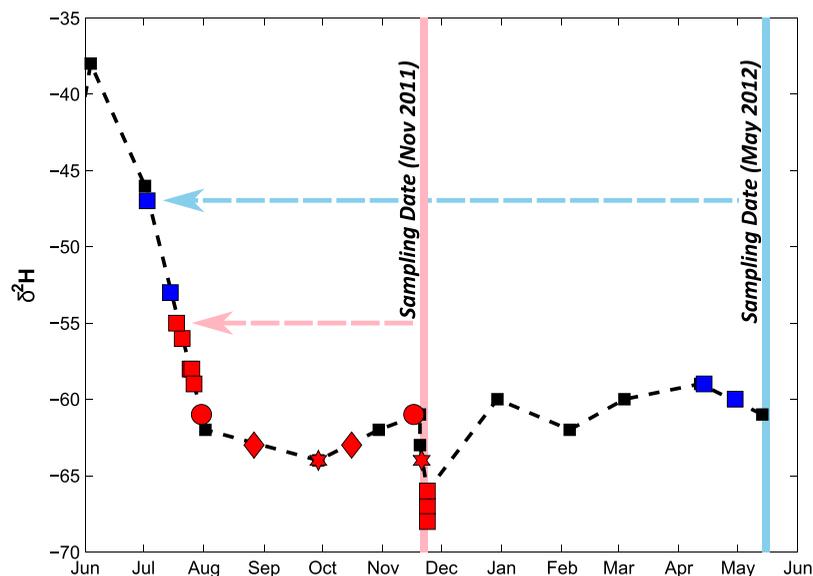


Figure 4. Time series of river stable water isotopes (black squares) and porewater stable isotopes versus estimated recharge date. Porewater samples with only one estimated recharge date are shown as squares (red if collected in Nov 2011 and blue if collected in May 2012) and samples with two estimated recharge dates are shown as stars, diamonds, or circles. The distance between the sampling date (indicated by the vertical bars; red bar for Nov 2011; blue bar for May 2012) and the estimated recharge date (indicated the red and blue symbols) gives the sample's residence time. To help illustrate this point arrows going from the sample date to the estimated recharge date are shown for two samples (red arrow for the sample collected in November 2011 and blue arrow for the sample collected in May 2012).

ferrhydrite dissolution and the subsequent release of arsenic and iron occurs as river water flows through riverbed sediments, are consistent with the findings from laboratory experiments using similar Red River sediments [Postma *et al.*, 2010] and suggest a more quantitative interpretation is reasonable for our pe/pH data.

3.3. Riverbed Sediment Arsenic Release Rates

The high levels of arsenic measured on our porewater samples and the direction of groundwater flow, which is from the river to the aquifer, indicate that arsenic is released as water flows through the riverbed sediments. We calculated rates of arsenic release on these samples to determine the time required to reach unsafe levels (i.e. > WHO guidelines) and to compare our results to rates calculated in other high arsenic settings in Vietnam.

Our estimated rates of arsenic release range from 0 to 0.15 $\mu\text{M}/\text{d}$, with a mean rate of 0.06 $\mu\text{M}/\text{d}$ (Table 1). Uncertainty in our arsenic release rate estimates is generally small (i.e., <5% of the estimated rate) (Table 1). Incorporation of three porewater samples with nonunique recharge date estimates yields qualitatively similar results, with estimated rates of arsenic release that range from 0 to 0.6 $\mu\text{M}/\text{d}$ and a mean rate of 0.1 $\mu\text{M}/\text{d}$. At the mean rate of arsenic release, river water recharging through the riverbed would exceed WHO guidelines for arsenic in approximately 2 days. Our field-derived rates of arsenic release rates are in agreement with rates determined by Postma *et al.* [2010] in laboratory incubations of Red River sediments. Our estimated mean and maximum rates of arsenic release fall between those of sands (0.07 $\mu\text{M}/\text{d}$) and river muds (1.36 $\mu\text{M}/\text{d}$), which were determined in laboratory experiments by Postma *et al.* [2010] (see section 2.5). These results are consistent with the fact that the riverbed sediment consists of alternating beds of sands and muds and thus we should expect a mean rate above those measured on sands and a maximum rate below those measured on muds.

3.4. Geomorphic Influence on Groundwater Arsenic

The study area of the Red River along Van Phuc included both depositional and nondepositional zones. We find a strong spatial correlation between the arsenic concentrations in local wells adjacent to the river and geomorphic settings of wells (Figure 1). Groundwater arsenic concentrations along depositional reaches of the river are generally 10–50 times greater than WHO guidelines, whereas arsenic concentrations along nondepositional reaches are almost uniformly below WHO guidelines (Figure 1). These results are consistent with a strong coupling between river geomorphology and groundwater pumping. The depositional environment controls the delivery and removal of young and reactive, arsenic-bearing sediments to the river-

Table 2. Riverbed Sediment Solid-Phase Arsenic

Adjacent Zone	As (mg/kg)
Zone 4	20
Zone 4	24
Zone 4	21
Zone 4	30
Zone 4	45
Zone 4	30
Zone 4	50
Zone 4	20
Zone 4	24
Zone 4	19
Zone 4	44
Zone 4	32
Zone 4	20
Zone 2	12
Zone 2	23
Zone 2	15
Zone 2	31
Zone 2	23
Zone 2	6
Zone 2	6

aquifer interface, and pumping draws newly released arsenic into the aquifer as river water flows through these sediments.

Solid-phase arsenic concentrations measured on riverbed sediments (Table 2) from a depositional reach (adjacent to Zone 4 in Figure 1) are 70% higher than sediments from a nondepositional reach (adjacent to Zone 2 in Figure 1). A two-sample *t*-test (homoscedastic and two-tailed) shows that the mean solid-phase arsenic concentration of 29 mg/kg (*n* = 13) from the depositional reach is significantly different at the 5% level (*p*-value = 0.017) from the mean concentration of 17 mg/kg (*n* = 7) from the nondepositional reach (only clay/silt-sized samples were compared between the depositional and nondepositional reach, to minimize the effect that grain size may have on total solid-phase arsenic).

3.5. Identification of Pleistocene Versus Holocene Sediments

The extent to which Pleistocene aquifers have been affected by the relatively recent (i.e. 50 years) introduction of large-scale groundwater pumping is presently unclear. This study site contains both Holocene and Pleistocene aquifers from both depositional and nondepositional environments (Figure 1), and thus is useful to examine the vulnerability of Pleistocene zones. Zones 1 and 2 are Holocene and Pleistocene, respectively [van Geen *et al.*, 2013], based on age dating of sediments. Zone 3 has not been previously studied but is identified as Pleistocene based on radiocarbon dating of a single sample supplemented with information obtained from its geochemical composition and comparison with published core logs [Winkel *et al.*, 2011]. Sediments from a representative core we collected in Zone 3 (Figure 1) had a small piece of wood collected at 18 m depth during coring that has been dated to $14,900 \pm 30$ years based on radiocarbon measurements. This representative Zone 3 core (Figure 1) also exhibits low Ca concentrations (in sands, median, and mean values of <50 and 740 mg/kg, respectively) and also is capped by a several meter thick layer of oxidized red/brown clay and sands (see Figure 5 for solid-phase Ca data). van Geen *et al.* [2013] found that the Holocene sediments had solid-phase Ca concentrations of >2000 mg/kg whereas the Pleistocene sediments typically had Ca concentrations <500 mg/kg and frequently much lower. van Geen *et al.* [2013] observed that the water within the Holocene aquifer was highly supersaturated with respect to calcite whereas the water within the Pleistocene aquifer was subsaturated and thus attributed the higher levels of solid-phase Ca in the Holocene sediments to authigenic precipitation of calcite in the Holocene aquifer. They also found that the Holocene sediments were capped by a gray surficial clay layer while a more oxidized red/yellow sand layer lay atop the Pleistocene sediments.

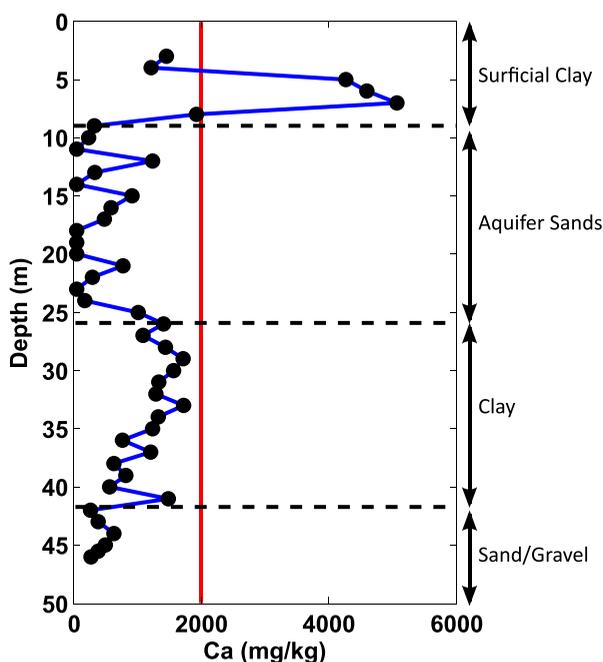


Figure 5. Depth profile of sediment calcium from Yen My (Zone 3) sediment samples. The solid red line indicates the lower bound of Ca concentrations for Holocene sands in Van Phuc as reported by van Geen *et al.* [2013].

They also found that the Holocene sediments were capped by a gray surficial clay layer while a more oxidized red/yellow sand layer lay atop the Pleistocene sediments.

4. Discussion and Conclusions

Our results suggest that aquifers throughout South and Southeast Asia may be vulnerable to arsenic contamination where riverine recharge flows through recently deposited sediments. Prior to the onset of substantial groundwater pumping, arsenic released in the porewater of reactive riverbed sediments would have discharged into

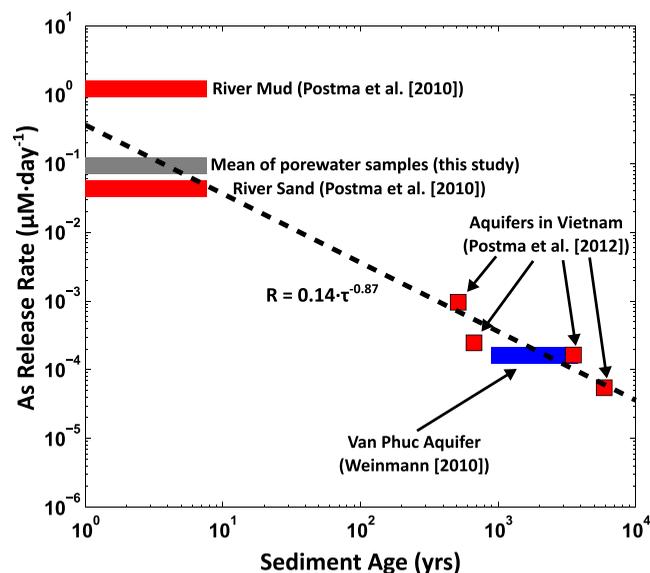


Figure 6. Plot of arsenic release rate versus age of sediment calculated from porewater and aquifer samples from Van Phuc (gray and blue bars, respectively); from aquifer samples near Hanoi, Vietnam (red squares, for site locations see map inset in Figure 1); from incubation of river sediments from Vietnam (red bars). Black-dashed line shows power law fit to aquifer data. See sections 2.5 and 2.6 for description of arsenic release rate calculations and determination of sediment age.

concentrations can be reached over short spatial scales (<1 m), our results also demonstrate that high arsenic concentrations (>100 $\mu\text{g/L}$) can be achieved over very short timescales (<1 year). *Roberts et al.* [2009] report a similar finding on rice field sediments in Bangladesh, where they observed arsenic concentrations in the upper 10 cm rose to 16 μM after inundation with monsoon floodwaters. The release of arsenic from these sediments is due to the onset of reducing conditions during flooding and the reduction of highly reactive arsenic bearing iron oxides that recently precipitated as a result of irrigation with iron and arsenic rich groundwater. However, a key difference is that at the study site of *Roberts et al.* [2009] there is no flow into the aquifer during the monsoon period when arsenic release occurs in these shallow sediments [*Harvey et al.*, 2006].

The mean arsenic release rate calculated on our riverbed porewater samples is two orders of magnitude greater than the maximum in situ rate of arsenic release previously reported for aquifers in the Red River Basin [*Postma et al.*, 2012; *Weinman*, 2010]. Since the riverbed sediments were more recently deposited than inland aquifer sediments, our results strongly suggest that sediment age influences that rate of arsenic release. Fitting a line to the log transformed arsenic release rate and sediment age data from *Postma et al.* [2012], we obtained a slope of -0.87 , implying that the rate of arsenic release scales inversely with the sediment age. Figure 6 shows this relationship, given by the equation $R = 0.14 \cdot \tau^{-0.87}$, where R is in units of $\mu\text{M/d}$, and τ is in years, along with arsenic release rates determined on sediments spanning a wide range of ages (see section 2.6) for discussion of sediment age data). Our measured arsenic release rate for the riverbed sediments agrees well with the fit obtained for the aquifer sediments from *Postma et al.* [2012] (Figure 6). This indicates that the relationship between sediment age and arsenic release rate is robust over an age range spanning four orders of magnitude. As an additional point of comparison, we plot our estimated age and rate of arsenic release for inland aquifer sediments at Van Phuc and find it to be consistent with our observed relationship. The much higher rate of arsenic release from the young riverbed sediments is consistent with findings of decreased organic matter and iron oxide reactivity over time [*Postma et al.*, 2012; *Thompson et al.*, 2006]. Furthermore, the power law relationship we find for arsenic release rate and sediment age (with an exponent of -0.87) is similar to power law relationships that have been observed between rates of mineral weathering and sediment age [*Taylor and Blum*, 1995; *White and Brantley*, 2003]. We recommend future research to further examine the relationship between sediment age and arsenic release rate. In particular, we envision a set of experiments where sediment samples spanning several

ivers and would not have influenced groundwater concentrations further inland. With large-scale groundwater pumping throughout South and Southeast Asia, it is likely that many aquifers are now experiencing net inflow from nearby rivers [*Berg et al.*, 2007; *Hoque et al.*, 2007] and at our field site we find that this riverine recharge becomes high in arsenic as it flows through recently deposited riverbed sediments. We observe arsenic concentrations which exceed WHO guidelines by two orders of magnitude after recharging river water flows through only 1 m of sediment. Arsenic concentrations in the shallow porewater is often at or in excess of concentrations found in inland wells, demonstrating that the arsenic concentrations observed in these inland wells could potentially emerge solely from the arsenic mobilization occurring in the riverbed sediments. In addition to observing that high arsenic

Table 3. Summary of Groundwater Arsenic Outcomes in Inland Aquifers for Combinations of Different Geomorphic Settings and Aquifer Types

Inland Aquifer Type		River Geomorphic Setting	
		Depositional	Nondepositional
Inland Aquifer Type	<i>Holocene</i>	Example: Zone 1 - High arsenic inflow -Continued arsenic release inland	No field example - Low arsenic inflow - Arsenic release inland
	<i>Pleistocene</i>	Example: Zone 3 - High arsenic inflow - Retardation of inflowing arsenic with potential for inland incursion of high arsenic over time	Example: Zone 2 - Low arsenic inflow - Possibility for onset of arsenic mobilization

orders of magnitude in age are tested for both the reactivity of the sedimentary organic matter (e.g., provide ample oxidizing agent) and the reactivity of the iron oxides (e.g., provide ample labile organic carbon). A set of experiments as described above would help to address the relative roles played by organic carbon and iron oxide reactivity in the decline in arsenic release rate with sediment age. We also recommend that the relationship between sediment age and arsenic release rate be examined over a broader geographic area (e.g., Bangladesh, India, and Cambodia).

Our finding of high rates of arsenic release (mean rate of 0.1 $\mu\text{M}/\text{d}$) on young riverbed sediments is cause for concern since it implies that river water recharging through recently deposited riverbed sediments will exceed WHO arsenic guidelines by one order of magnitude after only 14 days of contact with the sediment. Redox calculations along with the presence of aqueous iron provide strong evidence that the reductive dissolution of ferrihydrite is responsible for arsenic release within the riverbed sediments (Figure 2 and Figure 3). Given that ferrihydrite is a relatively unstable iron oxide (i.e., dissolves under mildly reducing conditions at near-neutral pH), it is likely that high aqueous arsenic is a common feature of groundwater recharged through riverbed sediments.

Under conditions of net river inflow, local geomorphology controls whether recharging water flows through freshly deposited riverbed sediments with high arsenic release rates or more weathered sediments with lower rates of arsenic release. Groundwater arsenic concentrations further inland are dependent on local hydrology, which influences the source of recharge and the connectivity with the river; the depositional environment and geomorphology, which influence arsenic levels in the recharge water; and the inland aquifer material, which controls the level of additional arsenic release or retardation [van Geen *et al.*, 2013; Postma *et al.*, 2012]. The different possible geomorphic settings and aquifer types with descriptions of arsenic contamination outcomes are presented in Table 3.

The Holocene aquifer (Zone 1 in Figure 1), which has the highest levels of groundwater arsenic in Van Phuc, abuts a depositional reach of the river. The high arsenic levels in aquifer Zone 1 are consistent with two observations: water recharging the aquifer flows through young and highly reactive riverbed sediments (Figure 6) and the aquifer sediments themselves are relatively young (< 4000 years) and likely still release arsenic at a moderate rate. In contrast, the Pleistocene aquifer (Zone 2 in Figure 1), [van Geen *et al.*, 2013] abuts a nondepositional reach of the river and has almost all uniformly low (<0.13 μM) arsenic concentrations. This finding agrees with previous observations on aquifers in Vietnam and Bangladesh that high arsenic groundwater is generally confined to Holocene aquifers. Furthermore, river water recharging along aquifer Zone 2 will flow through riverbed sediments that are currently being eroded and are not receiving input of young, highly reactive river sediments. The aquifer region labeled Zone 3 in Figure 1, offers a contrast to aquifer Zones 1 and 2 because it is Pleistocene in age (see section 3.5) but adjacent to fresh sediment deposited by the river (Zone 4). Aquifer Zone 3 may be a continuation of the Zone 2 Pleistocene aquifer unit. We suggest that groundwater arsenic levels in the Pleistocene aquifer Zone 3 are higher than levels in Pleistocene aquifer Zone 2 because it receives recharge from the active sediment deposition Zone 4. Prior to large-scale groundwater pumping—which has reversed the natural flow direction and is drawing riverine recharge into the aquifer—groundwater in aquifer Zone 3 was likely low in arsenic as is nearly always the case for Pleistocene aquifer in the region [BGS, 2001; Pal *et al.*, 2002; McArthur *et al.*, 2004; von Brömssen *et al.*, 2007; van Geen *et al.*, 2013]. Thus the high levels of groundwater arsenic that we measured

in aquifer Zone 3 are likely the result of the inflow of riverine recharge which becomes enriched in arsenic as it flows through the freshly deposited sediments (i.e. Zone 4) adjacent to aquifer Zone 3.

There are two distinct reasons that release rates could be elevated in these riverine sediments. First, the solid-phase arsenic levels of the riverbed sediments are high, and much of this arsenic appears to be labile. Sediment arsenic concentrations at this site exceed the 3–10 mg/kg levels normally observed on unconsolidated sediments [Smedley and Kinniburgh, 2002] and are greater than the 15 mg/kg mean value measured on sediments from the upper 20 m of the aquifer at our site [Eiche *et al.*, 2008]. Aqueous arsenic usually bears no clear relationship with total solid-phase arsenic [Eiche *et al.*, 2008; Zheng *et al.*, 2005]; however, a modest change in the quantity of labile arsenic can lead to significant increases in aqueous arsenic concentrations. van Geen *et al.* [2008] found that an increase in phosphate mobilizable arsenic from 0.3 to 1 mg/kg equates to an increase in aqueous arsenic concentrations from 10 to 300 $\mu\text{g/L}$. Thus even small changes in total solid-phase arsenic, if attributable to differences in phosphate mobilizable arsenic, can result in very large differences in aqueous arsenic concentrations. Second, the mineralogy of fresh sediments may be considerably different than of older sediments in erosional areas. Postma *et al.* [2010] observed that reactive iron minerals such as ferrihydrite resulted in arsenic release rates more than three orders of magnitude greater than observed during the reduction of stable oxyhydroxides like goethite or hematite.

The rapid release of arsenic from depositional environments may explain the high concentrations of arsenic observed inland of depositional environments, and places important constraints on the generation of arsenic contamination. Given the fast rates of arsenic release, active depositional areas are predisposed to flushing if the sediment supply is shut off. Assuming arsenic release rates are relatively constant, we calculate that for a freshly deposited sediment particle, arsenic will be depleted in roughly 30 years (for mean solid-phase arsenic levels measured in depositional reaches and mean arsenic release rate assuming porosity of 40% and sediment density of 2.65 g/cm^3) if sediment delivery is suspended, after which time the dissolved arsenic levels would be expected to drop in the porewater. Therefore changes in sediment delivery to the river will influence the amount of fresh sediment available for deposition and may ultimately effect groundwater arsenic concentrations. The product of the time to depletion (30 years) and the estimated rate of sediment deposition (0.1 m/yr, see section 2.6) gives us a rough estimate that the upper 3 m of riverbed sediment are actively mobilizing arsenic into solution. Thus, for a given groundwater velocity and arsenic release rate, an increased rate of sediment deposition will increase the thickness of the riverbed sediment actively mobilizing arsenic. The increased thickness of the reactive riverbed sediments leads to an increased contact time for the recharging water and thus increased arsenic concentrations in the recharging water. Conversely, a decreased rate of sediment deposition will decrease the thickness of the riverbed sediment actively mobilizing arsenic and thus lead to lower arsenic concentrations in the recharging water. At a given location, the rate of sediment deposition is likely to be dynamic due to seasonal flooding events, individual storm events, and longer term changes in sediment transport within the river. As a result we anticipate that arsenic concentrations in recharging river water will be similarly dynamic due to these changes in sediment deposition rates. Furthermore, changes in land management practices in the headwaters of the Red River in Yunnan, China, practices that enhance erosion [Fullen *et al.*, 2000] could affect groundwater arsenic levels downstream by providing additional sediments. Dam construction also could affect sediment delivery by decreasing sediment delivery [Le *et al.*, 2007], and by affecting the river stage and thus exchange between the aquifer and river. In riverbank deposits, arsenic and iron often accumulate into plaques at discharge points [Bone *et al.*, 2006; Charette and Sholkovitz, 2002]. The flow reversals caused by groundwater pumping may make these areas, which can contain thousands of mg/kg arsenic [Datta *et al.*, 2009], particularly important sources of aquifer arsenic contamination.

Our results also suggest that the interactions with the aquifer and river may explain some of the heterogeneity in arsenic levels in deltaic environments in that aquifers on the side of a river opposite to extensive groundwater pumping may be less vulnerable to arsenic contamination. Large rivers can act as specified head boundaries on an aquifer system and therefore the effects of intensive groundwater pumping on one side may not influence groundwater flow on the opposite side [Bear, 1979]. In Hanoi groundwater pumping takes place on the western side of the Red River and therefore net groundwater flow may still be toward the river on the eastern side of the river, a feature still observed at distances outside of Hanoi's drawdown cone [Larsen *et al.*, 2008]. In this case, high aqueous arsenic could still be generated in riverbank sediments, but not drawn into the aquifer except during high river stages. If the Hanoi drawdown cone extends beneath the river, it will only enhance flow towards the river on the other side.

These findings establish that shallow Red River sediments are a highly reactive arsenic source. As a result of intensive groundwater pumping, river water is recharging the aquifer in areas around Hanoi, and is becoming high in arsenic where it flows through the recently deposited river sediments. The delivery of highly reactive arsenic-bearing sediments along depositional reaches of the river sustains the release of arsenic to recharging river water. Thus, in areas of the aquifer inland of depositional reaches, we find high groundwater arsenic. Conversely, nondepositional reaches of the river eventually become leached of easily mobilizable sedimentary arsenic, and in areas of the aquifer inland of these reaches we find low groundwater arsenic. While our results suggest that riverine recharge can either contaminate or flush the aquifer of arsenic, the potential exists for low arsenic recharge to stimulate arsenic mobilization further inland. Furthermore, our results suggest that other arsenic contaminated aquifer systems located within large river networks (e.g., Bengal Delta) could be similarly impacted as growing groundwater withdrawals increase or induce riverine recharge.

Acknowledgments

This work was supported by NSF grants EAR 09-11557 and EAR 15-21356 and an NSF Graduate Research Fellowship. This is LDEO Contribution Number 8042. The authors thank the people of Van Phuc for their support of our project. Data associated with this manuscript are available upon request from B. C. Bostick at Bostick@LDEO.columbia.edu.

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