Hydrological and Sedimentary Controls Leading to Arsenic Contamination of Groundwater in the Hanoi Area, Vietnam: The Impact of Iron-Arsenic Ratios, Peat, River Bank Deposits, and Excessive Groundwater Abstraction

Michael Berg^{1,*}, Pham Thi Kim Trang², Caroline Stengel¹, Johanna Buschmann¹, Pham Hung Viet², Nguyen Van Dan³, Walter Giger¹, and Doris Stüben⁴

¹ Eawag, Swiss Federal Institute of Aquatic Science and Technology, Ueberlandstrasse 133, 8600 Dübendorf, Switzerland

² Center for Environmental Technology and Sustainable Development (CETASD), Hanoi University of Science, 334 Nguyen Trai, Hanoi, Vietnam

³ Vietnam Northern Hydrogeological and Engineering Geological Division (NHEGD), Ministry of Natural Resources and Environment, Tran Cung Street, Hanoi, Vietnam

⁴ Institute for Mineralogy and Geochemistry, University of Karlsruhe, Adenauerring 20, D-76131 Karlsruhe, Germany

* Corresponding author. Phone: +41-44-823 50 78; Fax: +41-44-823 50 28
E-mail: michael.berg@eawag.ch

Key words

Hydrology, water isotopes, iron-arsenic ratio, sediment extraction, seasonal fluctuations, irrigation

This document is the accepted manuscript version of the following article:
Berg, M., Trang, P. T. K., Stengel, C., Buschmann, J., Hung Viet, P., Van Dan, N., ... Stüben, D. (2008). Hydrological and sedimentary controls leading to arsenic contamination of groundwater in the Hanoi area, Vietnam: the impact of iron-arsenic ratios, peat, river bank deposits, and excessive groundwater abstraction. *Chemical Geology*, 249(1), 91-112.
<http://doi.org/10.1016/j.chemgeo.2007.12.007>

This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

Abstract

Groundwater contamination by arsenic in the Red River Delta (Vietnam) poses a serious health threat to millions of people consuming this water. In the larger Hanoi area, elevated arsenic levels are present in both the Holocene and Pleistocene aquifers. Family-based tubewells predominantly tap the Holocene aquifer for daily water needs, while the public drinking water supply of Hanoi city extracts more than 600'000 m³ of groundwater a day from the Pleistocene aquifer. Detailed groundwater and sediment investigations were conducted in three villages located in different settings, i) high levels of dissolved arsenic (av. 121 µg/L) at the river bank, ii) low levels of dissolved arsenic (av. 21 µg/L) at the river bank and, iii) medium levels of dissolved arsenic (60 µg/L) in an area of buried peat and excessive groundwater abstraction. In-depth chemical analyses were conducted in samples of groundwater from Holocene and Pleistocene tubewells, of surface water, of sediment material collected from 3 bore cores, of groundwater from wells nested around the sediment boreholes, as well as of extracts derived from sequential leaching of the sediment material. In addition, seasonal fluctuations in water chemistry were studied in 13 wells over a time span of 14 months.

The sediment-bound arsenic (1.3–22 µg/g) is in the natural range for alluvial sediments. It correlates with iron ($r^2 > 0.8$), with variation largely related to grain size (or surface area). Fractions of 23–84% (av. 56%) arsenic were extracted with 1 M phosphate from all sediments, indicating that arsenic can readily be mobilized at each of the three locations. Vertical migration of DOC-enriched groundwater from the young clayey sediments at the river bank to the aquifer below, or from the Holocene aquifer to the Pleistocene aquifer in the peat area, were found to promote iron-reducing conditions leading to arsenic contamination in the aquifers.

Low levels of arsenic in groundwater (<10 µg/L) generally exhibit manganese reducing conditions, with manganese levels reaching up to 8.7 mg/L. Elevated levels of dissolved arsenic are caused by reductive dissolution of sediment-bound arsenic under iron- and sulphate reducing conditions, with average arsenic concentrations in groundwater being twofold higher at the river bank than in the peat area. The lower levels of arsenic contamination in the peat area are likely controlled by the high abundance of iron present in both the aqueous and sediment phases. With median molar Fe/As ratios of 350 in water and 8'700 in the sediments of the peat area, reduced iron possibly forms new mineral phases that resorb (or sequester) previously dissolved arsenic to the sediment. Despite similar redox conditions, resorption is much less significant at the river bank (Fe/As(aq) = 68,

Fe/As(s) = 4'700), and hence, arsenic concentrations in groundwater reach considerably higher levels.

Drawdown of Holocene water to the Pleistocene aquifer caused by pumping of groundwater for the public drinking water supply of Hanoi did not show any observable increase of arsenic concentrations during the 14 months of this study. However, DOC, ammonium and iron were leaching down from the Holocene aquifer, thereby enhancing the reducing conditions in the Pleistocene aquifer. Seasonal fluctuations (11–66%) of redox sensitive species (As, Fe and Mn) in 70 m deep Pleistocene wells were concurrent with water table fluctuations, indicating shifted mixing ratios of deep groundwater with iron-reduced groundwater that is seeping down from the Holocene aquifer.

1. Introduction

Arsenic is a persistent contaminant in groundwater and drinking water in the Red River Delta of Vietnam (Berg et al., 2001; Trang et al., 2005; Berg et al., 2006; Berg et al., 2007). In the last 10–12 years, people have moved away from using surface water and water from shallow dug wells as sources for drinking water, in favour of groundwater pumped from individual private (family-based) tubewells. Long-term exposure to arsenic can affect human health and is a significant cause of skin pigmentation, hyperkeratosis, cancer, cardiovascular disease and may affect the mental development of children, among other possible adverse effects (Smith et al., 2000; Wasserman et al., 2004; Kapaj et al., 2006). The World Health Organization (WHO) recommends 10 µg arsenic per litre as drinking water guideline.

Vulnerable areas for arsenic contamination are typically young Quaternary deltaic and alluvial sediments containing highly reducing aquifers. Arsenic concentrations can have a very heterogeneous distribution, for which the reasons are not yet fully understood. The general geochemical mechanisms of arsenic mobilization under reducing conditions is widely attributed to microbial and/or chemical reductive dissolution of arsenic-bearing iron minerals in the aquifer sediments (Nickson et al., 2000; Dowling et al., 2002; Harvey et al., 2002; Stuben et al., 2003; Horneman et al., 2004; Islam et al., 2004; Zheng et al., 2004; Charlet and Polya, 2006; Postma et al., 2007). Others suggest that arsenic may be released from soil minerals at oxic–anoxic boundaries and could subsequently be drawn down from the near-surface through the aquifer to well-depths (Polizzotto et al., 2006). However, both theories do not explain why neighbouring wells can differ

in arsenic concentration by 1-2 orders of magnitude, or why some highly reducing areas have lower arsenic levels than others. This problem is partly due to the fact that geological and geochemical conditions are typically very patchy in unconsolidated sediments of young alluvial environments. Some studies have linked the mobility of arsenic in groundwater to the abundance of solid phase hosts such as carbonates (Akai et al., 2004), silicates, sulphates and iron(hydr)oxides (McArthur et al., 2001; Roman-Ross et al., 2002). Recent publications show that arsenic is not only reductively released from the sediments, but dissolved arsenic can again be reincorporated to solid-phase hosts. I.e., arsenic may be retained by evolving new phases that incorporate arsenic and iron (Herbel and Fendorf, 2006), the sorption density of As(III) on iron oxide phases increases with increasing Fe(II)(aq) (Dixit and Hering, 2006), and, reductive dissolution of arsenic-bearing ferrihydrite can promote arsenic sequestration rather than desorption (Islam et al., 2005; Coker et al., 2006; Kocar et al., 2006).

The Hanoi area can be categorized into three general situations of groundwater conditions, i) predominantly high arsenic (av. 121 $\mu\text{g/L}$) at the river bank (south of Hanoi), ii) predominantly low arsenic (av. 21 $\mu\text{g/L}$) close to the river (northwest of the city), and, iii) medium arsenic (av. 60 $\mu\text{g/L}$) in areas of abundant peat and high groundwater abstraction. Regarding the third situation, one can speculate that the groundwater abstraction in the Pleistocene aquifer causes vertical drawdown of water from the Holocene aquifer. This raises the question whether arsenic mobilization is influenced by anthropogenic activity and if arsenic concentrations might gradually increase over time in the Pleistocene aquifer.

With the aim to investigate these cases, we selected three villages representing the different hydrogeological and/or geochemical conditions for each of the above mentioned situations. The main objectives of this study were to i) delineate high and low arsenic concentrations at the river bank by comparison between the situations, ii) elucidate the connectivity of the Holocene and Pleistocene aquifers in the peat area and determine the impact of excessive groundwater abstraction, iii) find reasons for the lower magnitude of arsenic contamination in the peat area in comparison to the river bank, and, iv) investigate whether arsenic concentrations increase over time or fluctuate between the seasons. For this purpose, 23 parameters were measured in groundwater from randomly chosen tubewells in each of the three studied villages. Some of these wells were repeatedly investigated at intervals of 2–3 months over a time span of 14 months. In addition, we drilled sediment cores in each village and established nests of groundwater wells to study sediment-groundwater interactions.

2. Geological setting and hydrological features

A map of the Hanoi province with sedimentary cross-sections are shown in figure 1. The larger Hanoi area (south and west of the Red River) has sediments of both Pleistocene and Holocene age, with the latter being partly derived from postglacial marine transgressions (Trafford et al., 1996; NHEGD, 2002). Due to frequent riverbed migrations, the aquifers are not fully separated and in some locations are connected by sand lenses (Trafford et al., 1996). In a ~5 km wide zone along the Red River, the Holocene and Pleistocene aquifers today are mainly recharged from the river, with the more distant Pleistocene aquifer predominantly recharged by vertical percolation from the Holocene aquifer (Water-Master-Plan, 1993).

[insert Figure 1]

Due to its rapid growth of industry and urban population (3.5 Mio inhabitants in 2001, urban area 84 km²) Hanoi has a strongly increasing water demand. Drinking water treatment facilities in Hanoi exclusively exploit the lower (Pleistocene) aquifer containing variable levels of dissolved arsenic (5–430 µg/L), Fe(II) (1–25 mg/L), Mn(II) (0.2–3 mg/L), and NH₄⁺ (2–25 mg/L) (Duong et al., 2003; Dodd et al., 2006). Groundwater exploitation in the city began more than 100 years ago (1894), but besides iron, the quality of raw groundwater was not questioned until the early 1990s. Today, ten major well fields supply water to city treatment facilities which in 2005 processed 610'000 m³ of water per day (Cao et al., 2005).

Private households in rural areas pump groundwater from the upper (Holocene) aquifer where in the south-western region, arsenic concentrations are predominantly above 50 µg/L (Berg et al., 2001). An overlay of mapped arsenic, groundwater heads, peat and ammonium is shown in figure 2a. Arsenic concentrations range between 50 and 300 µg/L in the area of abundant peat and extensive groundwater abstraction, with higher arsenic levels (>300 µg/L) present in the south on both sides of the Red River where buried peat is less abundant.

Hanoi's high water demand is causing a significant drawdown of the groundwater in the Pleistocene aquifer. As illustrated in figure 2c, this is particularly severe in the west and south of the city where cones of depression reach down as far as 30 m below surface (NHEGD, 2002). In the south-western area, the Holocene sediments are rich in natural organic matter (NOM). The map presented in figure 2d shows that such sediment layers (indicated as peat) are up to 10 m thick (Trafford et al., 1996).

As a consequence of extensive pumping, ammonium concentrations in the Pleistocene aquifer have increased significantly between 1993–2001 (NHEGD, 2002). Levels exceeding 10 mg/L ammonium have become particularly abundant in the peat area over recent years (Figures 2e-2g).

[insert Figure 2]

3. Methods

3.1. Study areas

The locations of the three study areas are marked in figure 1a. Each area represents a different hydrological and geochemical situation, i) Thuong Cat village (TC) with low arsenic in the close vicinity of the river bank, ii) Van Phuc village (VP) with high arsenic in the river bank, and iii) Hoang Liet village (HL) with medium arsenic in areas of abundant peat and high groundwater abstraction. Geological and climatic conditions are given in the introduction and are summarized in Berg et al. (2001) and Duong et al. (2003).

3.2. Sample collection and preservation

Groundwater was collected at the tube by a hand- or electrical pump. Samples were taken after 10 minutes of pumping, i.e., after the oxygen concentration in the water reached a stable value. Redox potential (against SHE), pH, temperature, oxygen, and conductivity were recorded on-site by a portable system YSI 556 and a WTW Multi 340i (John Morris Scientific Pty Ltd). The samples were placed in polypropylene bottles (rinsed with 1% HNO₃ and 3 times with distilled water before shipping and 3 times with well-water before taking the sample). An aliquot (60 mL) for the analysis of metals, ammonium and phosphate was filtered (0.45 µm cellulose nitrate filter, Schleicher&Schuell, Germany) and acidified with approximately one millilitre of concentrated nitric acid (65%, Fluka, Switzerland) to reach a pH <2. Anions, alkalinity and DOC were determined in non-acidified and non-filtered water (120 mL). The samples were shipped to Switzerland by express mail and stored at 4°C in the dark until analysis. Control samples transported to Vietnam and back did not show any impact of transport on the analytical results (Berg and Stengel, 2004).

3.3. Water analysis and quality assurance

The chemical constituents in the groundwater samples were quantified from triplicate analyses. Arsenic concentrations were measured in parallel by atomic fluorescence spectroscopy (AFS,

Millennium Excalibur, PS Analytical, UK) and high resolution inductively-coupled-plasma mass spectrometry (HR ICP-MS, Element 2, Thermo Fisher, Bremen, Germany). Cross-evaluation of these methods agreed within 5% (Figure A-1 in Annex A1). Fe, Mn, Na, K, Ca, Mg, and Ba concentrations were measured by inductively-coupled-plasma optical emission spectroscopy (ICP-OES, Spectro Ciros CCD, Kleve, Germany); Co, Ni, Cu, Zn, Pb, Cr, Cd and Ba by ICP-MS; ammonium and phosphate by photometry; nitrate, sulphate and chloride by ion chromatography (Dionex, Switzerland); alkalinity by titration; and dissolved organic carbon (DOC) with a TOC 5000 A analyzer (Shimadzu, Switzerland).

The robustness of the measurements was assured by intermittent analysis of certified reference samples (SLRS-4 River Water Canada, TM-28.2 Lake Ontario, SPS-SW2 Surface Water Level 2 and reference samples from the interlaboratory quality evaluation ARS13-16 (Berg and Stengel, 2004)), as well as cross-evaluation between different analytical techniques, e.g. ICP-OES versus ICP-MS. The results of certified samples and cross-checking agreed within $\pm 5\%$. Calibration curves had $r^2 > 0.999$ with the exception of Na and K where r^2 were 0.990 (ICP-OES). Standard deviations of triplicates were always $< 5\%$. The limits of quantification (LOQ, 10 x standard deviation of noise) were 0.1 $\mu\text{g/L}$ for Co, Ni, Cu, Cr, U and Cd; 1 $\mu\text{g/L}$ for As (AFS); 2 $\mu\text{g/L}$ for Ba; 0.01 mg/L for $\text{NH}_4^+\text{-N}$; 0.03 mg/L for Mg; 0.05 mg/L for Fe; 0.1 mg/L for Mn, Na, Ca; 0.2 mg/L for $\text{PO}_4^{3-}\text{-P}$; 0.25 mg/L for $\text{NO}_3^-\text{-N}$; 0.5 mg/L for Cl^- ; 0.01 mg/L for SO_4^{2-} ; 1 mg/L for K, Si; 0.02 mmol/L for HCO_3^- .

3.4. Statistical analysis

In order to identify parameter associations for the three regions studied, principal component analysis (PCA) was performed using Systat 11. A detailed description and the results are given in the annex A 2 (Figure A-2).

3.5. Water isotope analysis

Samples of raw groundwater (non-filtered, non-acidified) were placed in 8 mL brown glass vials, sealed without headspace (PTFE-lined screw cap), and stored in the dark until analysis. Groundwater $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/\text{H}$ ratios were analyzed at Eawag Kastanienbaum by a Micromass Isoprime isotope ratio mass spectrometer (IRMS) in continuous flow mode. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope compositions of the water samples are conventionally expressed as a permil deviation from Vienna Standard Mean Ocean Water (VSMOW). The overall analytical errors are 0.2‰ and 2‰ for

$\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. Prior to analysis, the samples were equilibrated with a $\text{CO}_2\text{--He}$ and $\text{H}_2\text{--He}$ mixture, respectively, at 40 °C for at least 12 hours (Fette et al., 2005).

3.6. Sediment sampling

Boreholes for sediment sampling were drilled in April 2003 to depths of 30, 40, and 42 m in Thuong Cat, Van Phuc, and Hoang Liet, respectively. Freshly-drilled sediment cores were sampled on-site at intervals of 1 m with 20 g of wet sediment placed in polypropylene bags sealed airtight in the field. Water and sediment samples were stored at 4°C in the dark until analysis. Nests of 4–5 piezometers spaced no more than 1 m from the boreholes were installed the next day. The drilling locations are marked on the maps in figures 5, 7, and 9.

3.7. Sediment analysis and quality assurance

Sediment samples were freeze-dried, and digested with concentrated nitric acid and hydrogen peroxide in a microwave oven. Total arsenic was determined in the digests by AFS, with metals analysed by ICP-MS. The average recovery of iron was $90\pm 2\%$ (manganese $103\pm 3\%$) in Buffalo River Sediment 2704, and $92\pm 3\%$ in IMEP-14 using this microwave extraction method. Although clay minerals are not completely digested, the iron recoveries obtained for the reference materials are in an acceptable range. Affirmative measurements of total arsenic in sediment samples were carried out on the solid sediments with semi-quantitative wavelength dispersive X-ray fluorescence (WD-XRF) by the Swiss Federal Laboratories for Material Testing and Research. The WD-XRF results were calculated from arsenic impulse rates ($\text{PbL}\alpha/\text{PbL}\beta$ corrected) with a fitted one point calibration derived from the certified total arsenic concentration in BCR-320 ($77\text{ }\mu\text{g/g As}$) reference material. The estimated inaccuracy is $\pm 5\text{ }\mu\text{g/g}$. Sediment-bound total organic carbon (TOC) was measured with a CHN analyser by thermal oxidation.

3.8. X-ray diffraction (XRD)

The mineral composition of sediment samples was determined by x-ray diffraction using a Scintag XDS 2000 diffractometer at 45 kV and 40 mA with Cu K-alpha radiation at angles between 4 and $70^\circ 2\text{ Theta}$ and the graphical analysis program MacDiff 4.2.5. Machine parameters were: Scan type normal, start angle 4 deg, stop angle 70 deg, step size 0.02 deg, scan rate 2.000000, scan mode continuous, wavelength 1.540562.

3.9. Sediment leaching

Sequential extractions of sediment samples identified a variety of solid phase associations with arsenic. Leaching was carried out following a simplified procedure of (Keon et al., 2001). The sequence of extractants, the target phases of each extraction step and the possible mechanisms of dissolution are listed in table 1. Extracted amounts of arsenic and metals were quantified by the procedure described for water samples (section 3.3).

[insert Table 1]

4. Results

4.1 Groundwater

4.1.1. Sources of groundwater recharge

The piper diagrams in figure 3 show distinguishable hydrochemical features between the three studied villages. In general, the groundwaters of deltaic areas are of Ca-Mg-HCO₃ type (White et al., 1963; Stuben et al., 2003). Relatively low chloride concentrations and a predominance of Ca over Mg are found for the Red River and the majority of Van Phuc village (VP) (Figure 3a). Thuong Cat (TC) follows a trend to a higher ratio of Mg and some samples are elevated in chloride. The similarity with river water indicates that groundwater in VP and parts of TC is partly replenished by the river. Samples from Hoang Liet (HL) have a tendency towards Na-Cl type compared to river water (Figure 3b), reflecting anthropogenic infiltration from surface water. Pleistocene groundwaters have a higher ratio of Na+K over Ca in comparison to the Holocene aquifer which resembles surface water. The situation in the Holocene aquifer points to local surface water infiltration if one considers chloride levels.

[insert Figure 3]

The connectivity of the groundwater bodies with surface water was further investigated using isotopic signatures ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) measured in groundwater from VP (n=15), TC (n=12), and HL (n=14), as well as in surface water from HL (n=7). The variation of water isotopes in precipitation and Red River water was determined in 2003 and 2004 by the Institute of Nuclear Science and Technology in Hanoi (Nhan et al., 2005). Figure 4a shows that the Red River water lies on the global meteoric water line (GMWL, slope 8.17 (Rozanski et al., 1993)), while the local precipitation had a slightly tilted slope of 9.9. However, the precipitation line crosses the isotopic signatures of river water, thus demonstrating a similar average composition of these two water

resources, despite the Red River water being a mixture derived from the whole upstream catchment. In agreement with data published on the Internet website of Waterisotopes.org (www.waterisotopes.org), rain samples from September (warm rainy season) showed the lightest isotopic composition, and heaviest values in January (cool dry season).

[insert Figure 4]

The majority of the groundwater samples are not positioned on the GMWL (Figure 4b), but are shifted towards less negative $\delta^{18}\text{O}$ values (enriched in ^{18}O). This shift is particularly pronounced for HL groundwater and for some samples from TC. This implies groundwater recharge from evaporated water bodies, expressed by the so-called evaporation line (Rozanski et al., 1993). With fitted slopes of 5.6 and 5.1 for HL and TC, respectively, the evaporation lines are characteristic for theoretical evaporation occurring at climatic conditions of 75–80% humidity. This is an excellent match with the average annual humidity of 78% in Hanoi (www.bbc.co.uk/weather).

Infiltration of surface water into the HL Holocene aquifer is further corroborated by the isotopic signatures in HL surface water (see Figure 9 for sampling locations). They are situated on the same surface water evaporation line as the HL groundwater samples (SW 1 and SW 4), or on the GMWL (SW 5). In contrast, the water from the drainage channels (SW 2, 3, 6 and 7) lies on the precipitation line, reflecting drainage of local rain. The fact that two of the three samples from the Pleistocene aquifer (HL 23 and HL 25) are also positioned on the evaporation line, signifies that they receive a significant proportion of Holocene groundwater.

The following sources of groundwater recharge are concluded from analyses of major ions and isotopic signatures; (i) Groundwater in the Holocene aquifer of HL is largely replenished by lake water, with drainage channels playing a minor role, (ii) Holocene groundwater is seeping into the Pleistocene aquifer at some locations in HL, (iii) TC groundwater is partly replenished by standing surface water bodies that mix with water infiltrating from the nearby river, particularly inside the dike, with samples collected outside the dike lying on the GMWL and so mainly derived from infiltrated river water, and, (iv) the composition in VP groundwater points to a connection with river water.

4.1.2. Groundwater at Van Phuc village (Case 1: High arsenic at the river bank with seasonal flooding)

VP is located on the bank of the Red River on a 3.5 km² 'peninsula' surrounded by a river bend (10 km south of Hanoi, see Figure 1). The entire village lies outside of the dike system that protects the south-western Hanoi area from floods. VP therefore encounters occasional flooding during the rainy season, and has a natural and undisturbed hydrological situation. The aquifer reaches down to >40 m with a loose bedding of Holocene and Pleistocene depositions (Nguyen, 2005). Any influence from the Pleistocene groundwater drawdown as discussed above (Figure 2b+c) is minimal. Figure 5 illustrates the VP setting and shows arsenic concentrations in family-based tubewells. The database of 23 parameters determined in the groundwater samples (December 2002) is provided in table A-1 of the annex.

[insert Figure 5]

[insert Figure 6]

The distribution of arsenic concentrations in VP is patchy and ranged from <1–340 µg/L (average 121 µg/L, median 88 µg/L). Samples with elevated arsenic are iron-reducing in nature which was confirmed by principal component analysis (PCA) with low E_h and elevated Fe(II), DOC and ammonia, known to be triggers for arsenic release (factor 1, 27% of the variance, see annex A2 for details). Arsenic shows a noticeable correlation with ammonium (r^2 0.41) and dissolved organic carbon (DOC, r^2 0.60). The mean ratio of Fe/As amounts to 68 mol/mol (max 630). Iron and redox potential have weak numerical relations, but as shown in figure 6, they have similar distribution patterns to arsenic. Reductive dissolution of arsenic bound to iron minerals seems to be the cause for the elevated groundwater arsenic levels. An association of arsenic with manganese can not be seen as the two elements have an inverse relationship (a situation that is frequently observed (Buschmann et al., 2007; Stuben et al., 2003; Smedley and Kinniburgh, 2002;)). The magnitude and patchiness of arsenic concentrations in VP is a situation of groundwater arsenic contamination as reported in other affected areas (BGS and DPHE, 2001; Stuben et al., 2003; van Geen et al., 2003; Buschmann et al., 2007).

4.1.3. Groundwater at Thuong Cat village (Case 2: Low arsenic close to the river bank, no seasonal flooding)

Like VP, the village TC is situated on the Red River bank (10 km northwest of Hanoi), but in contrast to VP, the majority of the houses (and consequently tubewells) are built on the inner side of the dike and not exposed to seasonal flooding. Similar to VP, the river bank aquifer reaches down to

Pleistocene depositions that are not separated by an aquitard from Holocene sand (Nguyen, 2005). River water infiltration is enhanced in this area due to groundwater drawdown caused by the Hanoi water works (see Figure 2b). The setting of TC, the course of the dike, and the measured arsenic concentrations are depicted in figure 7. The concentrations determined in these groundwater samples are listed in table A-2 of the annex.

[insert Figure 7]

[insert Figure 8]

All tubewells inside the dike had low arsenic levels while the wells located outside the dike have elevated concentrations between 62 and 198 µg/L. Wells exhibiting >2 µg/L arsenic and >0.05 mg/L iron have a mean Fe/As ratio of 60 mol/mol (max 270). Ammonium is predominantly found in the western part of the village which is in agreement with the groundwater ammonium distribution mapped over the whole Hanoi area (Figures 2e-g). Ammonium levels (average 2.3 mg N/L) are three times lower than in VP, and phosphate is 5–10 times less abundant. Similarities in the distribution of parameters depicted in figure 8 are less pronounced than in VP (Figure 6). The prevalence of manganese (average 1.95 mg/L) over iron (average 1.0 mg/L, median <0.05 mg/L) and positive E_h values point to manganese reducing conditions inside the dike. Arsenic is not readily mobilized under such conditions since iron(hydr)oxides in the sediments still provide abundant sorption sites (McArthur et al., 2004; Dixit and Hering, 2006; Herbel and Fendorf, 2006; Kocar et al., 2006). This is substantiated by an anti-correlation of manganese with arsenic (r^2 -0.88), and confirmed by statistical analysis in the PCA factor 1 (see annex A2 for details). In contrast, the wells outside the dike have negative redox potentials and are iron-reducing, leading to dissolution of iron and arsenic. The setting of the wells outside the dike is comparable to the situation in VP where fresh sediments are deposited during seasonal flooding of the river bank.

4.1.4. Groundwater at Hoang Liet village (Case 3: Elevated arsenic in the area of abundant peat and high groundwater abstraction, no flooding)

The land surface in HL is characterized by eutrophic lakes of various size, as well as sewage and irrigation channels (Figure 9). Prominent features are the oxbow lake in the centre of the village and the lake in the east. The buried sediments contain peat layers of up to 10 m thickness (see Figure 2d). Samples were collected from both the Holocene and Pleistocene aquifers, representing depths

of 9–35 m (median 24 m, n=19) and 53–100 m (median 70 m, n=7), respectively. The parameters analyzed in groundwaters are listed in table A-3 of the annex.

Strongly reducing conditions are clearly driven by degradation of NOM which is expressed by a good relation of DOC with ammonium (r^2 0.91). The mean molar ratio of inorganic N/P in the peaty aquifer was 17.7, which is close to the Redfield ratio (N/P = 16) that is representative for degradation of vegetative sources (Redfield, 1958; McArthur et al., 2001). Arsenic concentrations ranged from 1–127 µg/L (average 63, median 69 µg/L), with similar concentrations in the Holocene and Pleistocene aquifers. Arsenic shows a relatively uniform pattern over large parts of the village, with lowest levels in the south. However, it must be emphasized that dissolved arsenic in the peat area of HL is 50% lower than at the river bank, despite the Holocene groundwater featuring very high levels of iron (18.8 mg/L), ammonium (17.0 mg/L), phosphate (1.2 mg/L), DOC (5.8 mg/L) and exclusively negative Eh (-55 mV). This is an indication that high dissolved levels of iron could be promoting resorption of arsenic to new phases that incorporate arsenic and iron (see sections 4.2.4.3, 5.2 and 6)). The mean molar ratio of Fe/As is 350 mol/mol (max 12'000) which is 5–6 times higher than at the river bank in VP and HL.

Contour plots in figure 10 illustrate the distribution pattern of selected parameters in the Holocene aquifer. Levels of sodium (average 60 mg/L) and chloride (average 40 mg/L) were 3–4 times higher than at the river bank in VP and TC. DOC, ammonium and alkalinity were highest in the tubewells located in the east, with concentrations below the oxbow lake being considerably lower. While the high DOC and ammonium concentrations could derive from organic-rich leachate sourced from the lake in the east, the chloride distribution does not support such a scenario. In contrast it implies a major source of anthropogenic chloride being from the channel to the south, while the contribution of the two lakes is less obvious.

[insert Figure 9]

[insert Figure 10]

[insert Figure 11]

In the Pleistocene aquifer, iron, manganese, chloride and phosphate were 2 times less the abundance of the Holocene aquifer, with average levels of 8.7, 0.34, 27 and 0.58 mg/L, respectively. Figure 11

illustrates that chloride levels are more uniformly distributed here than in the upper aquifer, with concentrations closer to the magnitude measured in the two villages located at the Red River bank. This is supported by the piper diagram showing the similarity of HL Pleistocene groundwater with river water (Figure 3b). Highest levels of DOC and ammonium in the Pleistocene aquifer are present below the location where these species were highest in the Holocene aquifer, i.e. in wells located in the east of the study area. Chloride has the same trend, although the distribution in the Holocene aquifer differs significantly from that in the Pleistocene. Therefore, downward migration of DOC and ammonium reaching the Pleistocene aquifer is derived either from the Holocene aquifer or from the aquitard between them. In addition, iron showed notable relations with phosphate, ammonium and alkalinity with coefficients of determination (r^2) being 0.68, 0.60, and 0.85, respectively. This indicates that dissolved iron is also leaching into the Pleistocene water.

4.1.5. Variation of groundwater composition during the 14-month study

The Hanoi authorities raised concern that arsenic concentrations might increase over time, analogous to the increase in ammonium concentrations observed in the Pleistocene aquifer. To clarify this issue, 13 wells in HL were repeatedly sampled in intervals of 2–3 months over a time span of 14 months. The groundwater table in the Holocene aquifer during the years 2002 and 2003 varied gently with only 1.0 m difference between the minimum and maximum levels (Figure 12a). In contrast, the seasonal fluctuation of groundwater heads in the Pleistocene aquifer was pronounced, despite its mean level being 14 m deeper than in the upper aquifer (Figure 12b). With a difference of 1.8 m between high and low levels, this variation reflects the hydraulic connectivity with the Red River as it mirrors the changing water level of the river (± 9 m) over the seasons.

The variations of arsenic concentrations and groundwater heads are plotted in figure 12 (Fe, Mn, NH_4^+ , Na, Ca, and chloride are shown in Annex A.3). The highest fluctuations in the Holocene aquifer were recorded in tubewells near the oxbow lake (HL 5–7), or situated close to a drainage channel (HL 16 and HL 17; see Figure 9 for well positions), indicating that these wells are directly influenced by surface water infiltration. However, the majority of the tubewells had a stable groundwater composition ($\pm 10\%$).

The four wells monitored in the Pleistocene aquifer showed higher dynamics in groundwater composition than in the Holocene aquifer (see Figure 12b). Pronounced fluctuations were found for iron and arsenic in the 70 m deep wells HL 1 and HL 21. Arsenic and iron were lower during the high water stand while manganese increased. Due to altered directions of the groundwater flow

(related to elevated groundwater heads), it is likely that these wells received somewhat less reduced groundwater from shifted flow paths over the seasons. Such variation at 70 m depth is surprising, but could reflect different mixing ratios of Pleistocene groundwater with arsenic-burdened leachate originating from the Holocene aquifer.

[insert Figure 12]

4.2. Sediment studies

4.2.1. Sediment cores

Sediment cores were drilled in each of the three villages, reaching down to depths of 30, 40 and 42 m in TC, VP and HL, respectively. Nests of 4–5 piezometers spaced no more than 1 m from the boreholes were installed the following day. Sediment samples were collected from these cores at 1-meter intervals, characterized for major minerals, digested for the analysis of chemical composition, and sequentially extracted (leached) with various reagents (see section 4.2.4). This allowed (i) to elucidate how sediment and pore water concentrations of arsenic and other parameters varied with depth, (ii) to determine the relation of groundwater arsenic concentrations with sediment-bound arsenic contents, and, (iii) to test if some sediments release arsenic more readily than others.

4.2.2. Lithology

Lithological logs for the three areas are shown in figure 13. Aquitards of various thickness of clay are present at all sites near the surface. The sediments from TC were brownish in colour from top to bottom of the core. The other two cores revealed reduced sediments of various grey colouring below the piezometric groundwater heads (redox boundary). The close vicinity to the river is reflected in the sediment architecture of TC and VP, where the aquifers consist of various sizes of sand and are more than 25 m thick. The Holocene aquifer at the borehole of HL exhibits fine sand with inter-bedded layers of plant remains. The aquitard between the Holocene and Pleistocene aquifers (clay and peat) is more than 20 m thick.

[insert Figure 13]

4.2.3. Major minerals in sediments

Based on the diffractograms obtained from qualitative XRD, the sediments from the three boreholes have a generally homogeneous composition consisting of quartz (main component), chlorites, mica and feldspars, with differences occurring between the abundance of chlorites, mica and feldspars.

Further investigation of selected samples revealed amphibole (8.45 Å, in TC 9–12, TC 22, HL 12, HL 18, and HL 30 m), K-feldspar (3.24 Å, in VP 22–40, and HL 1–42), as well as plagioclase (3.9 Å, in VP 1–8, and HL 1–42). Photographs of sediments collected at the three sites are printed in figures A-6 to A-8 of the annex.

4.2.4. Chemical species in sediments and corresponding groundwater

Depth profiles of sediment species and total arsenic concentrations in the nested piezometers are shown in figure 14. The contents of sediment-bound iron and arsenic were generally related to grain size (see annex A.4). Since small particles have larger surface areas than large grains, elements associated with surface coatings (such as arsenic and iron) are most abundant in clay and gradually less concentrated in coarser material. An association of arsenic with iron is also reflected by correlations of 0.93 (outlier at 28 m excluded), 0.85 and 0.80 in VP, TC and HL, respectively. Similar depth profiles were observed for most of the other elements analyzed (data not shown), resulting in correlations of arsenic with Mg, Ba, Co, U, Cr, Ni (≥ 0.80); Al, P, Pb, Cu (≥ 0.70); and Mn, K, Ca, Si (≥ 0.60). Total organic and inorganic carbon (TOC and TIC) and total nitrogen (TON) were less related with arsenic in VP and TC, but showed a correlation of ≥ 0.67 in the peat area of HL. Considering the world baseline concentrations of arsenic in sediments of 5–10 µg/g (Smedley and Kinniburgh, 2002), the average levels of 8.3 µg/g in VP, 7.4 µg/g in TC, and 4.9 µg/g in HL are in a natural range.

4.2.4.1. Van Phuc

Sediment arsenic concentrations in VP were 17.5 µg/g near the surface and gradually decreased with depth to values <5 µg/g below 20 m. The data depicted in figure 14a confirms that the reducing conditions in the sediments are driven by NOM buried with clay in 8–16 m depth (>1% TOC), and that these conditions are maintained in the sandy aquifer. The very narrow and sharply delimited layer of clayey silt at 28±0.2 m depth exhibited the highest recorded arsenic level of 22 µg/g. A similar, but somewhat less distinct peak was identified in the corresponding sediment layer at TC (see section 4.2.4.2). The median molar ratio of sediment-bound Fe/As was 4'700.

Pore water arsenic concentrations in samples from the four piezometers varied between 22–270 µg/L which is a typical range for VP groundwater. The lowest aqueous concentration (22 µg/L) was measured at the redox boundary (9–10 m) where sediment arsenic was 9.8 µg/g. In contrast, the three piezometers tapping the sandy aquifer at 19, 30 and 40 m depth had 8–12 times higher dissolved arsenic (180–270 µg/L), although the sediment-bound concentrations at corresponding

depths were 1.3–5.5 times lower (1.8–7.8 $\mu\text{g/g}$). This data illustrates that dissolved arsenic is not related to the magnitude of arsenic in the sediment material.

4.2.4.2. Thuong Cat

The profile of solid-bound arsenic in TC is less variable than in VP and HL (Figure 14b). The highest concentrations are again found in the top clay layer (1 m, 13.8 $\mu\text{g/g}$) and in the narrow band of clayey silt at 24.5 m (11.2 $\mu\text{g/g}$). NOM is mainly present between 9–13 m and 24.5–30 m with a sharp peak of 2.5% TOC and 0.60% TON at 9 m depth. The less pronounced decrease of arsenic with depth is not surprising considering the relatively coarse nature of the sediments present. Nevertheless, the concentrations are higher in the medium to coarse sand (>20m, average 4.4 $\mu\text{g/g}$, range 3.8–5.2 $\mu\text{g/g}$) as compared to VP (>24 m, average 2.7 $\mu\text{g/g}$, range 1.8–3.8 $\mu\text{g/g}$). Since these sediments were deposited during the same time period at both locations, they should originally have had the same sediment-bound arsenic levels. The 1.7 $\mu\text{g/g}$ (39%) difference between the average arsenic contents in VP and TC therefore possibly reflects the amount of arsenic leached from the aquifer sand in VP as a result of reductive dissolution. With a median molar Fe/As ratio of 3'900, sediment-bound fractions of arsenic and iron were similar in TC as in VP.

[insert Figure 14]

The arsenic concentrations in water of the five nested piezometers (14–28 $\mu\text{g/g}$) match the elevated levels measured in the groundwaters outside the dike (see Figure 7). There is clearly enough NOM to cause reductive dissolution of some arsenic. However, the brownish colour of the sediments is indicative of less reducing conditions than in VP and HL, which is further corroborated by the low iron (average 0.8 mg/L) and elevated manganese levels (average 1.7 mg/L). Like in VP, aqueous arsenic has no trend with depth, nor a relation with sediment-bound levels.

4.2.4.3. Hoang Liet

The sediment depth profile in HL has a distinctly different shape than in VP and TC. Arsenic concentrations are generally below 5 $\mu\text{g/g}$ in the sandy aquifer and >5 $\mu\text{g/g}$ in the underlying peaty clay and silt. As depicted in figure 14c, NOM is not only found in the clay and peat, but also abundant within the sandy aquifer itself, particularly between 10–17 m. Arsenic shows a remarkable correlation with TOC (0.71) and TON (0.87). This indicates that a considerable proportion of arsenic might have been co-deposited along with organic matter, possibly accumulated with iron

coatings on plant roots (Blute et al., 2004; Meharg et al., 2006). The ~2 times higher molar ratio of Fe/As (median 8'700, max 18'500) than at the river bank would support such a scenario.

The arsenic concentrations in the nested piezometers were in the range of 7–41 µg/L and were in agreement with the levels measured in groundwater from nearby tubewells (26–103 µg/L, see Figure 9). Considering the abundance of NOM in the sediments of HL, the aqueous arsenic concentrations in the aquifer (3–18 m) are rather low when compared to VP. However, the significantly higher ratios of Fe/As in both, the solid and aqueous phases, as well as the high levels of dissolved iron (median 18.7 mg/L) provide another indication that arsenic mobility could be controlled by increased sorption densities on iron phases (Dixit and Hering, 2006), and/or retained by evolving new phases that incorporate arsenic and iron (Herbel and Fendorf, 2006). Based on the results of the total sediment digestion one can also speculate that (i) easily mobilized arsenic was (to some extent) already leached from the sediments, and/or (ii) arsenic is associated with more crystalline phases and less adsorbed to amorphous iron, and/or (iii) there is enough sulphur in the system to precipitate arsenic with insoluble sulphides under the prevalent anoxic conditions (Spycher and Reed, 1989; Helz et al., 1995). However, the sequential leaching of the sediments presented below does not point to any of these three scenarios.

4.2.5. Mobilization of arsenic from sediment phases

Depth profiles of leached arsenic are plotted in figure 15, and the average fractions listed in table 2. The most important feature is the considerable amount of arsenic mobilized from all sediments with 1 M phosphate (overall average 56.7%, Table 2). This fraction of ionically bound and/or strongly adsorbed arsenic is particularly abundant in the sandy aquifers of VP (18–40 m, average 70%) and HL (3–18 m, 69%). Somewhat lower ratios of phosphate dissolved arsenic were present in TC (7–30 m, 45%) as well as in the clay and silt of the other two cores. Considering the good correlation of digested iron with arsenic (see section 4.2.4), the phosphate leaching confirms that major proportions of arsenic must be adsorbed to iron phases (Horneman et al., 2004; Van Geen et al., 2004).

The fractions of arsenic leached by HCl and oxalate were small (11.2% and 8.1%, respectively), with highest values found in extracts of fine grained material, as well as of the more oxic sediments of TC. The residual fraction of arsenic is incorporated in crystalline phases (average 24%) which do not readily release arsenic at ambient pH (McArthur et al., 2004).

In conclusion, sequential leaching revealed readily dissolvable arsenic (phosphate leached) in all sediments with a clear dominance in the aquifers of VP and HL. Hence, the amount of arsenic released to the groundwater is neither related to the bulk sediment arsenic contents, nor to the fraction associated with crystalline phases. Rather it is the predominance of reducing conditions, combined with a moderate Fe/As ratio that drives arsenic mobilization from the sediments.

[insert Figure 15]

[insert Table 2]

5. Discussion

5.1. Arsenic mobilization from young river deposits

The presented groundwater and sediment data imply that arsenic contamination of groundwater in the Hanoi area is driven by reductive mobilization of ionically bound and/or adsorbed arsenic from the sediments. This conclusion is drawn from sequential leaching of sediments and the iron-reducing conditions which were statistically confirmed by principal component analysis of the groundwater data (see annex A2). Arsenic concentrations released from the grey (iron-reduced) sediments in VP were significantly higher (max 340 µg/L) than those released from the brown sediments in TC (max 28 µg/L), as demonstrated from the corresponding sediment cores depicted in Figures 14a and 14b. The aquifer material at both river bank sites actually have a very similar lithology (fine to coarse sand), are made of the same mineralogical composition, have similar Fe/As ratios, and, comparable levels of TOC (Figures 14a and 14b). Furthermore, the similar amount of phosphate leached arsenic in the sandy material of these two aquifers demonstrate that arsenic can be released from both the grey (VP) and the brown sediments (TC). However, there is a significant difference between the river bank sites, with VP exhibiting a thick top layer of reduced clay and silt containing buried organic matter (TOC >1%), whereas the thin layer of surface clay (2 m) in TC is oxic and contains <0.4% TOC. Based on these facts, we conclude for the river bank site with high arsenic (VP) that anoxic and DOC burdened groundwater (potentially enriched by arsenic bound to DOC (Buschmann, 2006) is seeping from the reduced clay into the aquifer where it triggers (and maintains) the iron-reducing conditions in the aquifer. High arsenic concentrations in VP groundwater can thereby originate from the seepage as well as be released from the sandy material in the aquifer itself.

Based on a study with Bangladesh sediments, Polizzotto et al. (2006) suggested that arsenic is only released via redox cycling in surface soils/sediments and is then transported to well-depth through the sandy aquifer. Such a scenario is not likely at our site in VP as the shallow piezometer tapping groundwater from just below the redox boundary at 9–10 m depth had a low arsenic concentration (22 µg/L) while the levels were >180 µg/L at depths >18 m (see Figure 14a). Downward migration of DOC-enriched groundwater originating from surface water bodies was reported by Harvey et al. (Harvey et al., 2002) and made responsible for arsenic mobilization in Bangladesh. However, this has been questioned because the reported DOC concentrations were lowest near the surface and steadily increased to a depth of ~30 meters (McArthur et al., 2004). It should however be considered that the nature of the DOC may be more important than the absolute total concentrations (Rowland et al., 2006). A very small proportion of the total organic matter may be causing reducing conditions and subsequent As mobilization in the sediments (Rowland et al., 2007).

However, DOC migration can only be corroborated if DOC levels are high in the sediment layers above and decrease in the aquifer below. This situation is clearly present in VP, where depth profiles of DOC and sediment-bound TOC demonstrate highest levels in the anoxic clay, and, depletion of organic carbon in the sandy aquifer. Besides, it is well known that groundwater flow can locally be very heterogeneous, particularly in young alluvial sediments. The patchiness of arsenic concentrations in the wells of VP could hence be attributed to spatially varying mixing ratios of groundwater seeped vertically from the organic-rich clay layer (component 1) with less anoxic groundwater in the aquifer (component 2). Based on a detailed study investigating a transect of 100 wells on the river bank near Hanoi, Postma et al. (2007) showed that degradation of organic carbon in the sediments could explain the redox zoning throughout the studied aquifer, i.e. along the vertical groundwater flow component.

5.2. Arsenic mobilization and retention in the peat area

Arsenic concentrations in the Holocene aquifer of the peat area were twice as low than at the river bank, although iron, ammonium, phosphate and DOC were significantly higher than elsewhere. The stratigraphy of the HL sediment core presented in figure 14c is distinctly different from the two river bank cores. The main divergence is that NOM is embedded in the shallow sandy aquifer as well as in clay and silt beneath. Reducing conditions triggering arsenic release from sediments are therefore developed and maintained within the aquifer itself.

The higher arsenic levels found at the river bank in VP in comparison to the Holocene aquifer of the peat area in HL is likely related to the different molar Fe/As ratios present in the groundwaters (Table 3). Mean ratios in groundwater of the peat area in HL (350 mol/mol) were 7 times higher than in VP (68 mol/mol) and, most importantly, dissolved iron (>98% Fe(II)) is 3.5 times higher in the peat area (mean 18.7 mg/L). A recent laboratory study by Herbel and Fendorf (2006) found new sediment phases evolving under iron-reducing conditions that incorporated arsenic and iron from the groundwater. Furthermore, Dixit and Hering (2006) provided evidence that the sorption density of As(III) on iron oxide phases is increased at higher Fe(II) concentrations. In addition, the authors observed the absence of competition between As(III) and ferrous iron for sorption sites on goethite. By contrast, at higher As(III)(aq) concentrations the sorption density increased continuously with increasing Fe(II)(aq) concentration. Their observation suggests a possible formation of ternary surface complexes or surface precipitates that incorporate As(III) and Fe(II). Therefore, lower arsenic concentrations can be expected in aquifers exhibiting higher Fe/As ratios in groundwater and sediment, such as is the case in the Holocene aquifer of the peat area. These findings point to current limitations in the thermodynamic data base for arsenic, especially in the absence of solubility constants for ferrous As(III)/As(V) solid phases and restricts our ability to predict the mobility of arsenic in sediments containing iron oxides. Nevertheless, qualitative trends can be established by arguing with ratios of Fe(II)/As(III), as shown in this study.

[insert Table 3]

5.3. Impact of excessive groundwater abstraction

Groundwater abstraction from the Pleistocene aquifer for the public Hanoi water supply amounted to 610'000 m³ per day in 2005 (Cao et al., 2005) and is likely to increase as the population and industry grow. The authorities plan to extract up to 760'000 m³/day, covering additional needs from other sources. The Pleistocene aquifer is mainly composed of gravel with a low content of buried organic matter (Water-Master-Plan, 1993), with low contents of arsenic bound to the gravel surfaces. Although the hydraulic conductivity is high in gravel, the excessive pumping is causing massive drawdown of piezometric water heads in the Pleistocene aquifer (-30 m in 2003), thereby drawing down the groundwater heads of the Holocene aquifer as well (Figure 2a+b). Despite the sediment core at our location in HL containing a >20 m aquitard, there is enough evidence that the two aquifers are not well separated, as seen in the geological cross-section of figure 1b. Correspondingly, the Hanoi water master plan (Water-Master-Plan, 1993) states "at a distance of 5 km from the Red River, the Pleistocene aquifer is largely replenished by vertical percolation from

the Holocene aquifer". Our isotopic data and the piper plot presented in section 4.1.1 confirm mixing of Red River derived groundwater with Holocene water. In addition, the distribution pattern of ammonium, DOC and alkalinity was similar in the Holocene and Pleistocene aquifers of HL, where these species were highest in the eastward wells of both aquifers, further implies mixing of the aquifers.

Based on data presented in this paper, there is enough evidence to conclude that reduced groundwater is vertically seeping from the Holocene aquifer into the Pleistocene aquifer, thereby enriching the Pleistocene aquifer with DOC, ammonium, alkalinity and iron. This trend was not clear for arsenic, but regarding the iron-reducing conditions and the abundance of readily dissolvable arsenic in all sediments, downward migration of arsenic is likely. The seasonal fluctuations of dissolved arsenic, iron and manganese at wells depths of 70 m (Figure 12, A-6, and A-7) also indicate mixing of water with elevated arsenic and iron concentrations.

As demonstrated in the Hanoi area, drawdown of groundwater through Holocene sediments with abundant NOM may enhance or even be responsible for the iron-reducing conditions in the Pleistocene aquifer below the peat area. The observed steady increase of ammonium concentrations since 1993 is another indication for this situation (Figure 2). Untreated groundwater collected in the year 2000 from wells of the Hanoi water works contained 15–430 µg/L arsenic (Berg et al., 2001), yet it remains unknown how these concentrations developed prior to this date. A trend of increasing arsenic can not be seen in the data of our 14-month groundwater monitoring in HL (see Figure 12), but the situation must be observed over much longer periods to gain a clearer understanding. A 3-year monitoring of 20 wells in Bangladesh documented similar temporal fluctuations of groundwater composition, however, a noticeable increase of dissolved arsenic was only evident in one shallow well (Cheng et al., 2005). Considering a timescale of surface water infiltration into the aquifer in the order of 0.3 to 3 m/year as determined by tritium measurements of Dowling et al. (2002), then several tens of years might be needed to see such an increase over time.

6. Conclusions

Arsenic concentrations in groundwater were neither linked to bulk sediment arsenic (and iron), nor to the phosphate leached fraction of ionic and/or adsorbed arsenic. The magnitude of arsenic levels in groundwater could however be related to the dissolved Fe(II) concentrations. With a mean groundwater Fe/As ratio of 350 mol/mol in the peat area, it seems likely that resorption and/or

incorporation (sequestration) of arsenic to sediment phases is enhanced. Similar conclusions were made in several recent publications (Islam et al., 2005; Coker et al., 2006; Dixit and Hering, 2006; Herbel and Fendorf, 2006).

Vertical migration of reduced groundwater was observed in the excessively pumped peat area, but also at the river bank, where groundwater pumping has little impact on the natural hydrology. Iron-reducing conditions at the river bank emerge in the young clay layer from NOM degradation, thereby dissolving arsenic, iron, manganese and DOC from the sediments. DOC-loaded water then travels downwards through the clay to reach the aquifer, where it triggers and maintains reducing conditions. Once these aquifers become reduced, arsenic is released from the aquifer solids and also additionally derived from the arsenic-enriched groundwater seeping through the clay into the aquifer. This behaviour is an important mechanism for arsenic contamination in aquifers that might not necessarily contain enough organic matter in their sediments to induce reducing conditions independently (Harvey et al., 2002; McArthur et al., 2004; Zheng et al., 2004; Klump et al., 2006).

In the peat area, the aquifer itself contains enough NOM to build up highly reduced groundwater which is then drawn down to the Pleistocene aquifer by the excessive groundwater abstraction. In analogy to the river bank, the iron-reducing conditions are maintained in the Pleistocene aquifer, with groundwater remaining enriched with high concentrations of arsenic, ammonium, DOC and iron. This situation poses a major problem to the water treatment technology currently applied by the Hanoi water works. Arsenic is to some extent removed by oxidation and coprecipitation with iron (Berg et al., 2001; Dodd et al., 2006), but ammonium and DOC remain in the treated water and significantly hamper chlorine disinfection (Duong et al., 2003). Therefore we strongly recommend that the Hanoi water works should evaluate alternative water resources for drinking water production, be it either groundwater from uncontaminated areas, or ambient surface water.

The groundwater drawdown in the Hanoi area is certainly relatively extreme, but it serves to illustrate what might happen if deep and less anoxic groundwater is not sufficiently replenished. Surface water is still the dominant source for irrigation in the Red River Delta, but, in the arsenic burdened Bengal delta floodplain, large amounts of groundwater are pumped for irrigation purposes. The impact on arsenic mobilization is controversial and mainly discussed for irrigation wells tapping arsenic-rich water from about 30 m depth (McArthur et al., 2004; Zheng et al., 2004; Harvey et al., 2006; Klump et al., 2006). Evidence from this study in Hanoi shows that excessive abstraction of groundwater from deep wells, e.g., wells tapping water below the arsenic burdened

depth, can cause a downward shift of iron-reducing conditions and concurrently mobilize arsenic along the way. If such wells are installed, the development of reducing conditions and arsenic levels must be carefully monitored.

Acknowledgements

This project was substantially funded by the Swiss Agency for Development and Cooperation (SDC) in the framework of the Swiss-Vietnamese cooperation project ESTNV (Environmental Science and Technology in Northern Vietnam). We thank Bui Hong Nhat, Luu Thanh Binh, Nguyen Thi Minh Hue, Nguyen Trong Hai, Pham Minh Khoi, Vi Thi Mai Lan, Pham Thi Dau, and Tran Thi Hao for contributions in field and laboratory work. The field campaigns benefited from the kind support of Tong Ngoc Thanh and Nguyen Thanh Hai of the Vietnam Northern Hydrogeological and Engineering Geological Division. Dang Duc Nhan from the Vietnam Institute of Nuclear Science and Technology kindly provided isotope signatures of local meteoric water. We are grateful to Adrian Ammann, David Kistler, Jakov Bolotin, and Madeleine Langmeier with the AuA lab crew for analytical assistance, and Carsten Schubert for water isotope measurements. The authors also thank Roland Schertenleib, Stephan Hug, Zsolt Berner, Stephan Norra, and Elisabeth Eiche for valuable discussions and Helen Rowland for proofreading.

References

- Akai, J., Izumi, K., Fukuhara, H., Masuda, H., Nakano, S., Yoshimura, T., Ohfuji, H., Anawar, H.M. and Akai, K., 2004. Mineralogical and geomicrobiological investigations on groundwater arsenic enrichment in Bangladesh. *Appl. Geochem.*, 19(2): 215-230.
- Berg, M., Luzi, S., Trang, P.T.K., Viet, P.H., Giger, W. and Stuben, D., 2006. Arsenic removal from groundwater by household sand filters: Comparative field study, model calculations, and health benefits. *Environ. Sci. Technol.*, 40(17): 5567-5573.
- Berg, M. and Stengel, C., 2004. ARS13-16 Arsenic Reference Samples Interlaboratory Quality Evaluation (IQE), Report to Participants, Eawag, Swiss Federal Institute of Aquatic Science and Technology (Eawag), Dübendorf, Switzerland.
- Berg, M., Stengel, C., Trang, P.T.K., Viet, P.H., Sampson, M.L., Leng, M., Samreth, S. and Fredericks, D., 2007. Magnitude of arsenic pollution in the Mekong and Red River Deltas - Cambodia and Vietnam. *Sci. Total Environ.*, 372(2-3): 413-425.
- Berg, M., Tran, H.C., Nguyen, T.C., Pham, H.V., Schertenleib, R. and Giger, W., 2001. Arsenic contamination of groundwater and drinking water in Vietnam: A human health threat. *Environ. Sci. Technol.*, 35(13): 2621-2626.
- BGS and DPHE, 2001. Arsenic contamination of groundwater in Bangladesh. British Geological Survey Report WC/00/19, BGS Technical Report WC/00/19; British Geological Survey: Keyworth, U.K., Keyworth, UK.
- Blute, N.K., Brabander, D.J., Hemond, H.F., Sutton, S.R., Newville, M.G. and Rivers, M.L., 2004. Arsenic sequestration by ferric iron plaque on cattail roots. *Environ. Sci. Technol.*, 38(22): 6074-6077.

- Buschmann, J., Berg, M., Stengel, C. and Sampson, M.L., 2007. Arsenic and Manganese Contamination of Drinking Water Resources in Cambodia: Coincidence of Risk Areas with Low Relief Topography. *Environ. Sci. Technol.*, 41(7): 2146–2152.
- Cao, T.H., Le, V.C., Nguyen, V.K., Bui, V.M., Ngo, N.A. and Berg, M., 2005. Improving the supply water quality of Hanoi. Part 1: current situation of supply water and challenges for treatment technology. *Vietnam Water Suppl. Sewer.*, 7: 31–35.
- Charlet, L. and Polya, D.A., 2006. Arsenic in shallow, reducing groundwaters in southern Asia: An environmental health disaster. *Elements*, 2(2): 91-96.
- 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 Araiazar, Bangladesh. *Environ. Sci. Technol.*, 39(13): 4759-4766.
- Coker, V.S., Gault, A.G., Pearce, C.I., van der Laan, G., Telling, N.D., Charnock, J.M., Polya, D.A. and Lloyd, J.R., 2006. XAS and XMCD evidence for species-dependent partitioning of arsenic during microbial reduction of ferrihydrite to magnetite. *Environ. Sci. Technol.*, 40(24): 7745-7750.
- Dixit, S. and Hering, J.G., 2006. Sorption of Fe(II) and As(III) on goethite in single- and dual-sorbate systems. *Chem. Geol.*, 228(1-3): 6-15.
- Dodd, M.C., Vu, N.D., Ammann, A., Le, V.C., Kissner, R., Pham, H.V., Cao, T.H., Berg, M. and Von Gunten, U., 2006. Kinetics and mechanistic aspects of As(III) oxidation by aqueous chlorine, chloramines, and ozone: Relevance to drinking water treatment. *Environ. Sci. Technol.*, 40(10): 3285-3292.
- Dowling, C.B., Poreda, R.J., Basu, A.R., Peters, S.L. and Aggarwal, P.K., 2002. Geochemical study of arsenic release mechanisms in the Bengal Basin groundwater. *Water Resour. Res.*, 38(9).
- Duong, H.A., Berg, M., Hoang, M.H., Pham, H.V., Gallard, H., Giger, W. and von Gunten, U., 2003. Trihalomethane formation by chlorination of ammonium- and bromide-containing groundwater in water supplies of Hanoi, Vietnam. *Water Res.*, 37(13): 3242-3252.
- Fette, M., Kipfer, R., Schubert, C.J., Hoehn, E. and Wehrli, B., 2005. Assessing river-groundwater exchange in the regulated Rhone River (Switzerland) using stable isotopes and geochemical tracers. *Appl. Geochem.*, 20(4): 701-712.
- Harvey, C.F., Ashfaq, K.N., Yu, W., Badruzzaman, A.B.M., Ali, M.A., Oates, P.M., Michael, H.A., Neumann, R.B., Beckie, R., Islam, S. and Ahmed, M.F., 2006. Groundwater dynamics and arsenic contamination in Bangladesh. *Chem. Geol.*, 228(1-3): 112-136.
- Harvey, C.F., Swartz, C.H., Badruzzaman, A.B.M., Keon-Blute, N., Yu, W., Ali, M.A., Jay, J., Beckie, R., Niedan, V., Brabander, D., Oates, P.M., Ashfaq, K.N., Islam, S., Hemond, H.F. and Ahmed, M.F., 2002. Arsenic mobility and groundwater extraction in Bangladesh. *Science*, 298(5598): 1602-1606.
- Helz, G.R., Tossell, J.A., Charnock, J.M., Patrick, R.A.D., Vaughan, D.J. and Garner, C.D., 1995. Oligomerization in as(III) Sulfide Solutions - Theoretical Constraints and Spectroscopic Evidence. *Geochim. Cosmochim. Acta*, 59(22): 4591-4604.
- Herbel, M. and Fendorf, S., 2006. Biogeochemical processes controlling the speciation and transport of arsenic within iron coated sands. *Chem. Geol.*, 228(1-3): 16-32.
- Horneman, A., Van Geen, A., Kent, D.V., Mathe, P.E., Zheng, Y., Dhar, R.K., O'Connell, S., Hoque, M.A., Aziz, Z., Shamsudduha, M., Seddique, A.A. and Ahmed, K.M., 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part 1: Evidence from sediment profiles. *Geochim. Cosmochim. Acta*, 68(17): 3459-3473.
- Islam, F.S., Gault, A.G., Boothman, C., Polya, D.A., Charnock, J.M., Chatterjee, D. and Lloyd, J.R., 2004. Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. *Nature*, 430(6995): 68-71.
- Islam, F.S., Pederick, R.L., Gault, A.G., Adams, L.K., Polya, D.A., Charnock, J.M. and Lloyd, J.R., 2005. Interactions between the Fe(III)-reducing bacterium *Geobacter sulfurreducens* and arsenate, and capture of the metalloid by biogenic Fe(II). *Appl. Environ. Microbiol.*, 71(12): 8642-8648.
- Kapaj, S., Peterson, H., Liber, K. and Bhattacharya, P., 2006. Human health effects from chronic arsenic poisoning- A review. *J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng.*, 41(10): 2399-2428.
- Keon, N.E., Swartz, C.H., Brabander, D.J., Harvey, C. and Hemond, H.F., 2001. Validation of an arsenic sequential extraction method for evaluating mobility in sediments. *Environ. Sci. Technol.*, 35(13): 2778-2784.

- Klump, S., Kipfer, R., Cirpka, O.A., Harvey, C.F., Brennwald, M.S., Ashfaq, K.N., Badruzzaman, A.B.M., Hug, S.J. and Imboden, D.M., 2006. Groundwater dynamics and arsenic mobilization in Bangladesh assessed using noble gases and tritium. *Environ. Sci. Technol.*, 40(1): 243-250.
- Kocar, B.D., Herbel, M.J., Tufano, K.J. and Fendorf, S., 2006. Contrasting effects of dissimilatory iron(III) and arsenic(V) reduction on arsenic retention and transport. *Environ. Sci. Technol.*, 40(21): 6715-6721.
- McArthur, J.M., Banerjee, D.M., Hudson-Edwards, K.A., Mishra, R., Purohit, R., Ravenscroft, P., Cronin, A., Howarth, R.J., Chatterjee, A., Talukder, T., Lowry, D., Houghton, S. and Chadha, D.K., 2004. Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications. *Appl. Geochem.*, 19(8): 1255-1293.
- McArthur, J.M., Ravenscroft, P., Safiulla, S. and Thirlwall, M.F., 2001. Arsenic in groundwater: Testing pollution mechanisms for sedimentary aquifers in Bangladesh. *Water Resour. Res.*, 37(1): 109-117.
- Meharg, A.A., Scrimgeour, C., Hossain, S.A., Fuller, K., Cruickshank, K., Williams, P.N. and Kinniburgh, D.G., 2006. Codeposition of organic carbon and arsenic in Bengal Delta aquifers. *Environ. Sci. Technol.*, 40(16): 4928-4935.
- Nguyen, V.D., 2005. Personal communication. Northern Hydrogeological and Engineering Geological Division, Vietnam Geological Survey, Hanoi, Vietnam.
- Nhan, D.D., Giap, T.V., Lieu, D.B., Loan, D.T., Anh, V.T., Minh, D.M., Thinh, N.T.H. and Viet, D.D., 2005. Arsenic Contaminated Groundwater in the Hanoi Area and Its Studies Using Isotope Technique, Institute for Nuclear Science and Technology, Hanoi, Vietnam.
- NHEGD, 2002. Annual Report 2001, Northern Hydrogeological and Engineering Geological Division, Vietnam Geological Survey, Hanoi, Vietnam.
- Nickson, R.T., McArthur, J.M., Ravenscroft, P., Burgess, W.G. and Ahmed, K.M., 2000. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Appl. Geochem.*, 15(4): 403-413.
- Polizzotto, M.L., Harvey, C.F., Li, G.C., Badruzzaman, B., Ali, A., Newville, M., Sutton, S. and Fendorf, S., 2006. Solid-phases and desorption processes of arsenic within Bangladesh sediments. *Chem. Geol.*, 228(1-3): 97-111.
- Postma, D., Larsen, F., Minh Hue, N.T., Duc, M.T., Viet, P.H., Nhan, P.Q. and Jessen, S., 2007. Arsenic in groundwater of the Red River floodplain, Vietnam: Controlling geochemical processes and reactive transport modeling. *71(21)*: 5054-5071.
- Redfield, A.C., 1958. The biological control of chemical factors in the environment. 46: 205-221.
- Roman-Ross, G., Cuello, G., Tisserand, D. and Charlet, L., 2002. Arsenic removal by gypsum and calcite: the continuum between sorption and solid-solution phenomenon. *Geochim. Cosmochim. Acta*, 66(15A): A646-A646.
- Rowland, H.A.L., Pederick, R.L., Polya, D.A., Pancost, R.D., Van Dongen, B.E., Gault, A.G., Vaughan, D.J., Bryant, C., Anderson, B. and Lloyd, J.R., 2007. The control of organic matter on microbially mediated iron reduction and arsenic release in shallow alluvial aquifers, Cambodia. *Geobiology*, 5(3): 281-292.
- Rowland, H.A.L., Polya, D.A., Lloyd, J.R. and Pancost, R.D., 2006. Characterisation of organic matter in a shallow, reducing, arsenic-rich aquifer, West Bengal. *Org. Geochem.*, 37(9): 1101-1114.
- Rozanski, K., Aragus, L., Gonfiantini, R., Swart, P.K., Lohmann Kyger, C., McKenzie, J.A. and Savin, S., 1993. Isotopic patterns in modern global precipitation. In: P.K. Swart and e. al (Editors), *Geophysical Monograph 78*. American Geophysical Union, pp. 1-36.
- Smedley, P.L. and Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.*, 17(5): 517-568.
- Smith, A.H., Lingas, E.O. and Rahman, M., 2000. Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. *Bull. World Health Organ.*, 78(9): 1093-1103.
- Spycher, N.F. and Reed, M.H., 1989. As(III) and Sb(III) Sulfide Complexes - an Evaluation of Stoichiometry and Stability from Existing Experimental-Data. *Geochim. Cosmochim. Acta*, 53(9): 2185-2194.
- Stuben, D., Berner, Z., Chandrasekharam, D. and Karmakar, J., 2003. Arsenic enrichment in groundwater of West Bengal, India: geochemical evidence for mobilization of As under reducing conditions. *Appl. Geochem.*, 18(9): 1417-1434.
- Trafford, J.M., Lawrence, A.R., Macdonald, D.M.J., Nguyen, V.D., Tran, D.N. and Nguyen, T.H., 1996. The effect of urbanisation on the groundwater quality beneath the city of Hanoi, Vietnam. BGS Technical Report WC/96/22. British Geological Survey, Keyworth, UK.

- Trang, P.T.K., Berg, M., Viet, P.H., Van Mui, N. and Van Der Meer, J.R., 2005. Bacterial bioassay for rapid and accurate analysis of arsenic in highly variable groundwater samples. *Environ. Sci. Technol.*, 39(19): 7625-7630.
- Van Geen, A., Rose, J., Thorai, S., Garnier, J.M., Zheng, Y. and Bottero, J.Y., 2004. Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part II: Evidence from sediment incubations. *Geochim. Cosmochim. Acta*, 68(17): 3475-3486.
- 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 variability of arsenic in 6000 tube wells in a 25 km² area of Bangladesh. *Water Resour. Res.*, 39(5).
- Wasserman, G.A., Liu, X.H., Parvez, F., Ahsan, H., Factor-Litvak, P., van Geen, A., Slavkovich, V., Lolacono, N.J., Cheng, Z.Q., Hussain, L., Momotaj, H. and Graziano, J.H., 2004. Water arsenic exposure and children's intellectual function in Araihaazar, Bangladesh. *Environ. Health Perspect.*, 112(13): 1329-1333.
- Water-Master-Plan, 1993. Water Master Plan of Hanoi City for the Period of 1993–2010. Vol. 1, The Social Republic of Vietnam, Hanoi People's Committee. The Republic of Finland, Finnish International Development Agency FINNIDA, Hanoi, Vietnam.
- White, D.E., Hem, J.D. and Waring, G.A., 1963. Chemical composition of subsurface water, Data of Geochemistry. US Geological Survey.
- Zheng, Y., Stute, M., van Geen, A., Gavrieli, I., Dhar, R., Simpson, H.J., Schlosser, P. and Ahmed, K.M., 2004. Redox control of arsenic mobilization in Bangladesh groundwater. *Appl. Geochem.*, 19(2): 201-214.

Figures

Figure 1. a) Map of the Hanoi province and geological cross-sections derived from lithological logs of the Vietnam Geological Survey. Pink rectangles mark the locations of the investigated villages Thuong Cat (TC), Hoang Liet (HL) and Van Phuc (VP). **b)** Sedimentary cross sections illustrating the simplified sediment architecture below the city of Hanoi (A–B) and the southern suburbs (C–D).

Figure 2. Map of the Hanoi area depicting hydrological and sedimentary features as well as concentrations of arsenic (Berg et al., 2001) and ammonium (NHEGD, 2002) in the Holocene and Pleistocene aquifers. **a)** Arsenic, groundwater heads, peat and ammonium, **b)** drawdown of Holocene groundwater (2003), **c)** drawdown of Pleistocene groundwater (2003), **d)** sedimentary peat layers, and **e-g)** ammonium in the Pleistocene aquifers from 1993, 1995 and 2001.

Figure 3. Piper diagrams showing the main hydrochemical composition of the three studied areas. **a)** River water and groundwater in Van Phuc and Thuong Cat (located close to the river), **b)** groundwater from the Holocene and Pleistocene aquifers and surface water in Hoang Liet (located 5 km west of the Red River).

Figure 4. d^2H versus d^{18}O values in precipitation, Red River water and groundwater, expressed as ‰ enrichments relative to standard mean ocean water (SMOV). **a)** Red River water and precipitation collected in Hanoi in 2003 and 2004 (data from (Nhan et al., 2005)), **b)** groundwater collected in July 2003 in the three studied areas and surface water from Hoang Liet. The Global meteoric water line (GMWL) has a slope of 8.17 derived from the equation $\text{d}^2\text{H} = 8.17 \times \text{d}^{18}\text{O} + 10.35$ (Rozanski et al., 1993).

Figure 5. Map of Van Phuc village (VP) and vertical cross-section depicting arsenic concentrations in groundwater samples collected in December 2002 from family-based tubewells. Semi-transparent dots are measurements from a reconnaissance study conducted in March 2001. Results of the sediment core are discussed in section 4.2. The illustrated clay/silt layer in the cross-section is only implied. The well with 540 $\mu\text{g/L}$ (close by VP 6) and a number of other wells were abandoned by the owners after our reconnaissance study of March 2001.

Figure 6. Contour plots of selected parameters in VP groundwater collected in December 2002. The contours are spatially delimited by the groundwater wells indicated by black points (see also map in figure 5). Mapping software: Surfer 7.0, nearest neighbour algorithm.

Figure 7. Map of Thuong Cat village (TC) and vertical cross-section depicting arsenic concentrations in groundwater samples collected from family-based tubewells in December 2002. Results of the sediment core are discussed in section 4.2. The illustrated clay/silt layer in the cross-section is only implied.

Figure 8. Contour plots of selected parameters in TC groundwater. The contours are spatially delimited by the groundwater wells indicated by black points (see also map in figure 5). Mapping software: Surfer 7.0, nearest neighbour algorithm.

Figure 9. Map of Hoang Liet village (HL) and vertical cross-section depicting arsenic concentrations in groundwater samples collected from family-based tubewells in December 2002. Wells encircled by a thick line are tapping the Pleistocene aquifer (n=7). Surface water samples are indicated by white stars. Results of the sediment core are discussed in section 4.2. The illustrated clay/silt layer as well as the aquitard in the cross-section are only implied.

Figure 10. Contour plots of selected parameters in groundwater samples from HL (Holocene aquifer). The contours are spatially delimited by the groundwater wells indicated by black points (see also map in figure 5). Mapping software: Surfer 7.0, nearest neighbour algorithm.

Figure 11. Contour plots of selected parameters in groundwater samples from HL (Pleistocene aquifer). The contours are spatially delimited by the groundwater wells indicated by black points (see also map in figure 5). Mapping software: Surfer 7.0, nearest neighbour algorithm.

a) Holocene aquifer

b) Pleistocene aquifer

Figure 12. Variation of dissolved arsenic in 13 groundwater wells (top) and groundwater levels (bottom) in HL (2002–2003). **a)** Holocene aquifer, **b)** Pleistocene aquifer.

Figure 13. Lithological logs (hand drawn) of the three boreholes drilled in April 2003, with depths of associated nested piezometers. The colouring reflects the aspect of the sediments as they were brought to the surface. Dashed lines of correlation were derived from lithology and chemical composition. The triangles indicate groundwater heads at the time of drilling. **a)** Position E 105°44.084', N 21°05.859', **b)** position E 105°53.851', N 20°55.189', **c)** position E 105°50.221', N 20°58.046'. The locations are marked on the maps in figures 5, 7, and 9.

a) VP

b) TC

c) HL

Figure 14. Depth profiles of sediment-bound As, Fe, C and N, as well as total dissolved arsenic measured in groundwater from the nested piezometers in **a)** Van Phuc, **b)** Thuong Cat, and **c)** Hoang Liet.

Figure 15. Arsenic leached from the sediments by the sequence of extractants outlined in table 1.

Tables

Table 1. Procedure Applied for the Sequential Extraction of Arsenic-Bearing Sediment Phases^a

Step	Extractant	Conditions	Target phase	Mechanism ^b
PO4	1 M NaH ₂ PO ₄	pH 5, 16 and 24 h, 25 °C. One repetition of each time duration + one water wash	ionically bound As, strongly adsorbed As	Anion exchange of phosphate for arsenite and arsenate
HCl	1 M HCl	1 h, 25 °C. One repetition + one water wash	As coprecipitated with acid volatile sulfides, carbonates, Mn oxides, and As coprecipitated with very amorphous Fe oxyhydroxides	Proton dissolution Fe-Cl complexation
Ox	0.2 M ammonium oxalate/oxalic acid	pH 3, 2 h, 25 °C in dark (wrapped in Al foil) One repetition + one water wash	As coprecipitated with amorphous Fe oxyhydroxides	Fe oxyhydroxides ligand-promoted dissolution
rest	16 M HNO ₃ + 30% H ₂ O ₂	1 h microwave digestion, 100°C, 40 bar	As coprecipitated with crystalline Fe oxyhydroxides, silicates, pyrite and As ₂ S ₃ , orpiment and calcitrant As minerals	Digestion of the minerals as described in the experimental section

^a Simplified from (Keon et al., 2001). ^b According to (Keon et al., 2001).

Table 2. Average Fraction (%) of Arsenic in the Sequential Extracts.

Extractant	Target phase	Thuong Cat (TC)	Van Phuc (VP)	Hoang Liet (HL)	All
PO ₄	Ionically and/or strongly adsorbed As	44.3	59.4	61.1	56.7
HCl	Carbonates, Mn oxides, very amorphous FeOOH	12.2	11.2	10.4	11.2
Ox	Amorphous FeOOH	9.6	8.4	6.5	8.1
Rest	Crystalline FeOOH, pyrite, and other calcitrant phases	34.0	21.1	19.0	24.0

Table 3. Molar ratios^a of Fe/As in water and sediment of the three locations studied.

	River bank		Peat area
	Thuong Cat	Van Phuc	Hoang Liet
Water			
mean	60	68	350
average	96	120	740
max	270	630	3900
Sediment			
mean	3900	4700	8700
average	4200	4600	9100
max	7700	7500	18500

^a Values <2 µg/L As and <0.05 mg/L Fe are not considered