Arsenic Contamination of Groundwater and Drinking Water in the Red River Delta, Vietnam: Geochemical Investigations and Mitigation Measures

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Abstract

Natural contamination of anoxic groundwater by arsenic has become a crucial water quality issue in many parts of the world. The problem was first recognized in 1989 in West Bengal (Bengal Delta, India) and it took several more years to realize that large parts of neighboring Bangladesh are also affected, where some 30 million people are drinking this water without treatment. Consequently, as the worldwide awareness of geogenic arsenic contamination of groundwater increased, the problem was found to be widespread in several other countries and >100 million people are now believed to be at risk of arsenic poisoning. Arsenic contamination of groundwater and drinking water in the city of Hanoi and in the rural areas of the Red River Delta was discovered in 1998. The studies presented here focus on i) the first assessment of the occurrence and distribution of arsenic contamination in groundwater of the Red River Delta and in Hanoi's drinking water supply, ii) in-depth investigations on the geochemical causes and mechanisms leading to elevated groundwater arsenic levels regarding local hydrogeological situations, and, iii) the examination of a low-cost and easy to use arsenic removal system for rural households, capable to significantly mitigate the arsenic burden of the people.

For the first assessment (*Chapter 2*), 5 sediment cores and 68 private tubewells tapping the upper (Holocene) aquifer in rural areas were investigated over an area of 700 km^2. The groundwaters are strongly reducing with high concentrations of Fe, Mn and ammonium. With an average of 159 μg/L (range 1–3000 μg/L) the majority of tubewells yielded arsenic concentrations above the current WHO guideline of 10 μg/L and the concentrations varied greatly within the studied area. Arsenic was generally higher in the south of Hanoi where alarming levels of >500 μg/L were measured on both sides of the Red River. The results indicated that the sources of contamination are distributed over a large area potentially affecting 10 million people. Analysis of raw groundwater pumped from the lower (Pleistocene) aquifer for the Hanoi water supply yielded arsenic levels between 15 and 430 μg/L. Aeration and sand filtration that are applied in the treatment plants for iron removal significantly lowered the arsenic concentrations in the treated water, but arsenic occasionally remained above 50 μg/L. Extracts of sediment samples showed a correlation of arsenic and iron contents (r^2 0.700, n=64), indicating that arsenic bound to the sediments is associated with iron oxy(hydr)oxides and released to the groundwater by reductive dissolution of iron.

A more detailed geochemical groundwater and sediment investigation was conducted in three villages located in different settings (*Chapter 3*), i.e., high arsenic at the river bank, low arsenic at the river bank, and medium arsenic in an area of buried peat and excessive groundwater abstraction. In-depth chemical analysis of water from Holocene and Pleistocene tubewells, surface water, sediment cores (>30 m), sites of nested wells, as well as sequential leaching of sediment samples were conducted. Seasonal fluctuations in water chemistry were studied over a time span of 14 months. The sediment-bound arsenic (1.3–22 µg/g) was in a natural range of alluvial sediments. Fractions of 23–84% (av. 56%) arsenic were extracted with 1 M phosphate from all sediment layers, indicating that arsenic can readily be mobilized at each of the three locations. Vertical migration of DOC-enriched groundwater from the young clayey sediments to the aquifer at the river bank, or from the Holocene to the Pleistocene aquifer in the peat area, were found to promote iron-reducing conditions which lead to arsenic contamination in the aquifers. Arsenic levels averaged 121 µg/L at the river bank and 60 µg/L 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 iron/arsenic ratios of 350 in water and 8'700 in the sediments of the peat area, reduced iron possibly forms new mineral phases that resorb previously mobilized arsenic to the sediment. Drawdown of Holocene water to the Pleistocene aquifer caused by the pumping for the public drinking water supply of Hanoi (>600'000 m^3/day) did not show an observable increase of arsenic during the 14 month study. However, there are indications that DOC, ammonium and iron are leaching down from the Holocene aquifer, thereby enhancing the reducing conditions in the Pleistocene aquifer. This situation should alert the local authorities to evaluate better groundwater management practises.

Finally, with the goal to propagate a suitable mitigation measure, arsenic removal efficiencies of 43 household sand filters were studied in rural areas of the Red River Delta (*Chapter 4*). The average arsenic removal amounted to 80% from the broad range of groundwaters containing 10–382 µg/L As, <0.1–48 mg/L Fe, <0.01–3.7 mg/L P, and 0.05–3.3 mg/L Mn. The filtering process requires only a few minutes. Removal efficiencies of Fe, phosphate and Mn were >99%, 90% and 71%, respectively. Phosphate concentrations >2.5 mg P/L slightly hampered the sand filter efficiencies. Iron/arsenic ratios of ≥50 or ≥250 were required to ensure arsenic removal to levels below 50 or 10 µg/L, respectively. Interestingly, the overall arsenic elimination was higher than predicted from model calculations based on sorption constants determined from co-precipitation experiments with artificial groundwater. This observation is assumed to result from enhanced As(III) oxidation in the natural groundwaters, possibly involving Mn, microorganisms and dissolved organic matter. Clear evidence of lowered arsenic burden for people consuming sand-filtered water was demonstrated from hair analyses. The easily observable removal of iron from the pumped water makes the effect of a sand filter immediately recognizable even to people who are not aware of the arsenic problem.

Arsenkontamination von Grund- und Trinkwasser im Red River Delta, Vietnam: Geochemische Untersuchungen und Linderungsmassnahmen

Kurzfassung

Arsenbelastetes Grundwasser stellt in mehreren Ländern ein ernstes Wasserqualitätsproblem dar. Dieser Sachverhalt wurde 1989 erstmals in West Bengalen (Bengal Delta, Indien) erkannt. Einige Jahre später stellte sich heraus dass auch weite Teile im benachbarten Bangladesh stark betroffen sind wo geschätzte 30 Millionen Leute dieses Grundwasser ohne vorherige Aufreinigung trinken. Nach der Erkenntnis dass anoxisches Grundwasser mit geogenem Arsen kontaminiert sein kann, wurde das Problem in mehreren Ländern erkannt. Die Zahl betroffener Leute wird heute auf mehr als 100 Millionen geschätzt. In Hanoi und den ländlichen Gebieten des Red River Deltas wurde 1998 erstmals Arsen in Grund- und Trinkwasser analysiert. In der vorliegenden Arbeit wurden folgende Untersuchungen durchgeführt: i) Erste Studie über das Vorkommen und die Verbreitung der Arsenkontaminationen in Grundwässern des Red River Deltas und in der Wasserversorgung von Hanoi; ii) Eingehende Erkundung der geogenen Ursachen die zu erhöhten Arsengehalten führen, unter Berücksichtigung lokaler hydrogeologischer Gegebenheiten; iii) Evaluation einer kostengünstigen und anwenderfreundlichen Technologie zur Arsenentfernung in ländlichen Haushaltungen, welche die Arsenbelastung der Leute signifikant vermindern kann.

Für die erste Studie wurden 5 Sedimentkerne und Grundwasser in einem 700 km^2 grossen Gebiet untersucht (*Kapitel 2*). Dazu wurden handbetriebene Grundwasserpumpen in 68 ländliche Haushalten beprobt, welche ausschliesslich Wasser aus dem oberen (holozänen) Aquifer förderten. Das Grundwasser ist sehr reduzierend mit hohen Konzentrationen von Eisen, Mangan und Ammonium. Bei einer durchschnittlichen Konzentration von 159 μg/L (Bereich 1–3000 μg/L) wies die Mehrheit der Proben Arsenkonzentrationen über dem WHO Grenzwert von 10 μg/L auf, wobei die Werte örtlich stark variierten. Im Süden von Hanoi war Arsen grundsätzlich höher wobei alarmierende Gehalte von >500 μg/L auf beiden Seiten des Red Rivers gemessen wurden. Die Resultate zeigten auf dass die Arsenkontaminationen über grosse Gebiete verbreitet sind und potentiell 10 Millionen Leute davon betroffen sind. Unbehandeltes Grundwasser aus dem unteren (pleistozänen) Aquifer welches für die Trinkwasseraufbereitung von Hanoi gepumpt wird lagen die Arsenkonzentrationen zwischen 15 bis 430 μg/L. Während der Enteisenung in den Wasserwerken (Belüftung und Sandfiltration) werden die Arsengehalte stark vermindert, in einigen Fällen lagen die Konzentrationen im aufbereiteten Trinkwasser jedoch über 50 μg/L. In den

Sedimentaufschlüssen zeigten Arsen und Eisen eine Korrelation von r^2 0.700 (n = 64). Sedimentgebundenes Arsen ist demnach mit Eisenoxi(hydr)oxiden assoziiert und gelangt bei der reduktiven Auflösung von Eisenmineralen ins Grundwasser.

Im zweiten Teil dieser Arbeit wurden ausführliche geochemische Untersuchungen von Grundwasser und Sedimenten an drei Standorten durchgeführt (*Kapitel 3*), die sich wie folgt in lokalen Gegebenheiten unterscheiden: i) Hohe Arsenwerte in Grundwasser nahe beim Fluss; ii) Tiefe Arsenwerte in Grundwasser nahe beim Fluss; iii) Mittlere Arsenkonzentrationen in einem Gebiet mit torfhaltigen Sedimenten und übermässiger Grundwasserabstraktion. Grundwasser von holozänen und pleistozänen Aquiferen, Oberflächenwasser, sowie Sedimentkerne (>30 m tief) und korrespondierendes Porenwasser wurden beprobt und eingehenden geochemischen Analysen unterzogen. Zudem wurden saisonale Schwankungen der Grundwasserzusammensetzung über eine Zeitspanne von 14 Monaten verfolgt. Die Gehalte von sedimentgebundenem Arsen (1.3–22 μg/g) waren in einem durchaus normalen Bereich für alluviale Sedimente. Allerdings liessen sich 23–84% (Durchschnitt 56%) Arsen mit 1 M Phosphat aus den Sedimenten extrahieren, was auf eine hohe Mobilität des Arsens an allen drei Standorten hinweist. Weitere Untersuchungen zeigten dass DOC-angereichertes Grundwasser aus den jungen, lehmigen Flusssedimenten in den Aquifer sickert, und im Torfgebiet vom holozänen in den pleistozänen Aquifer gelangt. Diese Gegebenheit führt zu eisenreduzierenden Bedingungen in den nicht sehr kohlenstoffhaltigen Aquiferen was letztlich die Mobilisierung von Arsen begünstigt. Durchschnittlich betrugen die Arsenkonzentrationen 121 μg/L in Flussnähe und 60 μg/L im Torfgebiet. Die tiefere Arsenkontamination im Torfgebiet ist wahrscheinlich auf die außerordentlich hohen Eisengehalte in Grundwasser und Sedimenten zurückzuführen. Bei den mittleren molaren Eisen/Arsen Verhältnissen von 350 in Grundwasser und 8'700 in den Sedimenten des Torfgebietes ist scheinbar genügend reduziertes Eisen vorhanden um neue Mineralphasen auszubilden, welche gelöstes Arsen binden und somit immobilisieren. Der forcierte Abfluss von Grundwasser aus dem holozänen in den pleistozänen Aquifer, bedingt durch die extensive Grundwasserentnahme für die Trinkwasserproduktion von Hanoi (>600'000 m^3/Tag), führte während der 14-monatigen Studie nicht zu ansteigenden Arsenkonzentrationen im pleistozänen Aquifer. Es gibt aber Anzeichen dass DOC, Eisen und Ammonium aus dem oberen in den unteren Aquifer sickert, was eine Verstärkung der reduzierenden Bedingungen im pleistozänen Aquifer zur Folge hat. Dieser Umstand sollte die lokalen Behörden dazu bewegen das Grundwasser nachhaltiger zu bewirtschaften.

Die dritte Studie widmete sich der Evaluation einer geeigneten Technologie zur Arsenlinderung in ländlichen Gebieten, wozu die Tauglichkeit von Sandfiltern in 43

Haushaltungen untersucht wurde (*Kapitel 4*). Die Zusammensetzung der Grundwässer an den verschiedenen Standorten deckte eine sehr grosse Spannweite ab mit Konzentrationen von 10–382 μg/L Arsen, <0.1–48 mg/L Eisen, <0.01–3.7 mg/L Phoshat-Phosphor und 0.05–3.3 mg/L Mangan. Mit den Sandfiltern konnte durchschnittlich 80% Arsen aus dem Wasser entfernt werden, obwohl der Filterungsprozess nur wenige Minuten dauert. Die Entfernungsraten waren auch für Eisen (>99%), Phosphat (90%) und Mangan (71%) gut. Bei Phosphatkonzentrationen >2.5 mg P/L war die Effizienz der Sandfilter 15–20% schlechter, was in Laborexperimenten bestätigt werden konnte. Um sicherzustellen dass die Arsengehalte in gefiltertem Wasser unter 50 μg/L beziehungsweise 10 μg/L liegen, sollte gelöstes Eisen gegenüber Arsen einen mindestens 50-, respektive 250-fachen Überschuss aufweisen. Anhand von Sorptionskonstanten die im Labor mit künstlichem Grundwasser ermittelt wurden, konnte die Entfernungseffizienz der Sandfiltern modelliert werden. Die effektive Arsenentfernung war in den Sandfiltern jedoch höher als die Modellvorhersage. In natürlichem Grundwasser wird die Arsenentfernung wahrscheinlich durch oxidative Prozesse begünstigt die im Modell nicht berücksichtigt sind, wie z.B. Oxidation von As(III) zu As(V) durch Manganspezies, durch Mikroorganismen, sowie durch DOC Bestandteile. Abschliessend konnte anhand von >200 Haaranalysen aufgezeigt werden dass sandgefiltertes Wasser die Arsenbelastung der Leute deutlich herabsetzt. Die beobachtbare Eisenfällung im Sandfilter veranschaulicht dessen Nützlichkeit selbst für Leute die wenig über die Arsenproblematik wissen.

Nichts in der Welt ist weicher und schwächer als Wasser, und doch gibt es nichts, das wie Wasser Starres und Hartes bezwingt, unabänderlich strömt es nach seiner Art.
(Lao-tse, "Dao de dsching", 6. Jahrhundert v. Chr.)

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TABLE OF CONTENTS

2. ARSENIC CONTAMINATION OF GROUNDWATER AND DRINKING WATER IN VIETNAM
(published in *Environmental Science and Technology*)

3. HYDROLOGICAL AND SEDIMENTARY CONTROLS LEADING TO ARSENIC CONTAMINATION OF GROUNDWATER IN THE HANOI AREA
(submitted to *Chemical Geology*)

4. ARSENIC REMOVAL FROM GROUNDWATER BY HOUSEHOLD SAND FILTERS
(published in *Environmental Science and Technology*)

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

Arsenic-enriched groundwater is used as drinking water by millions of households in several parts of the world (SMEDLEY & KINNIBURGH 2002). Figure 1 depicts countries affected by geogenic arsenic contamination of groundwater that is often consumed without treatment. The problem of arsenic intoxication by contaminated drinking water emerged in the past two decades, when surface water and groundwater from open dug wells, formerly used to cover the drinking water supply in rural areas of many regions, were abandoned for groundwater pumped through small-scale tubewells. As documented, chronic arsenic exposure can lead to severe health problems, such as skin lesions, hyperkeratosis, melanosis, skin cancer and cancer of internal organs (SMITH et al. 2000; HUGHES 2002; YOSHIDA et al. 2004).

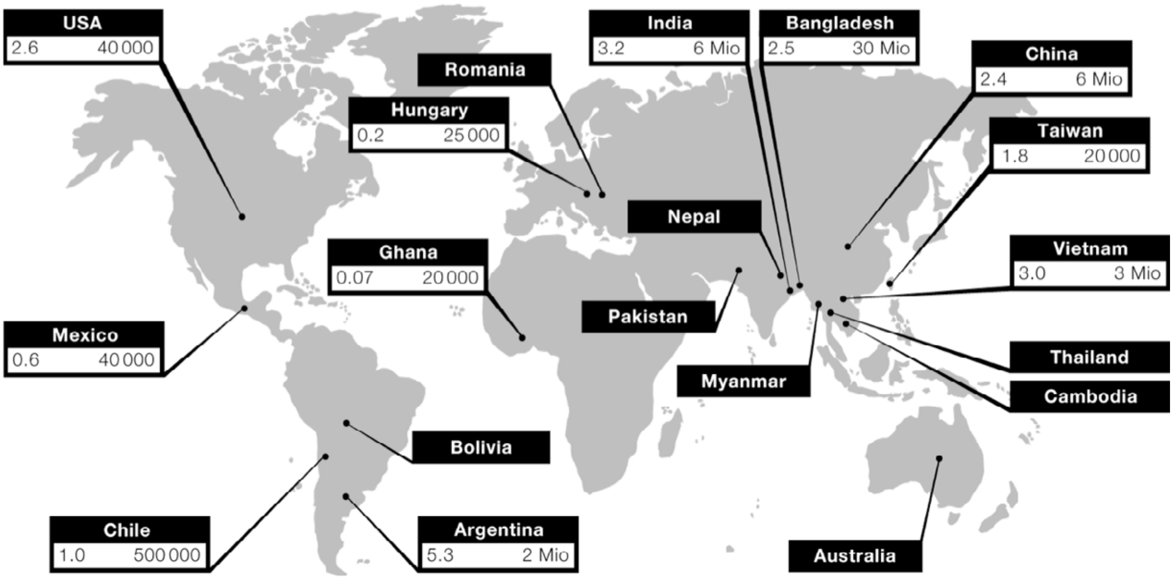


Figure 1. Countries affected by natural (geogenic) arsenic contamination of groundwater. The numbers below the country name list, (left) the highest reported arsenic concentration in mg/L, and (right) the estimated number of affected people (data from SMEDLEY & KINNIBURGH 2002).

1.1. Origin of Arsenic

Groundwater contamination by arsenic is often a natural phenomenon attributed to subsurface sediments containing small amounts of arsenic. The sediments of alluvial deltas originate from the mountains in the upstream river catchment and have been deposited during thousands of years (TANABE et al. 2006). Mountain erosion leads to a release of rock-forming minerals and arsenic into the hydrosphere (see Figure 2). Eroded iron turns to rust, iron(hydr)oxide, and forms particles as well as coatings on the surface of particles such as silt and sand. These iron(hydr)oxides are capable of scavenging dissolved arsenic from water and binding it to its surface (inner-sphere bidentate complexes, Manning & Goldberg 1997). Suspended particles with iron(hydr)oxide coatings and adsorbed arsenic are washed into rivers and transported downstream. Arsenic is thus brought to the river deltas bound to suspended solids and deposited in the soil with the settling sediments. River water with high loads of particles generally exhibits a characteristic red to yellowish brown colour caused by the iron, a phenomena that gave the Red River its name.

In the flat lowlands of the Red River Delta, suspended particles are usually deposited during floods. This was particularly the case in ancient times when the flow of the river water was not controlled by dykes. For thousands of years, deposits of river sediments have created the soil layers (sediments) that form the delta as it is known today. These sediments reach more than a hundred meters below the today's topsoil layer (Tanabe et al. 2006). Arsenic adsorbed on the surface of sediment particles is thus buried in the structure of the delta underground. The present Red River Delta was largely formed by sediments deposited in the Holocene period (last 10,000–12,000 years).

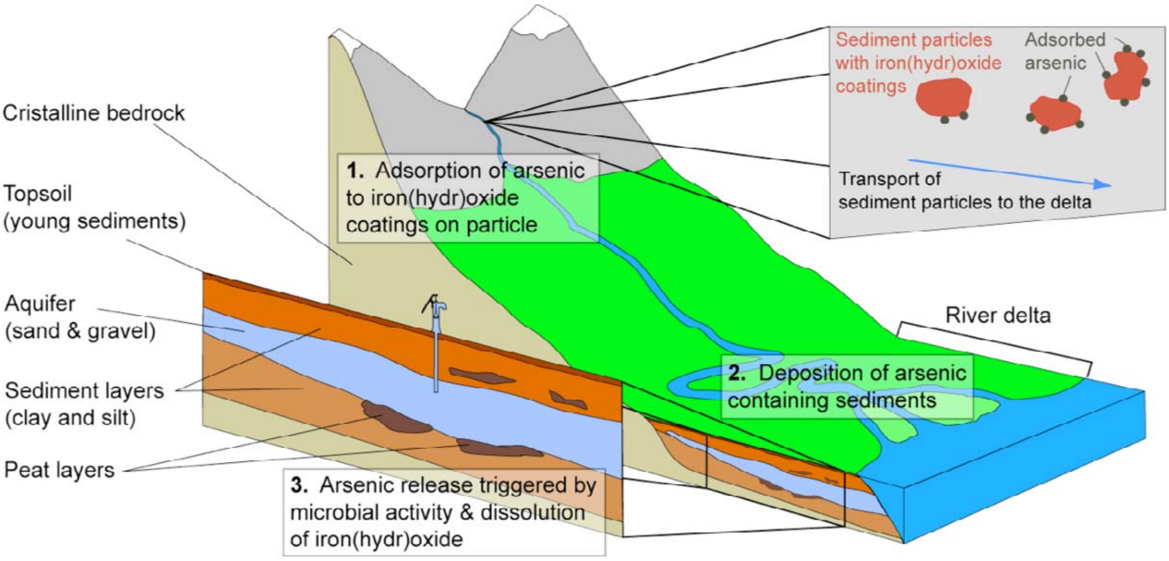


Figure 2. Simplified illustration of the widely accepted theory on the origin of arsenic in groundwater of river deltas.

1.2. Dissolution of Arsenic from Anoxic Sediments

The most widely accepted geochemical theory on the presence of arsenic in groundwaters is anoxic dissolution of iron(hydr)oxides and release of previously adsorbed arsenic (Figure 2). The arsenic remains fixed in the sediments as long as the groundwater contains sufficient dissolved oxygen. However, arsenic is released from the sediments if these come into contact with oxygen-depleted groundwater (NICKSON et al. 2000; SMEDLEY & KINNIBURGH 2002; HARVEY et al. 2002; STÜBEN et al. 2003; MCARTHUR et al. 2004; ZHENG et al. 2004; MEHARG et al. 2006). During the inundation periods, high loads of river sediments (suspended particles) are frequently covering of the topsoil layers including its vegetation. This process results in the entrapment and subsequent burial of natural organic matter (rotting plants, peat) in the sediment structure. Organic matter can serve as substrate ("food") for microorganisms to thrive on. These microorganisms consume dissolved oxygen to degrade organic material, thereby leading to an oxygen depletion in the groundwater (anoxic conditions). Under anoxic conditions, some microorganisms can use iron(hydr)oxides as a source of energy instead of oxygen. Degradation of solid iron(hydr)oxide particles releases arsenic formerly attached firmly to the particle surface.

Arsenic deposition with sediments in the delta and dissolution under anoxic conditions created by high levels of organic matter can hence lead to the high concentrations of dissolved arsenic in groundwater. This natural process leads to arsenic contamination of groundwater in, for example, the Bengal Delta (Bangladesh and West Bengal) (BGS & DPHE 2001; NICKSON et al. 2000; SMEDLEY & KINNIBURGH 2002; STÜBEN et al. 2003,), the Mekong Delta (Cambodia and Southern Vietnam) (BUSCHMANN et al. 2007; BERG et al. 2007), and in the Red River Delta (Northern Vietnam), which is demonstrated in the chapters 2 and 3 of this thesis.

1.3. Arsenic Species in Natural Waters

SMEDLEY & KINNIBURGH (2002) wrote a comprehensive review on the occurrence of arsenic in natural waters. The following section on arsenic speciation is largely rendered from this publication.

Arsenic is perhaps unique among the heavy metalloids and oxyanion-forming elements (e.g. arsenic, selenium, antimony, molybdenum, vanadium, chromium, uranium) in its sensitivity to mobilisation at the pH values typically found in groundwaters (pH 6.5–8.5) and under both oxidising and reducing conditions. Arsenic can occur in the environment in several oxidation states but in natural water it is mostly found in inorganic forms as oxyanions of trivalent arsenite (As(III), $As(OH)_3$) or pentavalent arsenate (As(V), $H_2AsO_4^-$). Organic arsenic forms may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important.

Most toxic trace metals occur in solution as cations (e.g. Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}) which generally become increasingly insoluble as the pH increases. At the near-neutral pH typical of most groundwaters, the solubility of most trace-metal cations is severely limited by precipitation as (or coprecipitation with) an oxide, hydroxide, carbonate or phosphate mineral, or more likely by their strong adsorption to hydrous metal oxides, clay or organic matter. In contrast, most oxyanions tend to become less strongly sorbed as the pH increases (DZOMBAK & MOREL 1990), whereas arsenic is among the most problematic in the environment because of its relative mobility over a wide range of pH and redox conditions. It can hence be found at concentrations in the mg/L range when all other oxyanion-forming metals are present at *µ*g/L levels.

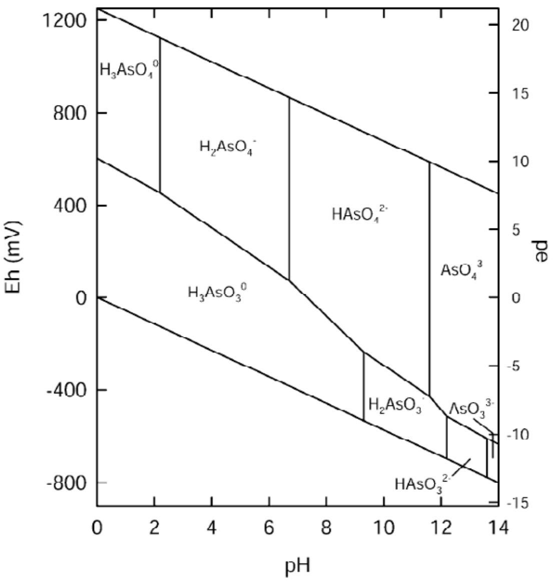


Figure 3. Eh-pH diagram for aqueous arsenic species in the system $As–O_2–H_2O$ at 25 °C and 1 bar total pressure (SMEDLEY & KINNIBURGH 2002).

Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Under oxidising conditions, the single negatively charged arsenate species $H_2AsO_4^-$ is dominant at low pH (less than about pH 6.9), whilst at higher pH, $HAsO_4^{2-}$ becomes dominant (see Figure 3). $H_3AsO_4^0$ and AsO_4^{3-} may be present in extremely acidic and alkaline conditions respectively. Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species $H_3AsO_3^0$ will predominate (Brookins 1988; Yan et al. 2000). The distributions of the species as a function of pH are given in figure 4. In practice, most studies in the literature report total arsenic concentrations without consideration the speciation and the degree of protonation.

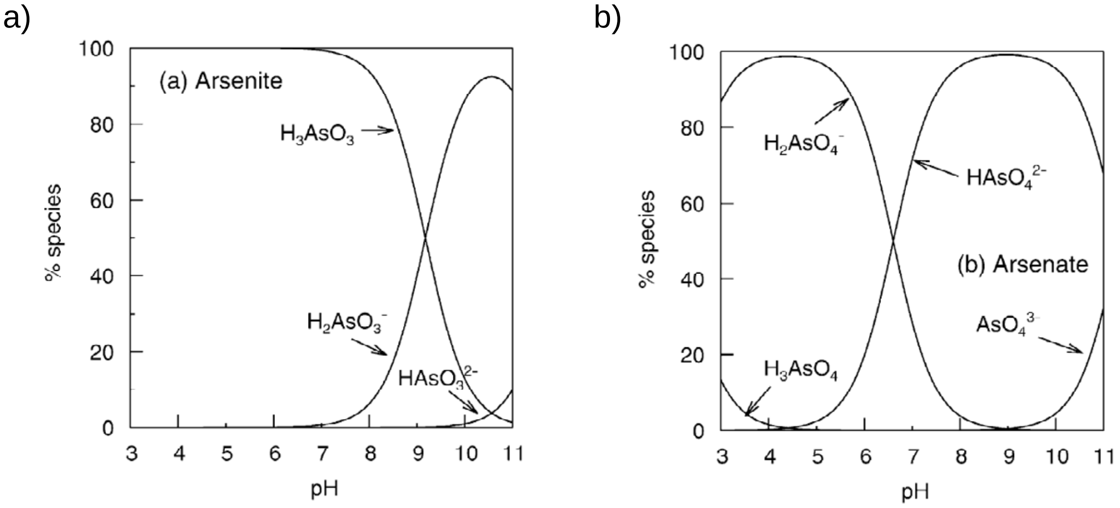


Figure 4. a) Arsenite, and b) arsenate speciation as a function of pH at an ionic strength of about 0.01 M (Smedley & Kinniburgh 2002).

1.4. Health Problems Caused by Chronic Arsenic Poisoning (Arsenicosis)

Arsenic concentrations of 50 μg per litre of water were shown to cause chronic health problems if such water is consumed over a period of 5–10 years (Smith et al. 2000). The European maximum admissible concentration, the World Health Organization guideline, and the United States maximum contaminant level are all set at 10 μg/L (Table 1). Many developing countries apply 50 μg/L as a threshold, but Vietnam has lowered it to 10 μg/L in 2002. Development of the disease is strongly dependent on exposure time and arsenic accumulation in the body, whereas age, nutritional habits and lifestyle of the exposed person may also have an influence on the occurrence of health problems (Hughes 2002; Yoshida et al. 2004).

Table 1. Thresholds for arsenic in drinking water.

WHO guideline	10 µg/L
EU	10 µg/L
USA (since 2006)	10 µg/L
Australia	7 µg/L
Bangladesh / India	50 µg/L
Cambodia	50 µg/L
Vietnam (since 2002)	10 µg/L


Hyperpigmentation

Melanoma

Black foot disease

Figure 5. Photos of patients from Bangladesh affected by various stages of arsenicosis.

Skin ailments are generally the first symptoms which develop after a few years of continued arsenic ingestion, i.e., hypopigmentation (white spots on skin), hyperpigmentation (dark spots on skin), keratosis (break up of the skin on hands and feet), and melanoma (Figure 5). More serious health problems such as skin cancer or cardiovascular and nervous affections are known to appear with a latency of 10 or more years. After 15–30 years of exposure, victims often suffer from lung, kidney or bladder cancer (Mazumder 2003). The exposure of some people in Vietnam seems particularly alarming since hyperpygmentation was diagnosed in children that were exposed to arsenic-contaminated water for only 3 years (NIOEH 2007). Hence, the expected number of arsenic-related health problems occurring in the future in Vietnam should not be underestimated. Further studies on health effects are currently carried out by the Vietnam National Institute of Occupational and Environmental Health (Ngoc et al. 2006).

1.5. Arsenic Contamination in the Red River Delta

The Red River Delta is one of several regions in the world where high arsenic concentrations in groundwater threaten human health. Chapter 2 of this thesis reports the discovery and first assessment of arsenic contamination in groundwater and drinking water in Vietnam. Similar to the high levels found in Bangladesh (BGS & DPHE 2001), the measurements from the Red River Delta revealed arsenic concentrations of 1 to >1000 μg per litre of groundwater (BERG et al. 2007). UNICEF estimates that 17% of Vietnam's population is dependent on groundwater from private tubewells as drinking water supply (UNICEF 2002).

1.5.1. Influence of Extensive Groundwater Abstraction

A study conducted in Bangladesh describes the influence of human activity on elevated arsenic levels in groundwater (HARVEY et al. 2002). This study is based on the theory of arsenic release from iron(hydr)oxides as described above, and attributes the arsenic problem partly to groundwater pumping for irrigation purposes. Extensive groundwater pumping rapidly lowers the groundwater table and draws down water containing organic material, which may stimulate microbial activity, thereby accelerating oxygen depletion and arsenic release. Due to the high groundwater demand in the Red River Delta, the groundwater table of its aquifers has locally been lowered by 20–30 meters. The study presented in chapter 3 demonstrates that this situation is particularly susceptible to future dissolution and mobility of arsenic.

1.5.2. Spatial Arsenic Variations

The investigated areas reveal an extremely heterogeneous distribution of arsenic levels. An example is given in figure 6. The water of neighbouring households within the same village may exhibit arsenic levels of both, below as well as significantly above the drinking water threshold (see Chapter 3). This unpredictable variability requires not only simple and efficient arsenic removal technologies on a household level, but also an effective monitoring program to decide on the design and application of mitigation measures such as the one presented in chapter 4.

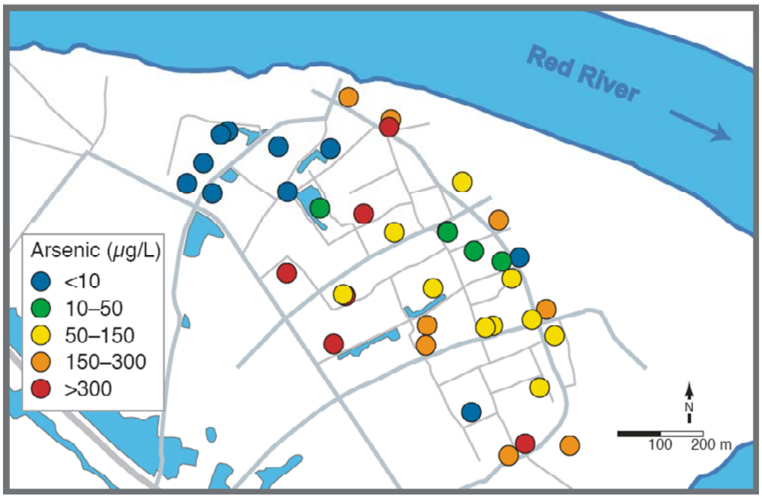


Figure 6. Spatial variability of arsenic concentrations in a small village of the Red River Delta. This example shows that low and high arsenic levels of <10 µg/L and >300 µg /L, respectively, can be just a few meters apart.

1.5.3. Sources of Drinking Water in Rural Areas

A. Groundwater

The vast majority of households cover their drinking water needs by groundwater which is often consumed without treatment.

Dug well. Vertical pit of 1–5 m depth for groundwater accumulation, and the traditional system for groundwater collection. Water from dug wells is generally low in arsenic (<20 μg/L) as it is constantly aerated through its contact with air. The water may be contaminated by microbial or chemical pollutants (e.g. bacteria, pesticides).

Settling tank. Water containers used for iron precipitation from anoxic groundwater (e.g. groundwater from tubewells). Two adjacent tanks are used for consecutive particle precipitation and settling. Groundwater is pumped into the first tank and a day later scooped into the second tank for an additional settling period. Chapter 4 reports on the arsenic removal capability of iron precipitates that are formed in these settling tanks and compares the efficiency with sand filters.

Sand filter. Efficient treatment process for groundwater exhibiting iron concentrations above 5 mg/L. In the peri-urban villages around Hanoi, this process is increasingly widespread among households affected by iron-rich groundwater. Sand filters should frequently run dry in order to prevent growing of harmful bacteria in standing water. The treated water can be stored and used for several days. The study presented in chapter 4 demonstrates that sand filters are a very feasible system to lower arsenic at the point of use (i.e. in rural households).

Supplied water. Predominant supply of drinking water in the major cities. Some villages have also put communal groundwater treatment facilities in place, although such systems require considerable investment, trained operators, as well as a robust distribution network. Groundwater is usually submitted to iron removal and disinfection, but not to enhanced arsenic removal (DODD et al. 2006). Although the iron removal process can also lower arsenic levels, arsenic concentrations may still remain above 50 μg/L (see Chapter 2).

B. Other sources of drinking water

Surface water. The percentage of people in the Red River Delta using surface water as drinking water is nowadays very small. But it may still be a considerable source in remote areas.

Rainwater. Rainwater runoff is collected from the house roofs. This water, free of iron and arsenic, is particularly used for cooking and drinking purposes. Stored in large tanks (1–5 m^3) it allows to cover the needs of a family during the dry season. Construction of a rainwater tank is rather expensive and the water must be protected from light, dust, animals and insects. Rainwater is occasionally used in households of areas with iron-rich groundwater. If properly protected, rainwater can be stored and used for several month.

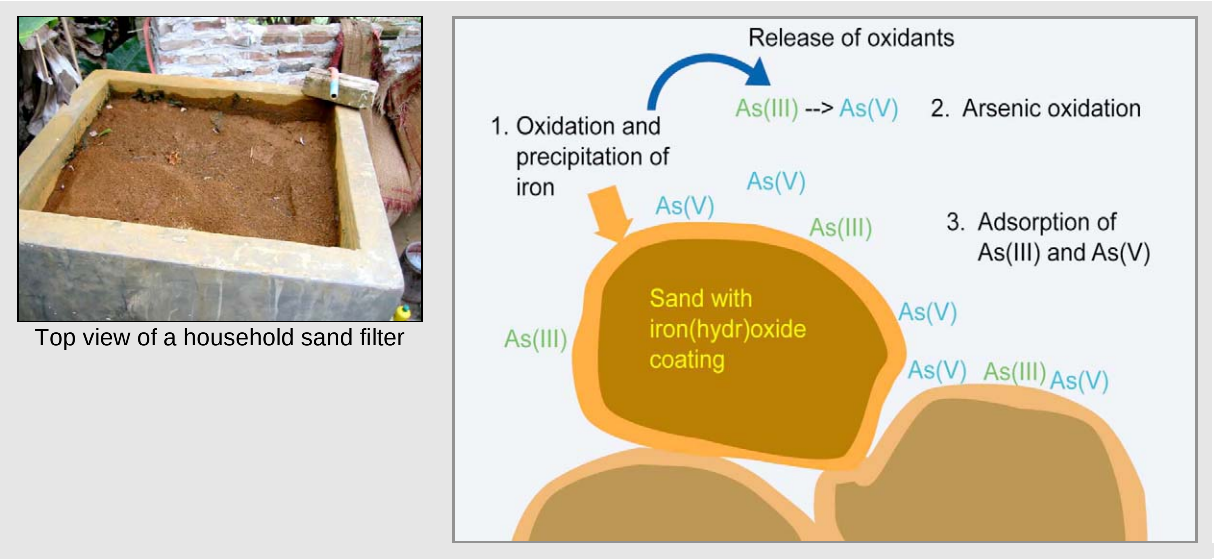
1.6. Arsenic Mitigation for Private Households

Arsenic mitigation approaches on a household level face several difficulties. An appropriate system for arsenic removal should be efficient, cheap, socially accepted, user-friendly, locally available and operated without the use of chemicals. None of the arsenic removal techniques described in the international literature meet all of these criteria. Arsenic removal technologies are often limited to small study areas and therefore do not contribute to regional progress in arsenic mitigation (USEPA 2000).

Elevated concentrations of arsenic in groundwater are often accompanied by high levels of dissolved iron. Iron concentrations (>5 mg/L) convey a bad taste to the groundwater, which in Vietnam is sometimes described as "fishy". Some households in rural areas of the Red River Delta have thus started to use simple sand filters or settling tanks to remove the iron from the groundwater. Household sand filters are simple to operate and, most important, besides iron they remove arsenic from the water to a remarkable extent, as could be shown in chapter 4 of this thesis.

1.6.1. Principle of Sand Filter Arsenic Removal

Arsenic removal in sand filters is governed by precipitation of initially dissolved iron on the surface of sand grains. Dissolved Fe(II) is oxidised by oxygen to Fe(III), which quickly forms insoluble iron(hydr)oxide and precipitates to be readily adsorbed to the sand surface to form a coating. Subsequently, such coatings catalyse further oxidation and precipitation of dissolved iron (Figure 7). The oxidation of Fe(II) triggers the formation of reactive oxygen species such as e.g. hydroxy radicals, which can oxidise As(III) to more strongly adsorbable As(V) (Hug & Leupin 2003). As(V) and - to a lesser extent - As(III) then adsorb to the coated sand particles where arsenic remains immobilised under oxic condition. In other words, a sand filter reverses the process of arsenic release occurring in anoxic groundwater. If anoxic groundwater comes into contact with air (after pumping), oxygen is rapidly dissolved and leads to oxygen-rich (oxic) water, where iron is precipitating as insoluble iron(hydr)oxides to which the arsenic is adsorbed.



Top view of a household sand filter

Figure 7. Illustration of arsenic oxidation and adsorption to iron(hydr)oxide coatings on sand grains.

Arsenic removal is thus highly dependent on the iron concentration, i.e., if more iron is initially present, larger surface areas are formed and more oxidants are produced for arsenic oxidation. The effect of other groundwater constituents can be rationalised by the following considerations. Phosphate, silicate, and other anions behave in a similar way as arsenic species (oxyanions). They also adsorb to iron(hydr)oxide surfaces and, therefore, compete with arsenic for the available adsorption sites (ROBERTS et al. 2004). Of all the relevant anions present in natural groundwaters, phosphate has the highest adsorption capacity to iron(hydr)oxide surfaces, and is thus a key factor governing arsenic removal as is outlined in chapter 4.

The key parameters characterising arsenic removal in the evaluated sand filters are as follows:

- Arsenic removal rates amount to 80–99% for groundwater containing more than 12 mg/L iron, and to less than 60% if iron concentrations are below 3–4 mg/L.
- Phosphate concentrations exceeding 2.5 mg P/L can hinder the arsenic removal efficiency, as phosphate competes with arsenic for adsorption sites on the iron(hydr)oxide surfaces. However, this was only the case in 3 of 43 (7%) tested sand filters.
- The effect of silicate is negligible since it has a 100 times lower sorption affinity to iron(hydr)oxide surfaces than phosphate or arsenate (ROBERTS et al. 2004).
- Arsenic(V) can better be removed than arsenic(III) species.

1.6.2. Benefit from Sand Filters

As a socially accepted groundwater treatment system in Vietnam, sand filters have advantages in their simplicity, low operation costs, and locally available construction material. They are operated without chemicals, can treat a reasonable amount of groundwater within a short time, and are easily replicated by the affected communities. The observable removal of iron from the pumped water makes the effect of a sand filter immediately recognizable even to people who are not aware of the arsenic problem. Thus, sand filters are a good option (at least until better mitigation options become available) for arsenic mitigation in Vietnam with a high potential to be successfully applied in other arsenic affected regions.

Two years after studying the sand filter efficiencies, concentrations of arsenic in hair of people drinking sand filter treated water or untreated groundwater were analysed (Chapter 4). The hair analysis showed that the arsenic burden of people drinking sand filtered water was below an elevated risk to develop pathological skin problems(>1 μg/g). The demonstration of this health benefit is particularly important to convince local authorities to widely promote sand filters.

1.7. Implications

Besides valuable information for the scientific community, the studies presented in this thesis generated important knowledge for the welfare of the people living in the Red River Delta. The finding that groundwater and drinking water in this area are prone to arsenic contamination (Chapter 2) was widely communicated with the national authorities and stakeholders in several meetings and workshops. Being suspicious at first and in order to verify the situation, the former president of Vietnam (a geologist by training) requested the Geological Survey to test arsenic in some 500 groundwater wells. After the arsenic contamination was confirmed, the government initiated a national action plan to address the problem and nominated three vice ministers, as well as water authorities, natural scientists and epidemiologists to form an arsenic committee. One of their first goals was to find a low-cost arsenic removal system which could be recommended as a mitigation measure in areas without access to public water supply. Hence, our encouraging results with the sand filter system came very timely (Chapter 4) and led to a technical report (in English and Vietnamese) on the applicability and point of use household sand filters in collaboration with three ministries and our local partner, the Hanoi University of Science. The arsenic threat has since been openly communicated by the authorities.

Planned arsenic mitigation programs in Vietnam address the arsenic problem on various levels. The government action plan initiated the training of water supply and health staff, as well as projects to intensify communication, information and cooperation. A large monitoring program comprising arsenic measurements in 20'000 wells in the Red River and Mekong Deltas started in early 2007 with the participation of our local partners at the Hanoi University of Science.

The action plan also addresses the need to improve arsenic removal in the urban waterworks. The findings derived from the study presented in chapter 3, i.e. the extensive groundwater abstraction for the Hanoi water supply might enhance arsenic mobilization in the exploited aquifer, need to be considered in the search for sustainable management of the groundwater resources.

1.8. References

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CHAPTER 2

Arsenic Contamination of Groundwater and Drinking Water in Vietnam: A Human Health Threat

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Arsenic Contamination of Groundwater and Drinking Water in Vietnam: A Human Health Threat

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This is the first publication on arsenic contamination of the Red River alluvial tract in the city of Hanoi and in the surrounding rural districts. Due to naturally occurring organic matter in the sediments, the groundwaters are anoxic and rich in iron. With an average arsenic concentration of 159 μg/L, the contamination levels varied from 1 to 3050 μg/L in rural groundwater samples from private small-scale tubewells. In a highly affected rural area, the groundwater used directly as drinking water had an average concentration of 430 μg/L. Analysis of raw groundwater pumped from the lower aquifer for the Hanoi water supply yielded arsenic levels of 240−320 μg/L in three of eight treatment plants and 37−82 μg/L in another five plants. Aeration and sand filtration that are applied in the treatment plants for iron removal lowered the arsenic concentrations to levels of 25−91 μg/L, but 50% remained above the Vietnamese Standard of 50 μg/L. Extracts of sediment samples from five bore cores showed a correlation of arsenic and iron contents ($r^2 = 0.700$, $n = 64$). The arsenic in the sediments may be associated with iron oxyhydroxides and released to the groundwater by reductive dissolution of iron. Oxidation of sulfide phases could also release arsenic to the groundwater, but sulfur concentrations in sediments were below 1 mg/g. The high arsenic concentrations found in the tubewells (48% above 50 μg/L and 20% above 150 μg/L) indicate that several million people consuming untreated groundwater might be at a considerable risk of chronic arsenic poisoning.

Introduction

Natural contamination of groundwater by arsenic has become a crucial water quality problem in many parts of the world, particularly in the Bengal Delta (Bangladesh and West Bengal, India) (*1*−*8*). Smith et al. (*9*) have stated that “the contamination of groundwater by arsenic in Bangladesh is the largest poisoning of a population in history, with millions of people exposed”. In the United States, the Environmental Protection Agency has proposed lowering the maximum contaminant level for arsenic in drinking water from 50 to 10 μg/L, but the feasibility of the proposed standard is currently being evaluated (*10*). The European maximum admissible concentration and the World Health Organization guideline for arsenic in drinking water are both set at 10 μg/L. On the other hand, developing countries are struggling to find and implement measures to reach standards of 50 μg/L in arsenic affected areas.

The Vietnamese capital of Hanoi is situated at the upper end of the 11 000 km^2 Red River Delta of northern Vietnam, which is inhabited by 11 million people and is one of the most populous areas in the world. Together with the Mekong Delta, the Red River Delta (Bac Bo Plain) has become one of the most productive agricultural regions of Southeast Asia. The rural population is growing rapidly and has, in the last 5−7 yr, moved away from using surface water or water from shallow dug wells as sources for drinking water in favor of groundwater pumped from individual private (family based) tubewells. Groundwater exploitation in the city of Hanoi began 90 yr ago. Today, eight major well fields supply water to city treatment facilities, which process 500 000 m^3 of water per day (*11*).

The Red River Basin stretches from 20°00′ to 25°30′ N and from 100°00′ to 107°10′ E and is bounded by the Truong Giang and Chau Giang River Basins in the north, the Mekong River in the west, the Ma River Basin in the south, and the Gulf of Tonkin in the east. The Red River Basin has a gross catchment area of 169 000 km^2 (*12*), and a total length of 1,150 km. It is dominated by tropical monsoon climate and is subject to rainy (May−September) and dry seasons (October−April). The average temperature in Hanoi is 23.4 °C, and the average rainfall is 1800 mm/yr (*13*). During the rainy season, the Red River in Hanoi may reach a water discharge of 9500 m^3/s (*14*). The long-term average flow is 3740 m^3/s (*13*), but the river volume is highly variable throughout the year. The Red River carries huge quantities of silt, rich in iron oxide, because of the large proportion of easily crumbled soil in its basin (*14*). The suspended solid load may reach over 6 kg/m^3 in the lower Red River during food seasons when over 90% of the annual load is transported (*13*).

The Bac Bo Plain is a flat area with a ground level of 5−8 m above mean sea level. It has a complicated geological history with up and down movements, transgressions, erosion, and stream activities that formed the alluvial sediments (*13*, *15*). The result of these geological processes is a relatively thick Quaternary formation (50−90 m in Hanoi) with loose and altering sediment beds (*13*), often containing organic material (*15*). In general, the Quaternary formation can be divided into two sequences: (i) the upper, composed of fine sediment clay, sandy clay, and fine sand; and (ii) the lower part, containing gravel with cobbles and coarse sand (*13*, *15*). The Quaternary sediments are underlain by Tertiary deposits of Neogene age that are composed of conglomerate sandstone, clay, and siltstone (*13*). In total, the deposits exceed 400 m. More detailed information can be found in refs *13* and *16*.

Naturally anoxic conditions in the aquifers are due to peat deposits (*15*), and consequently, the groundwaters contain large amounts of iron and manganese that are removed in the Hanoi drinking water plants by aeration and sand filtration (*13*). The urban water treatment plants exclusively exploit the lower aquifers at 30−70 m depth,

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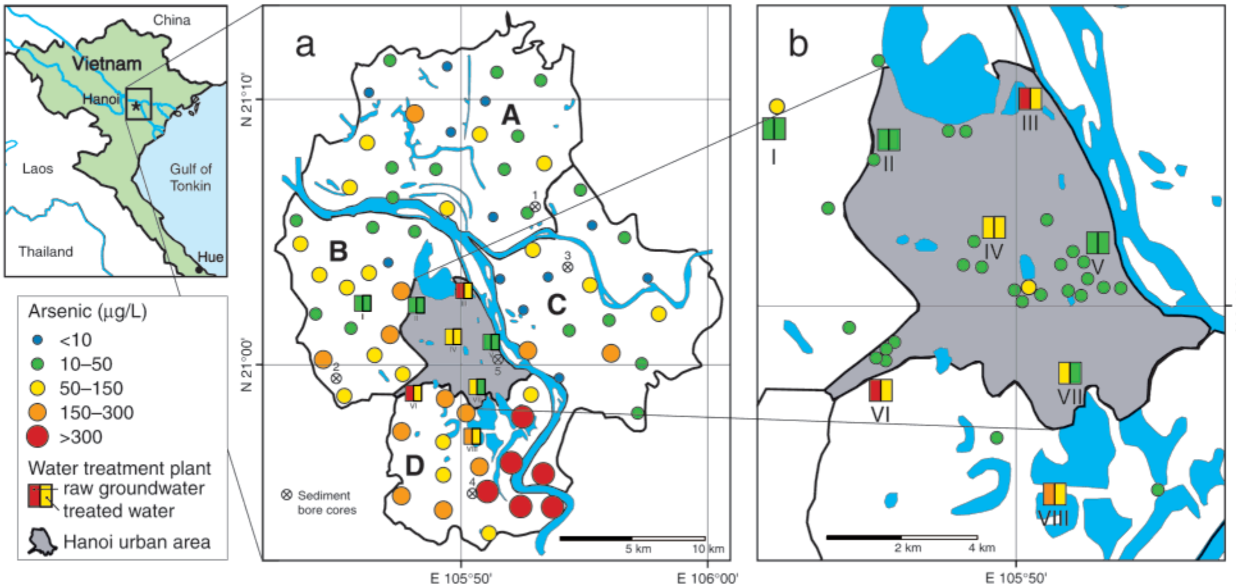

FIGURE 1. Arsenic concentrations in the Hanoi area in September 1999. (a) In the rural districts A−D, arsenic concentrations were measured in groundwaters pumped from the upper aquifer by private tubewells (dots). (b) In the city of Hanoi, arsenic concentrations were analyzed in raw groundwater of the lower aquifer and in treated water of the eight major water treatment plants (split rectangles) as well as in tap water of supplied households (dots). The numbers I−VIII refer to the following water treatment plants: I, Mai Dich; II, Ngoc Ha; III, Yen Phu; IV, Ngo Si Lien; V, Luong Yen; VI, Ha Dinh; VII, Tuong Mai; VIII, Phap Van.

whereas private tubewells predominantly pump groundwater from the upper aquifer at 12−45 m depth (*11*).

On the basis of geological analogies to the Bengal Delta (i.e., relatively young alluvial sediments and anoxic groundwater) and similar composition of the groundwater as in Bangladesh (*17*), we anticipated elevated arsenic concentrations in the aquifers of the Red River Basin. Thus, the objective of our study was to survey arsenic levels in the aquifers of the region around Hanoi. Our initial overview provides preliminary conclusions regarding the sources and mechanisms for arsenic release to the groundwater that have resulted in the high arsenic concentrations we have recently discovered in the groundwaters and drinking waters of the Hanoi area.

Methods

Sample Collection. Figure 1 shows the sampling locations for raw groundwater and of drinking water plants in Hanoi and the surrounding rural districts A−D. On the basis of a projected density of one sample per 10 km^2, we randomly selected 68 private tubewells of the districts A−D over the 700-km^2 area. Groundwater samples from the tubewells were collected three times in September 1999, December 1999, and May 2000. Prior to sampling, the tubewells were flushed with 2−3 tubewell volumes of groundwater (e.g., 70 L for 20 m depth, tube i.d. 4 cm). The generally crystal clear water samples were collected in 50-mL polypropylene flasks and acidified with 1 mL of concentrated nitric acid. The few turbid samples (i.e., less than 5%) were filtered (0.45 μm) in the laboratory and acidified thereafter. In water treatment plants, mixed raw groundwater derived from the operating pumps of the wellfields were sampled before aeration. Treated drinking water was collected from the storage tanks after chlorination. Tap water was sampled from randomly selected households that are supplied with treated drinking water from treatment plants. Water samples for tritium measurements were sampled directly at the wellheads of pumps in drinking water plants (Mai Dich pump H4, Ha Dinh pump 8, Phap Van pump 2) and in the Henninger Beer factory (pump 2) in pinched-off copper tubes (*18*).

Sediment bore cores of 12−40 m depth were drilled in July 2000 in each of the four rural districts and in Hanoi next to the Luong Yen well field. The bore core locations are marked in Figure 1a. Visually distinct vertical sections of the freshly drilled bore cores were sampled on-site at 1−2-m interval, and 20 g of the wet sediment was collected in polypropylene bags, which were sealed airtight on the spot. The bore cores were photographed, and the layers were visually classified. Water and sediment samples were stored at 4 °C.

Water Analysis. Water samples were analyzed for total arsenic and total iron at the Hanoi University of Science by atomic absorption spectroscopy (AAS) using a Shimadzu AA-6800 instrument (Kyoto, Japan). For arsenic measurements, an on-line hydride generation device was coupled to the AAS (HG-AAS). The instrument was calibrated from 1 to 6 μg/L, and the samples were diluted with deionized and distilled water (sometimes several times) to this concentration range. For comparison, 20% of the samples were sent to Switzerland, and total arsenic was analyzed by an independent contract laboratory with a hydride generation-atomic fluorescence spectroscopy (HG-AFS) system from PS Analytical (Kent, England; calibration range 2−50 μg/L). Tritium was analyzed by mass spectrometry as described elsewhere (*18*).

Sediment Analysis. Sediment samples were freeze-dried, extracted, and analyzed at EAWAG. The sulfur content was evaluated in dry sediments with X-ray fluorescence by the Swiss Federal Laboratories for Material Testing and Research. Aliquots of 100 mg of dried sediment were extracted in Teflon cups with a microwave extraction device (1200 mega, MLS GmbH, Leutkirch, Germany) using a solution of 2 mL of water, 4 mL of concentrated nitric acid (65% suprapur, Merck), and 1 mL of hydrogen peroxide (30% suprapur, Merck). The following microwave sequence was applied: 250 W (10 min), 0 W (2 min), 600 W (4 min), 0 W (1 min), 400 W (7 min), and 60 min vent/cool down. Before analysis, the sediment extracts were diluted to 50 mL with purified water (Nanopure water purification device, Skan, Basel, Switzerland). Total arsenic in sediment extracts was determined by HG-AFS (PS Analytical, Kent, England; calibration range 0.5−20 μg/L), and total iron and manganese were measured by inductively coupled plasma−optical emission spectroscopy (ICP−OES, Spectroflame, Spectro, Kleve, Germany; calibration range

TABLE 1. Average Arsenic Concentrations Measured in Three Sample Series of Groundwaters from Private Tubewells in Rural Districts around Hanoi

district[a]		n	arsenic concn (μg/L) average	range
Dong Anh	A	48	31	<1−220
Tu Liem	B	48	67	1−230
Gai Lam	C	55	127	2−3050
Thanh Tri	D	45	432	9−3010
	all	196	159	<1−3050

[a] The boundaries of the administrative districts A−D are shown in Figure 1a.

0.5−40 mg/L Fe and 0.5−4 mg/L Mn). Total organic carbon (TOC) and total organic nitrogen (TON) contents in the sediment samples were measured by thermic oxidation with a CHN analyzer (EA 1108, Carlo Erba, Milano, Italy).

Quality Assurance. As mentioned above, 20% of the water samples were sent to Switzerland for quality control. The arsenic concentrations determined by a Swiss contract laboratory and at the Hanoi University of Science agreed within 20% deviation. To further ensure the quality of the measurements, recoveries were determined before every sample series in certified water samples (SPS-SW1, Merck VI standard) or in reference sediments (Buffalo River Sediment 2704, IMEP-14, BCR-320). Recoveries in water samples were in the range of 92−109% (As) and 90−110% (Fe, Mn). With the microwave extraction method used, the average recovery of Fe was 90 ± 2% (Mn 103 ± 3%) in Buffalo River Sediment 2704 and 92 ± 3% in IMEP-14. Although clay minerals are not fully digested with the microwave extraction method, the Fe recoveries obtained for the reference materials are in an acceptable range. Confirmatory measurements of total arsenic in sediment samples were carried out in the solid sediments with semiquantitative 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 (PbLα/PbLβ corrected) with a fitted one-point calibration derived from the certified total arsenic concentration in BCR-320 (77 μg/g As) reference material. The estimated inaccuracy is ±5 μg/g.

Results and Discussion

Arsenic Concentrations in Upper and Lower Aquifers. We sampled 68 private tubewells in the rural districts and the eight major drinking water plants of Hanoi. Figure 1a shows the arsenic concentrations measured in samples collected in September 1999 from the upper aquifers in tubewells of the rural districts. Table 1 summarizes the arsenic concentrations measured in three sample series of the 68 private tubewells (see Supporting Information for the full database). The majority (72%) of the tubewells yielded arsenic concentrations above the current WHO guideline of 10 μg/L and the concentrations varied greatly (1−3050 μg/L) within the studied area. In district D, 89% of the arsenic concentrations exceeded the Vietnamese standard of 50 μg/L. In the southern parts of districts C and D, high arsenic concentrations of 1000−3000 μg/L were measured on both sides of the Red River. These results indicate that the sources of contamination are distributed over a large area.

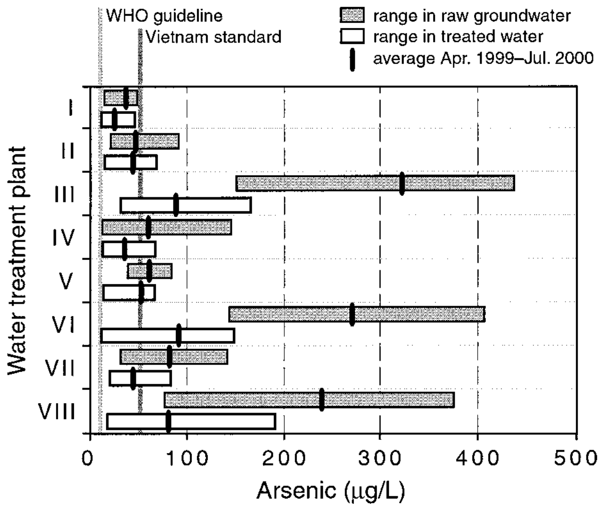

FIGURE 2. Arsenic concentration ranges in raw groundwaters from the lower aquifer and in treated Hanoi waters of eight water treatment plants. Seven sample series were analyzed from April 1999 through July 2000 (7 × 16 samples). The numbers I−VIII of the water works refer to Figure 1. The full database is available as Supporting Information.

Raw groundwaters pumped for the public water supply from the lower aquifer and treated waters from the eight Hanoi water treatment plants were sampled seven times between April 1999 and July 2000 (7 series of 16 samples). The concentrations in September 1999, depicted as split rectangles in Figure 1b, show that two of the analyzed raw groundwaters contained more than 300 μg/L arsenic. Figure 2 summarizes the arsenic concentrations measured in raw groundwater and in treated water of the Hanoi water treatment plants during the 15-month study period. The full database is provided as Supporting Information. Concentrations found in raw groundwater (15−430 μg/L) were substantially reduced in treated water, yet average concentrations of 25−91 μg/L remained (range 11−190 μg/L). Interestingly, 27 of the 29 tap water samples collected at individual homes (see Figure 1b) contained arsenic concentrations below 50 μg/L (range 7−82 μg/L; average 31 μg/L), suggesting that additional arsenic removal may be occurring in the distribution system, possibly by adsorption to iron oxide surfaces in the pipes. Under the conditions of piped supply water (average pH 7.30; Fe 1−13 μM; As ~1 μM), sorption of arsenic is plausible (*19*).

Arsenic Concentrations in Sediments. In July 2000, we sampled sediments from freshly drilled bore cores of 12−40 m depth (mainly upper aquifer). The locations of the five cores are marked in Figure 1a. The cores 1−4 were drilled next to groundwater monitoring wells of the Vietnam Hydrogeological Division II, and water from these wells were sampled concurrently. Core 5 was drilled in urban Hanoi next to the Luong Yen water plant (no. V in Figure 1a). We attempted to measure the sulfur content in the dried sediment material by X-ray analysis; however, only traces of sulfur below the quantification limit were detected (LOQ ~1 mg/g). On the basis of the low sulfur concentrations, we inferred that arsenic-containing sulfide minerals are not very abundant in the investigated sediments.

Extracted arsenic and iron concentrations varied with depth in stratigraphically different sediment layers. Peak arsenic concentrations of 6−33 mg/kg were primarily associated with brown to black-brown clay layers, followed by gray clay (2−12 mg/kg) and brown to gray sand (0.6−5 mg/kg). Figure 3 shows the correlation ($r^2 = 0.700$, two outlyers excluded) of extracted arsenic with extracted iron, suggesting that arsenic could be associated with iron phases. The extreme outlyer marked by an open diamond in Figure 3 was measured in a peat layer. The full database listing As, Fe, Mn, TOC, and TON values measured in the sediment samples is provided as Supporting Information. The arsenic concentration pattern in the sediments was confirmed with WD-XRF measurements, although the total arsenic contents obtained by WD-XRF were somewhat higher than the extracted arsenic measured with AFS analysis (average difference 3.8 μg/g).

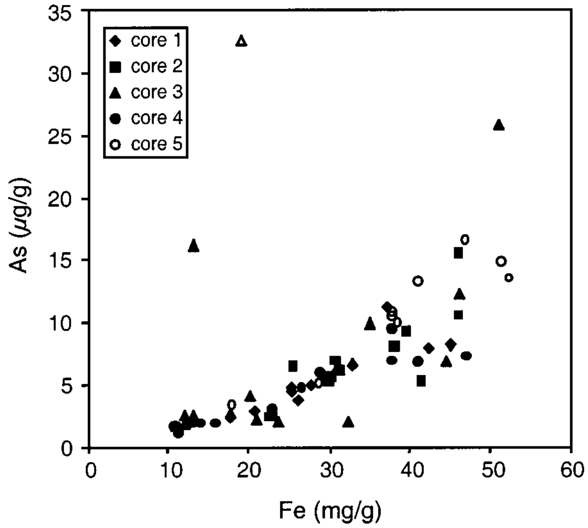

FIGURE 3. Correlation of total arsenic with total iron in sediment layers of five bore cores of July 2000 from districts A–D and urban Hanoi ($n = 64$). The 12–40 m deep cores were sampled at 1- or 2-m intervals. The extreme outlyer marked by an open triangle was associated with a peat layer.

This difference might be due to incomplete extraction of arsenic from clay minerals but should not be overinterpreted because WD-XRF values are subject to an inaccuracy of ± 5 μg/g (see Methods section). No correlation was observed between sediment-bound arsenic and dissolved arsenic in groundwater collected from the corresponding depth of the adjacent monitoring wells (data not shown).

Aspects of Arsenic in Anoxic Groundwater. Although there is no evidence for an anthropogenic origin of arsenic in the subsurface in and around Hanoi, the possibility of pollution by landfill leakage, agricultural fertilizers, or mining wastes carried by the Red River cannot be excluded. However, the widespread arsenic occurrence in the investigated aquifers points to natural geogenic sources similar to the situation in the Ganges Delta (*1, 3–5, 7, 8, 20*). Sediment-bound arsenic most probably originates from erosion and weathering processes, which result in the fluvial transport and sedimentation of arsenic-enriched iron oxyhydroxides (*21–23*). Several studies (*1, 7, 8, 20, 24–26*) have suggested that elevated arsenic levels in anoxic groundwater are caused by reductive dissolution of arsenic-rich iron oxyhydroxides occurring as dispersed phases in the aquifer rocks. Under oxic conditions, the release of arsenic from sulfide phases such as arsenian pyrite [naturally occurring (*5, 26*), in deposits of gold mining wastes (*27*)], in pegmatite-hosted arsenic sulfides (*21*), or from a sulfide-bearing secondary cement horizon (*28*) have been reported. In anoxic environments, sulfide minerals including arsenopyrite can incorporate arsenic and are therefore considered a sink for arsenic (*8, 26*). Kim et al. (*29*) hypothesized that bicarbonate ions cause the leaching of arsenic into groundwater by carbonation of arsenic sulfide minerals. However, the process would not be significant at the bicarbonate concentrations commonly found in the Hanoi aquifers (<10–20 mM).

The anoxic conditions in the Red River sediments are probably maintained by natural organic matter (NOM) present in the subsurface (*15, 30, 31*). Using data obtained from the Vietnam Hydrogeological Division II, Trafford et al. (*15*) have mapped peat layers in the districts B and D and showed that these layers are very abundant and are often over 10 m thick in district D. In the upper 8 m of the bore cores 2 and 3, we have found peat layers (2–3 m thick) with NOM concentrations of up to 15% total organic carbon. Dissolved oxygen is rapidly consumed by microbiological oxidation of NOM, resulting in the formation of bicarbonate and inorganic nitrogen species. This is consistent with high alkalinity [31–810 mg/L (*15, 32*)] and high nitrogen concentrations [10–48 mg of N/L (*15, 30*)] measured in the studied aquifers. Inorganic nitrogen was mainly found in the reduced form of ammonium that reached particularly high levels of 48 mg/L (*15*) in the severely arsenic-contaminated district D. These findings suggest that the oxidation of the buried peat material is responsible for the highly reducing conditions in the aquifers. As a result of the low redox potential, As(V) is most likely reduced to the more mobile As(III) (*19, 24, 31*).

Geological and Hydrogeological Conditions. To explain the significantly different arsenic levels of districts A and D (Figure 1a), the different geological settings and actual hydrogeological conditions of these areas must be considered (see also Introduction). The geology of the Red River Delta is complex with considerable variation in lithology within short distances (*15*). The sediments in district A (predominantly of Pleistocene age) are not as thick as in the other districts and form mainly one aquifer at 10–25 m depth (*11*). The other districts have sediments of both Pleistocene and Holocene age, with the latter being partly derived from postglacial marine transgressions (*11, 15*). Due to frequent riverbed migrations, the aquifers are not fully separated and are in some locations connected through sand lenses (*15*). In an approximately 10 km wide zone along the Red River, the upper and lower aquifers are today mainly recharged from the river, and the rest of the lower aquifer is mainly recharged by vertical percolation from the upper aquifer (*13*). Even without the pumping of groundwater, recharge in the upper two aquifers can partly originate from Red River bank filtration (*15*). However, Hanoi's high water demand is causing a significant drawdown of the groundwater. This is particularly severe in the districts B and D where depression cones go down as far as 30 m (*11*). As a consequence, the ammonium contamination increased significantly in district D from 1992 to 1995 (*33*), and land subsidence of more than 20 mm/yr has been reported for many years in the Hanoi area (*13, 34*). The authors of ref *13* established a groundwater flow model for districts B and D and attributed the recharge of the lower aquifer to 30–35% from surface water bodies, 60–65% to vertical percolation, and 2–3% to lateral inflow.

For this study, we have measured tritium concentrations in raw groundwater samples from districts A, B, and D. The samples collected in April 1999 at water treatment plants I, VI, and VIII (districts B and D, see Figure 1 and Methods section) yielded ^{3}H concentrations of 1.2 ± 0.3, 1.8 ± 0.3, and 1.9 ± 0.3 tritium units, respectively, Comparing these data with the (nearest) Bangkok station of the IAEA/WMO network shows that the likely period of infiltration lies between 1985 and 1995. If Red River water is assumed to be the only source of recharge, considerable groundwater flow velocities on the order of meters per day can be inferred. A very different situation was found in district A where the aquifers are only slightly disturbed. The groundwater sample collected from the Henninger Beer factory (8 km north of the Red River in district A) had a tritium unit of only 0.1, indicating that this water is much older (i.e., more than 50 yr).

Spatial and Seasonal Variations of Arsenic Concentrations. Extremely high arsenic concentrations were found in district D, an area of substantial groundwater abstraction. There is evidence that the groundwater tables in this area have been drastically lowered, which would result in a downshift of the redox boundaries. Thus, peat layers that were formerly water-saturated and anoxic can be expected to be exposed to oxygen in the unsaturated zone. If the (partial) oxidation of peat were accelerated, downward migration of NOM-rich leachates could maintain anoxia in the aquifers below the peat layers. We suggest that high

TABLE 2. Average Arsenic Concentrations Measured in September 1999, December 1999, and May 2000 in the Upper Aquifers (Private Tubewells in Rural Districts)

	September 1999		December 1999		May 2000	
district[a]	*n*	As (μg/L)	*n*	As (μg/L)	*n*	As (μg/L)
A	19	45	9	56	19	4
B	16	90	16	84	16	26
C	18	216	18	131	19	40
D	15	466	15	676	15	154
all	68	194	58	247	69	52

[a] The administrative districts A–D are shown in Figure 1a; corresponding names are given in Table 1.

groundwater abstraction from peat-rich aquifers may enhance dissolution of arsenic-rich iron oxyhydroxides and, thus, lead to increased arsenic concentrations in the upper aquifer of district D. However, the release of arsenic from the oxidation of arsenic-bearing sulfide minerals must also be considered. More detailed investigations are necessary to understand the arsenic pollution mechanism(s) in the Hanoi area.

In addition to the regional differences, seasonal variations of arsenic concentrations have been observed in the upper aquifers. We have analyzed the same 68 tubewells in September 1999, December 1999, and May 2000. As shown in Table 2, the highest arsenic concentrations occurred at the transition of the rainy season to the dry season (September, December) and the lowest at the end of the dry season (May). These variations may be related to the pronounced seasonality of the Red River discharge. The average seasonal difference of the water level is 10 m (8.9 m in 1999), which causes significant fluctuations in the groundwater table (*11*). Notably, the seasonal variation was most pronounced in district A (see Table 2), which experiences higher groundwater table fluctuations than the intensely pumped aquifers in district D. The variations in redox conditions associated with fluctuating groundwater levels could enhance release of arsenic to the groundwater through either reductive or oxidative mechanisms. Our database is undoubtedly too limited to draw conclusions regarding the processes governing the observed variability in arsenic concentrations.

Health Aspects. To the best of our knowledge, symptoms of chronic arsenic exposure have not yet been reported in Vietnam despite the fact that several million Vietnamese may be consuming arsenic-rich drinking water (>50 μg/L) and are therefore at risk of chronic arsenic poisoning. Figure 4 illustrates the cumulative frequency distribution of the arsenic concentration ranges measured in this study. In the four districts A–D, 25–90% (average 48%, $n = 196$) of the investigated groundwaters exceed the Vietnamese arsenic standard of 50 μg/L, and 50–98% (average 72%) were above the WHO guideline value of 10 μg/L. Thus, the Hanoi area and possibly larger areas of the Red River Delta may be as severely affected as Bangladesh (25% above 50 μg/L, $n = 3534$) (*7*).

Especially the alarmingly high concentrations in the upper aquifer of district D raise the question of why arsenicosis has not been detected in this area so far. The groundwater pumped through the family based tubewells are often used directly as drinking water. However, the first private tubewells were installed only 7 yr ago, and the first cases of chronic arsenic poisoning from ingestion of contaminated water are typically observed only after 5–10 yr of exposure (*35, 36*). Furthermore, the early manifestations are difficult to diagnose, particularly in the absence of the awareness of potential problems (*37*). Consequently, we urgently propose further and thorough evaluation of the extent of the groundwater and drinking water contamination by arsenic and early mitigation actions in order to reduce the risk of chronic arsenic poisoning of millions of people in Vietnam. Besides the Red River Delta, potential areas for arsenic-rich groundwater in Vietnam include the Ma, Ca, Gianh, Huong, Da Rang, and Mekong River deltas.

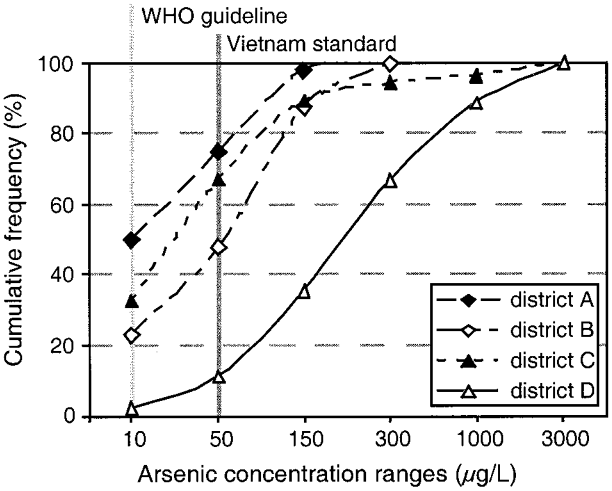

FIGURE 4. Cumulative frequency distributions of arsenic concentration ranges in groundwaters from the upper aquifer pumped by private tubewells (rural districts) in September 1999, December 1999, and May 2000. The administrative districts A–D are shown in Figure 1a. Numbers of samples are given in Table 1.

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Supporting Information Available

Three tables showing the results of arsenic in water samples and As, Fe, Mn, TOC, and TON measurements in sediment cores. This material is available free of charge via the Internet at http://pubs.acs.org.

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CHAPTER 3

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

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

Abstract

Groundwater contamination by arsenic in the Red River Delta (Vietnam) poses a serious health threat to millions of people consuming this water without treatment. 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 >600 000 m^3 of groundwater per day from the Pleistocene aquifer. Detailed groundwater and sediment investigation were conducted in three villages located in different settings, i.e., high arsenic at the river bank, low arsenic at the river bank, and medium arsenic in an area of buried peat and excessive groundwater abstraction. In-depth chemical analysis of water from Holocene and Pleistocene tubewells, surface water, sediment cores (>30 m), sites of nested wells, as well as sequential leaching of sediment samples were conducted. Seasonal fluctuations in water chemistry were studied over a time span of 14 months.

The sediment-bound arsenic (1.3–22 μg/g) is in a natural range of alluvial sediments, it correlates with iron (r^2 >0.8), and its variation is 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 to the aquifer at the river bank, or from the Holocene to the Pleistocene aquifer in the peat area, were found to promote iron-reducing conditions leading to arsenic contamination in the aquifers.

Low groundwater arsenic levels (<10 μg/L) generally exhibit manganese reducing conditions with manganese levels reaching up to 8.7 mg/L. Elevated arsenic levels are caused by reductive dissolution of sediment-bound arsenic under iron- and sulphate reducing conditions. They averaged 121 μg/L at the river bank and 60 μg/L 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 previously mobilized arsenic to the sediment. Despite similar redox conditions, resorption is much less significant at the river bank (Fe/As(aq) = 68, (s) = 4'700), and hence, arsenic levels reach considerably higher levels.

Drawdown of Holocene water to the Pleistocene aquifer caused by the pumping for the public drinking water supply of Hanoi did not show an observable increase of arsenic during the 14 month study. However, DOC, ammonium, and iron are leaching down from the Holocene aquifer, thereby enhancing the reducing conditions in the Pleistocene. Seasonal fluctuations (11–66%) of redox sensitive species in 70 m deep Pleistocene wells were concurrent with water table fluctuations. This indicates 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 or 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 considered to be 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 with highly reducing aquifers. Arsenic concentrations can be very heterogeneously distributed 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 sediments (Nickson et al., 2000; Dowling et al., 2002; Harvey et al., 2002; Stüben et al., 2003; Horneman et al., 2004; Islam et al., 2004; Zheng et al., 2004; Charlet and Polya, 2006). 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 usually very patchy in unconsolidated sediments of young alluvial environments. 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). This is in accordance with recent publications investigating the arsenic mobilization under iron reducing conditions. 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 (Kocar et al., 2006).

The Hanoi area can be categorized in three general situations of groundwater conditions: i) predominantly high arsenic at the river bank (south of Hanoi), ii) predominantly low arsenic close to the river (northwest of the city), and iii) medium arsenic in areas of abundant peat and high groundwater abstraction. Regarding the third situation, one can speculate that the groundwater abstraction from the Pleistocene aquifer causes vertical drawdown of water from the Holocene aquifer. This raises the question whether arsenic mobilization is influenced by this situation, and if arsenic concentrations might gradually increase in the Pleistocene aquifer over time.

With the aim to elucidate 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 i) to delineate high and low arsenic concentrations at the river bank by the comparison of these situations, ii) to elucidate the connectivity of the Holocene and Pleistocene aquifers in the peat area and the impact of excessive groundwater abstraction, iii) to find reasons for the lower magnitude of arsenic contamination in the peat area than at the river bank, and, iv) to investigate whether arsenic concentrations increase over time or fluctuate over 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 in intervals of 2–3 months over a time span of 14 months. Besides, we drilled sediment cores in each village and established nests of groundwater wells to elucidate sediment-groundwater interactions.

2. Geological Setting and Hydrological Features

A map of the Hanoi province, and 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 are in some locations connected through sand lenses (Trafford et al., 1996). In an approximately 5 km wide zone along the Red River, the Holocene and Pleistocene aquifers are today mainly recharged from the river, and, the more distant Pleistocene aquifer mainly by vertical percolation from the Holocene aquifer (Water-Master-Plan, 1993).

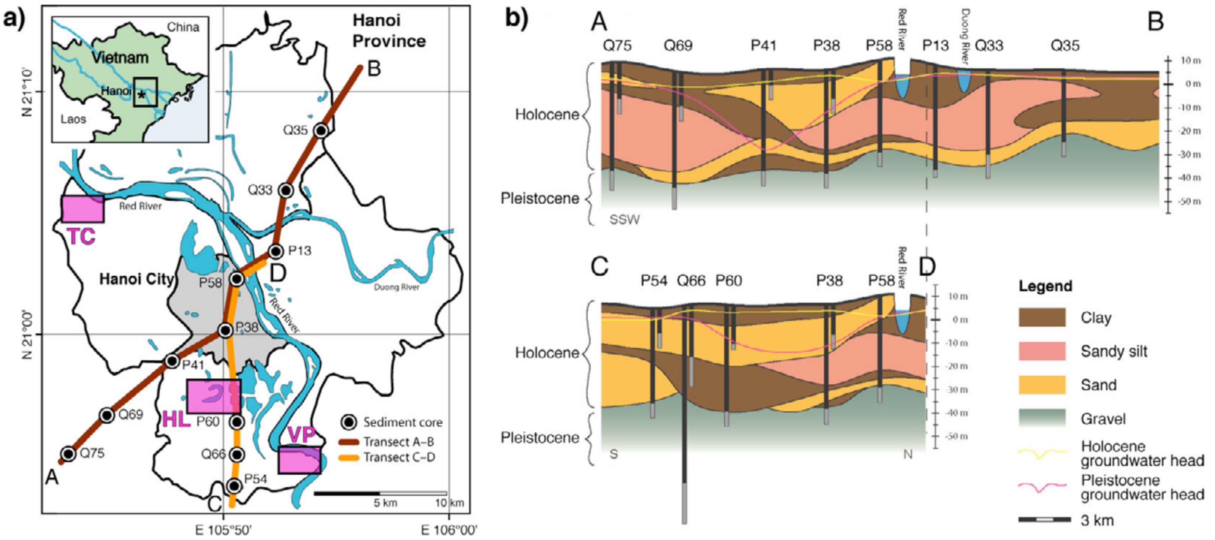


Figure 1. a) Map of the Hanoi province and geological transects derived from lithological logs of the Vietnam Geological Survey. Pink rectangles mark the locations of the investigated villages, namely Thuong Cat (TC), Hoang Liet (HL), and Van Phuc (VP). **b)** Sedimentary cross sections illustrating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

Hanoi has a strongly increasing water demand due to the rapid growth of industry and urban population (3.5 Mio inhabitants in 2001, urban area 84 km^2). The Hanoi drinking water treatment facilities exclusively exploit the lower (Pleistocene) aquifer containing variable levels of dissolved arsenic, Fe(II), Mn(II), and NH_4^+ ranging from 5–430 μg/L, 1–25 mg/L, 0.2–3 mg/L, and 2–25 mg/L, respectively (Berg et al., 2001, 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 has not been questioned until the early 1990s. Today, ten major well fields supply water to city treatment facilities which in 2005 processed 610 000 m^3 of water per day (Cao et al., 2005).

Private households in rural areas pump groundwater from the upper (Holocene) aquifer where arsenic levels >50 μg/L are predominantly present in the south-western region (Berg et al., 2001). An overlay of mapped arsenic, groundwater heads, peat and ammonium is presented in figure 2a. It depicts arsenic concentrations between 50 and 300 μg/L in the area of abundant peat and extensive groundwater abstraction, while even higher arsenic levels (>300 μg/L) are 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 (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 became particularly abundant in the peat area (see Figures 2e-2g).

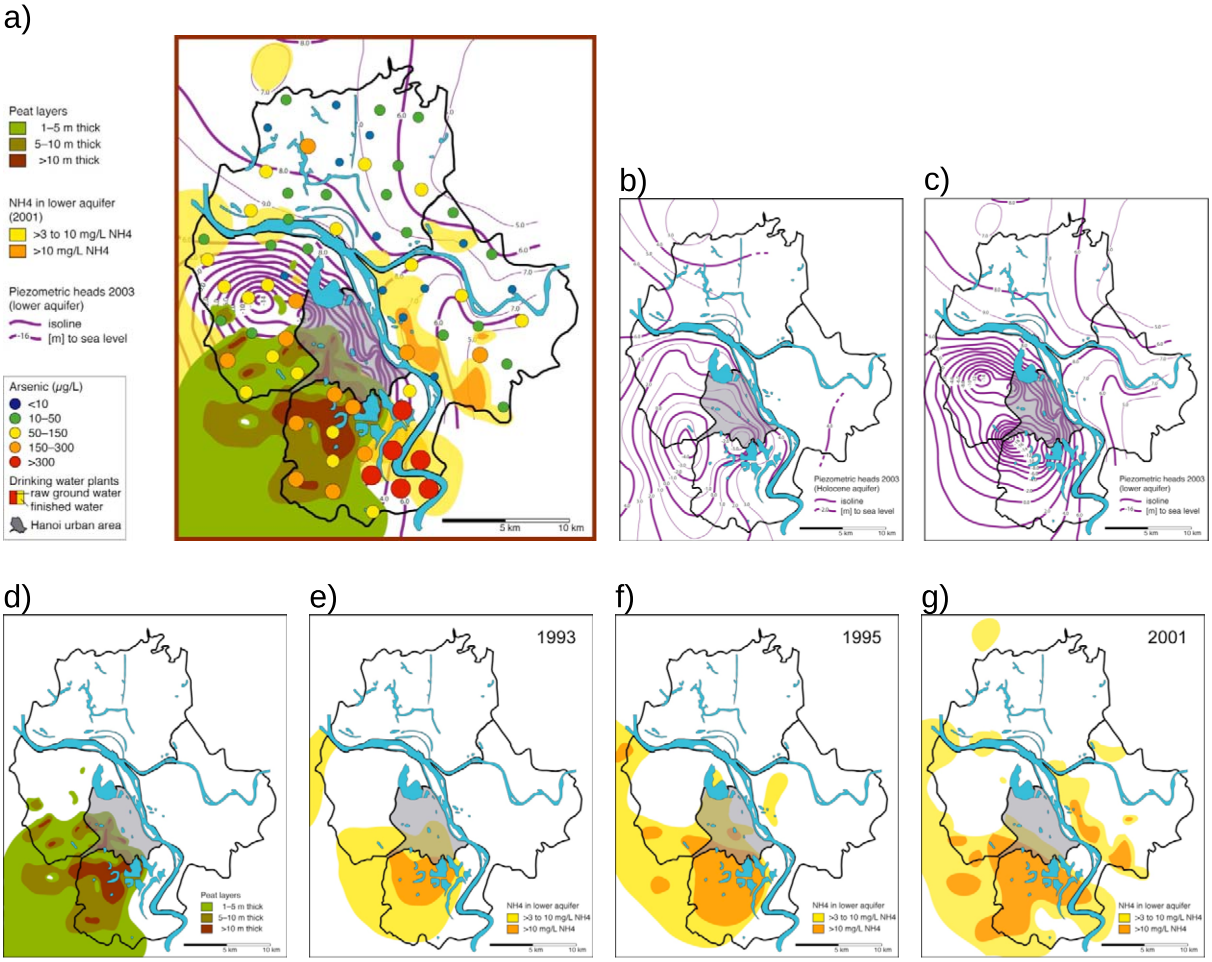


Figure 2. Map of the Hanoi area depicting hydrological and sedimentary features as well as concentrations of arsenic (Berg et al., 2001) and ammonium (NHEGD, 2002) concentrations in the Holocene and Pleistocene aquifers. **a)** Arsenic, groundwater heads, peat and ammonium, **b)** drawdown of Holocene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

3. Experimental Section

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.e., Thuong Cat village (TC) with low arsenic in the close vicinity of the river bank, Van Phuc village (VP) with high arsenic in the river bank, and, 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; 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 filled in polypropylene bottles (rinsed with 1% HNO_3 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 0.45 μm filtered (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, Quality Assurance, and Detection Limits. The chemical constituents in the groundwater samples were quantified from triplicate analysis. Arsenic concentrations were measured in parallel by atomic fluorescence spectroscopy (AFS, Millennium Excalibur, PS Analytical, UK) and inductively-coupled-plasma mass spectrometry (ICP-MS, Element 2, Thermo Electron, 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, 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 ±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 detection (LOD) were 0.1 μg/L for Co, Ni, Cu, Cr, U and Cd; 1 μg/L for As (AFS); 2 μg/L for Ba; 0.01 mg/L for NH_4^+-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 PO_4^{3-}-P; 0.25 mg/L for NO_3^--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 were analyzed at Eawag Kastanienbaum for $^{18}O/^{16}O$ and $^{2}H/H$ ratios by a Micromass Isoprime isotope ratio mass spectrometer (IRMS) in continuous flow mode. The $\delta^{18}O$ and $\delta^{2}H$ 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 $\delta^{18}O$ and $\delta^{2}H$, respectively. Prior to analysis, the samples were equilibrated with a CO_2–He and H_2–He mixture, respectively, at 40 °C for at least 12 hours (Fette et al., 2005).

3.6 Sediment Sampling. Boreholes for sediment sampling were established in April 2003, reaching down 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 and 20 g wet sediment was filled in polypropylene bags, which were 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 on 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. Subsequently, total arsenic was determined in the digests by AFS and metals by ICP-MS. With the microwave extraction method used, the average recovery of iron was 90±2% (manganese 103±3%) in Buffalo River Sediment 2704, and 92±3% in IMEP-14. Although clay minerals are not completely digested with the applied microwave extraction method, the iron recoveries obtained for the reference materials are in an acceptable range. Confirmatory measurements of total arsenic in sediment samples were carried out in 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 (PbLα/PbLβ corrected) with a fitted one point calibration derived from the certified total arsenic concentration in BCR-320 (77 μg/g As) reference material. The estimated inaccuracy is ±5 μg/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° 2 Theta and the graphical analysis program MacDiff 4.2.5. 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 allowed to identify a variety of solid phase associations of 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 (chapter 3.3).

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_2PO_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_2O_2	1 h microwave digestion, 100°C, 40 bar	As coprecipitated with crystalline Fe oxyhydroxides, silicates, pyrite and As_2S_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).

4. Results

4.1 Groundwater

4.1.1 Sources of Groundwater Recharge. The piper diagrams in figure 3 depict distinguishable hydrochemical features for the three studied villages. In general, the groundwaters of deltaic areas are of Ca-Mg-HCO_3 type (White et al., 1963; Stüben 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 infiltrate from surface water. Holocene and Pleistocene groundwaters are distinguished by a higher ratio of Na+K over Ca in the Pleistocene aquifer, which resembles surface water. The situation in the Holocene aquifer points to local surface water infiltration if one considers chloride levels. Faster migration of K and Na compared to Cl might explain these findings.

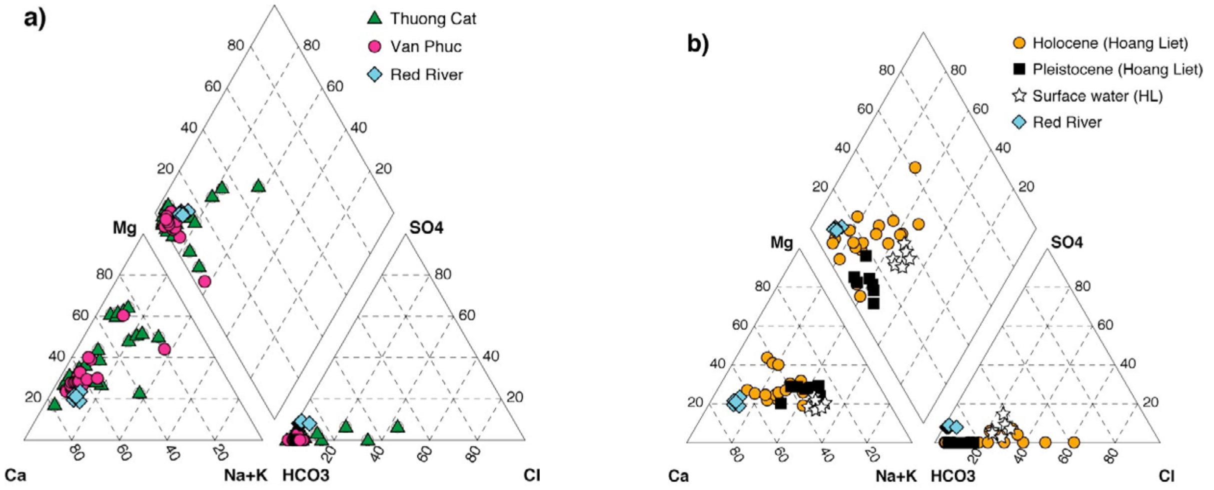


Figure 3. Piper diagrams depicting the main hydrochemical composition of the three studied areas. **a)** River water and groundwater in Van Phuc and Thuong Cat (located close to the river). **b)** Groundwater from the Holocene and Pleistocene aquifers, and surface water in Hoang Liet (located 5 km west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

The connectivity of the groundwater bodies with surface water was further elucidated by isotopic signatures (δ^2H and $\delta^{18}O$) 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 (over a period of 12 month) by the Institute of Nuclear Science and Technology in Hanoi (Nhan et al., 2005). Figure 4a reveals that 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 fact that Red River water is 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 were heaviest in January (cool dry season).

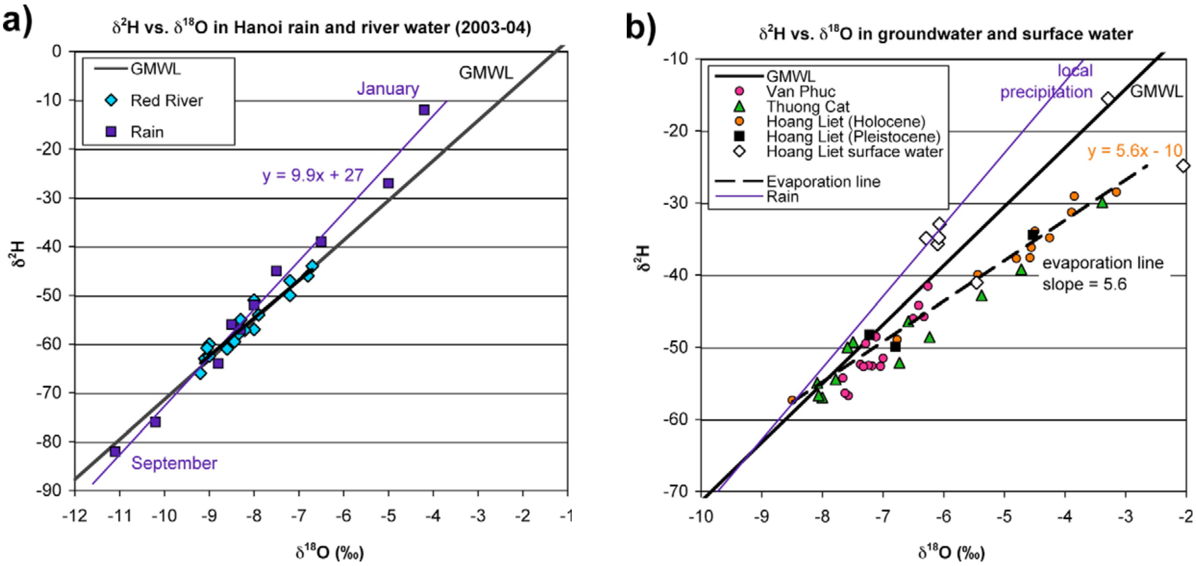


Figure 4. δ^2H versus δ^{18}O values in precipitation, Red River water, and groundwater, expressed as ‰ enrichments relative to standard mean ocean water (SMOV). **a)** Red River water and precipitation collected in Hanoi in 2003 and 2004 (data from (Nhan et al., 2005)). **b)** Groundwater collected 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 $d^2H = 8.17 \times d^{18}O + 10.35$ (Rozanski et al., 1993).

The majority of the groundwater samples are not positioned on the GMWL (Figure 4b), but are shifted towards less negative δ^{18}O values (enriched in ^{18}O). This shift is particularly pronounced for HL groundwater and also the case 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). But the water from the drainage channels (SW 2, 3, 6, 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 the analyses of major ions and isotopic signatures: (i) Groundwater in the Holocene aquifer of HL is largely replenished by lake water, while drainage channels play 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. Samples collected outside the dike are lying on the GMWL and are hence mainly derived from infiltrated river water. (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 km^2 '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, seen as a natural and undisturbed hydrological situation. This aquifer reaches down to >40 m with a loose bedding of Holocene and Pleistocene depositions (Nguyen, 2005). An influence from the Pleistocene groundwater drawdown discussed above (Figure 2b+c) is minimal, if any. Figure 5 illustrates the VP setting and depicts 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.

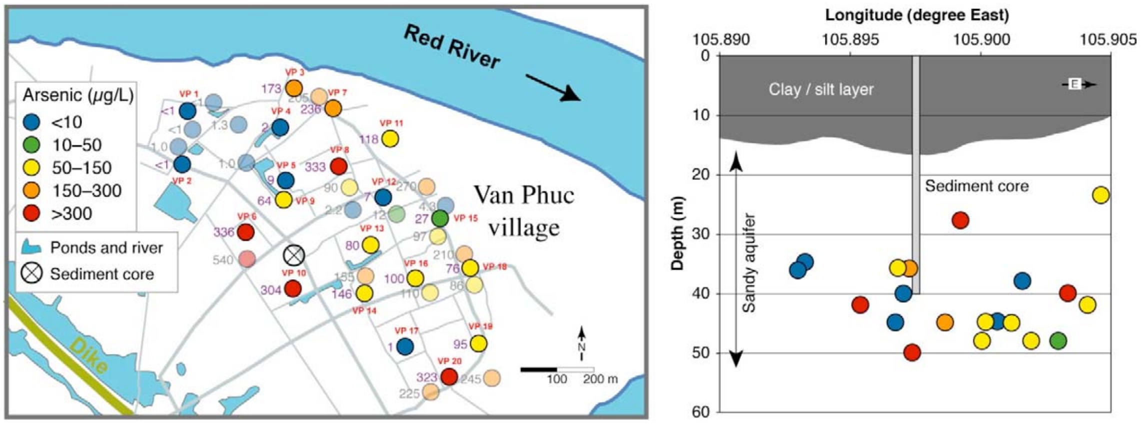


Figure 5. Map of Van Phuc village (VP) and vertical cross-section depicting arsenic concentrations in groundwater samples from family-based tubewells in December 2002. Semi-transparent dots are measurements from a reconnaissance study conducted in March 2001. Results of the sediment core are discussed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

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 week numerical relations, but as can be seen in figure 6, they show a similar distribution pattern as 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 occurrence (a situation that is frequently observed (Smedley and Kinniburgh, 2002; Stüben et al., 2003; Buschmann et al., 2007). 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; Stüben et al., 2003; van Geen et al., 2003; Buschmann et al., 2007).

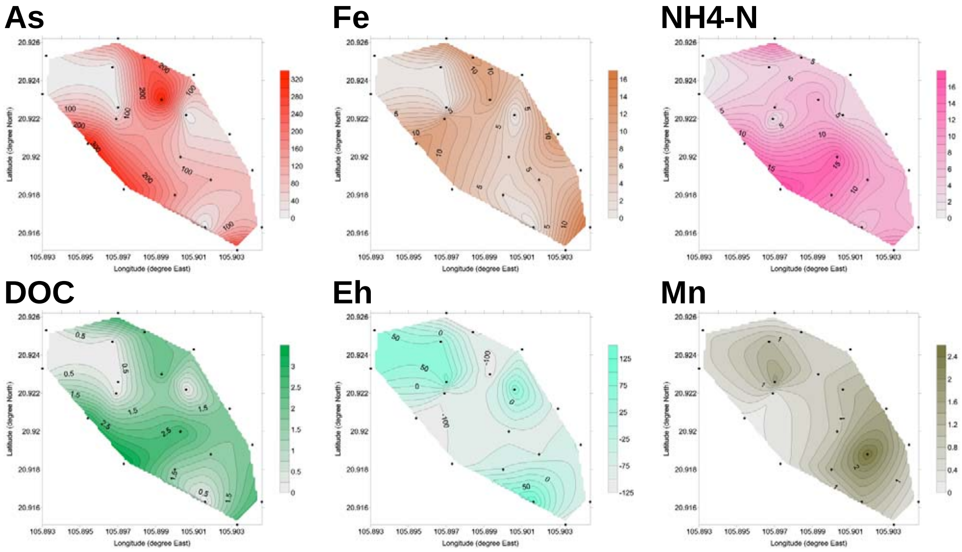


Figure 6. Contour plots of selected parameters in VP groundwater of December 2002. The contours are spatially delimited by the groundwater wells indicated by black points (see also map in figure 5). Mapping software: Surfer 7.0, nearest neighbour algorithm.

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 the majority of the houses (and consequently tubewells) are built on the inner side of the dike that is 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.

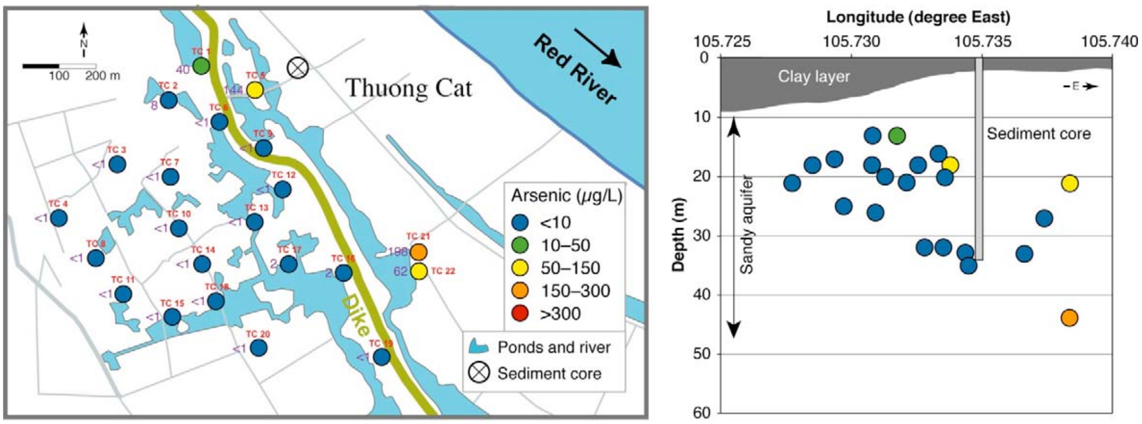


Figure 7. Map of Thuong Cat village (TC) and vertical cross-section depicting arsenic concentrations in groundwater samples collected from family-based tubewells in December 2002. Results of the sediment core are discussed in chapter 4.2. The illustrated clay/silt layer in the cross-section is only of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

All tubewells inside the dike had low arsenic levels while the wells located outside the dike reveal 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 distribution of the 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 arsenic with iron. 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.

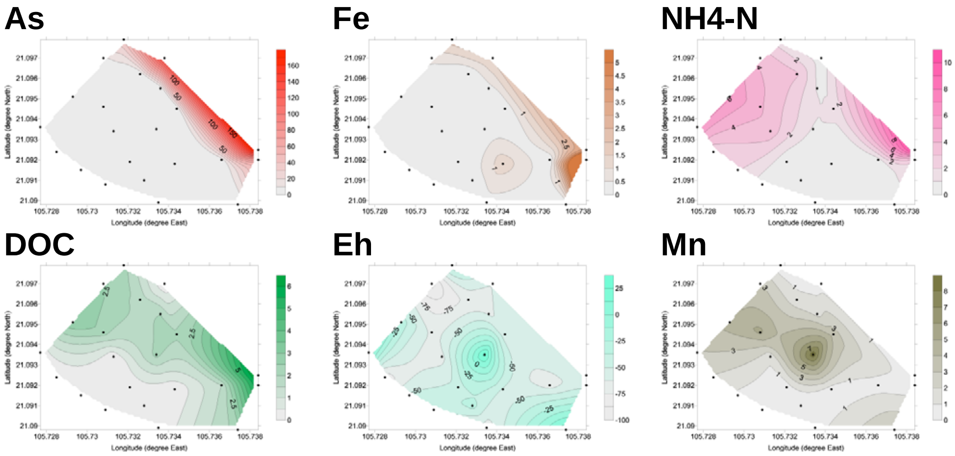


Figure 8. Contour plots of selected parameters in TC groundwater of December 2002. The contours are spatially delimited by the groundwater wells indicated by black points (see also map in figure 7). Mapping software: Surfer 7.0, nearest neighbour algorithm.

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.

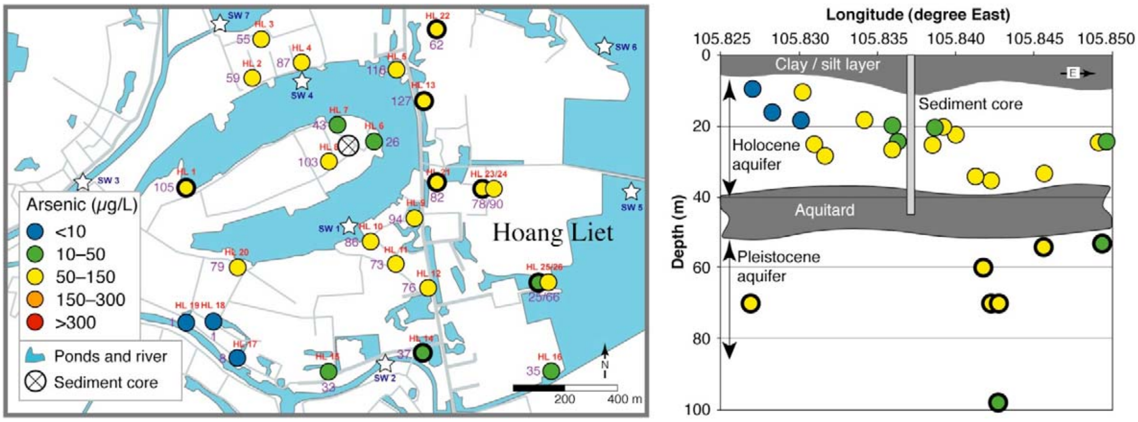


Figure 9. Map of Hoang Liet village (HL) and vertical cross-section depicting arsenic concentrations in groundwater samples collected from family-based tubewells in December 2002. Wells encircled by a thick line are taping the Pleistocene aquifer (n=7). Surface water samples are indicated by white stars.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

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. They show a relatively uniform pattern over large parts of the village, with lowest levels in the south. Yet, 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 features 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 Discussion below). The mean molar ratio of Fe/As amounted to 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 Na (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, while concentrations below the oxbow lake were considerably lower. One might speculate that the high DOC and ammonium concentrations derive from organic-rich leachate from the lake in the east, however, the chloride distribution does not support such a scenario. It rather appoints a major source of anthropogenic chloride from the channel in the south, while the contribution of the two lakes is less obvious.

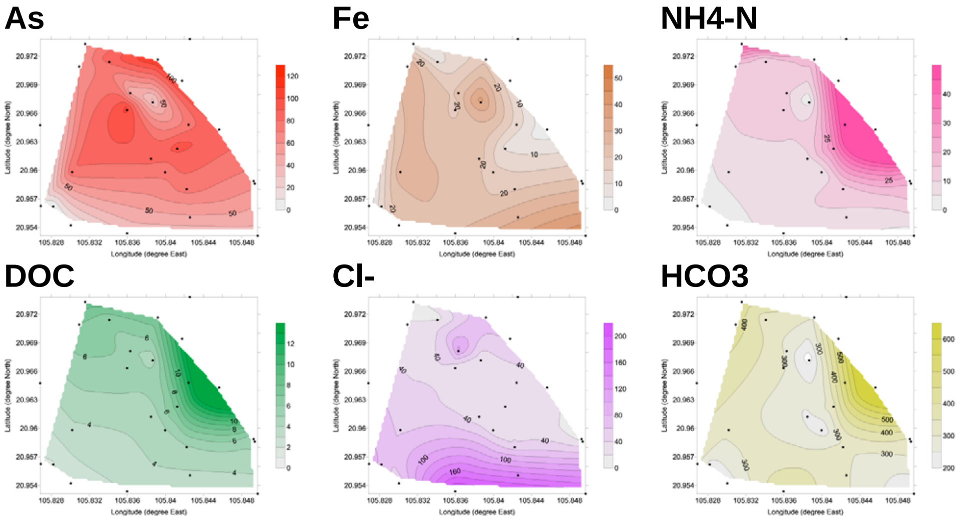


Figure 10. Contour plots of selected parameters in groundwater samples from HL in December 2002 (Holocene aquifer). The contours are spatially delimited by the Holocene groundwater wells indicated by black points (see also map in figure 9). Mapping software: Surfer 7.0, nearest neighbour algorithm.

In the Pleistocene aquifer, iron, manganese, chloride and phosphate were 2 times less abundant 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 than in the upper aquifer, and its concentrations closer to the magnitude measured in the two villages located at the Red River bank, which is supported by the piper diagram showing the similarity of HL Pleistocene groundwater with river water (Figure 3b). Highest levels of DOC and ammonium are present in the same corner 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. Hence, downward migration of DOC and ammonium reaching the Pleistocene aquifer is likely, be it derived 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.

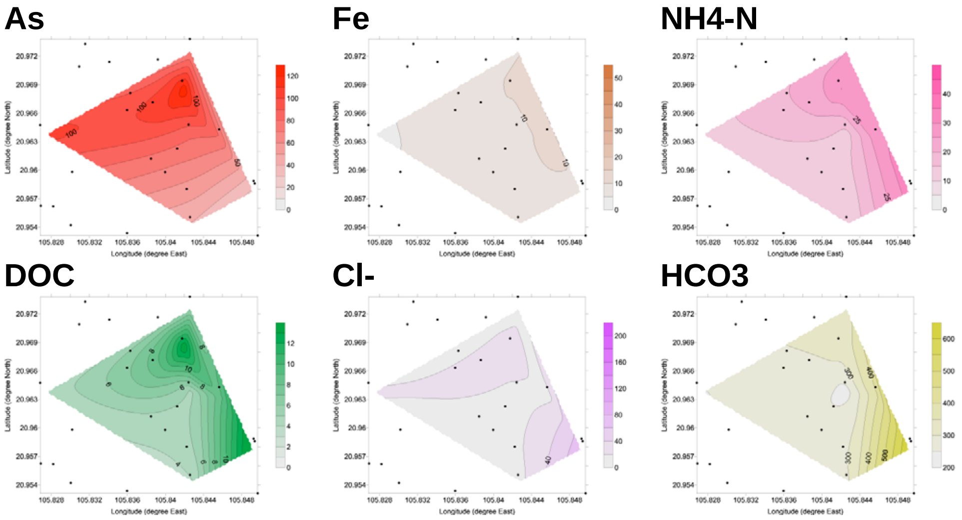


Figure 11. Contour plots of selected parameters in groundwater samples from HL in December 2002 (Pleistocene aquifer). The contours are spatially delimited by the Pleistocene groundwater wells indicated by black points (see also map in figure 9). Mapping software: Surfer 7.0, nearest neighbour algorithm.

4.1.5 Variation of Groundwater Composition during the 14-Month Study

The Hanoi authorities raised concern that arsenic concentrations might increase over time in analogy to the increase in ammonium concentrations that was observed in the Pleistocene aquifer. To elucidate this issue, selected wells were repeatedly sampled in intervals of 2–3 month. 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 was 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 rise of the river (max +9 m) over the seasons.

The variations of arsenic levels 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 (±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 variations at 70 m depth are surprising, but could reflect different mixing ratios of Pleistocene groundwater with arsenic-burdened leachate originating from the Holocene aquifer.

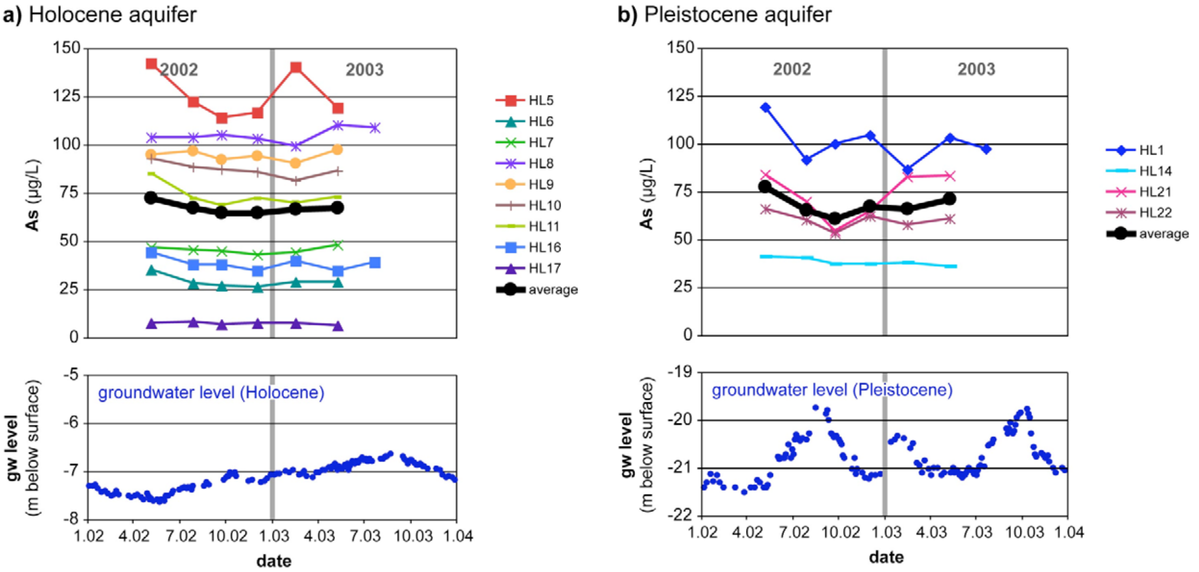


Figure 12. Variation of arsenic and groundwater levels in HL (2002–2003). **a)** Holocene aquifer, **b)** Pleistocene aquifer.

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 on the next 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 chapter 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. The lithological logs 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 is more shallow with 15 m thickness. It 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.

4.2.3 Major Minerals in Sediments. Based on the diffractograms obtained from qualitative XRD, the sediments from the three boreholes generally have a homogeneous composition of quartz (main component), chlorites, mica, and feldspars. Differences are obvious in the abundance of chlorites, mica, and feldspars. Some samples allowed further identification and 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).

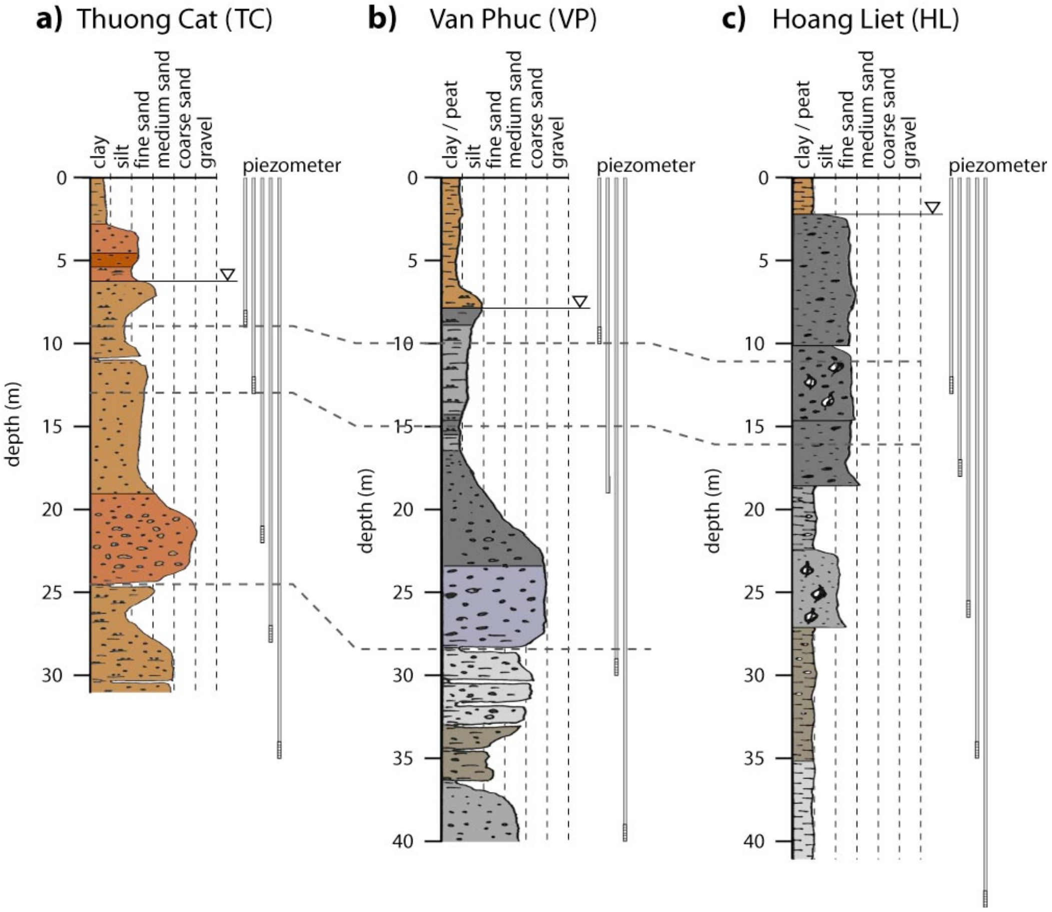


Figure 13. Lithological logs (hand drawn) of the three boreholes drilled in April 2003, and depths of the nested piezometers. The colouring reflects the aspect of the sediments as they were brought to the surface. Dashed lines of correlation were derived from lithology and chemical composition. The triangles 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.

4.2.4 Chemical Species in Sediments and Corresponding Groundwater. Depth profiles of sediment species are plotted in figure 14. Total arsenic concentrations in the nested piezometers are depicted in the same figures. Sediment-bound iron and arsenic were largely related with grain size (see annex A.4). Since small particles generally exhibit larger surface areas than bigger ones, 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 therefore substantiated and also reflected in 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 in 28±0.2 m depth exhibited the highest recorded arsenic level of 22 μg/g. The same but somewhat less distinct peak was identified in the corresponding sediment layer at TC (see below). The median molar ratio of sediment-bound Fe/As was 4'700.

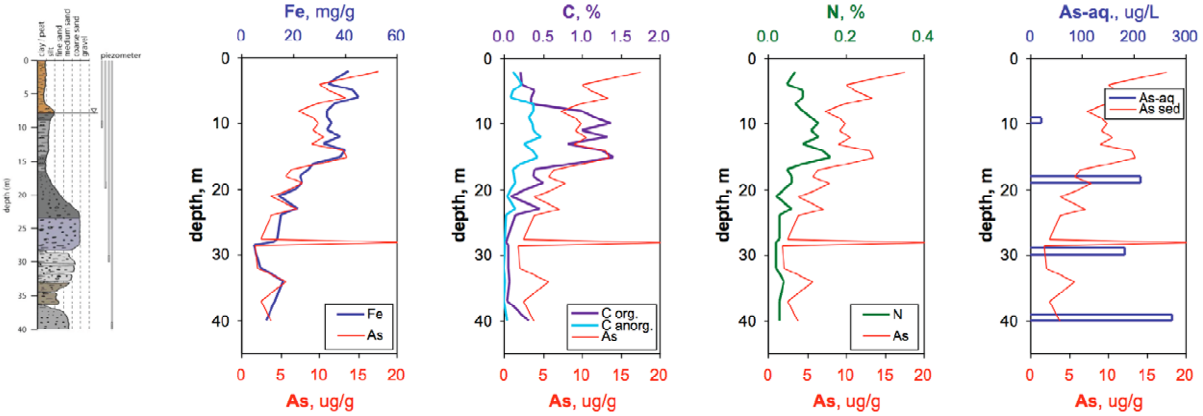
Pore water arsenic concentrations in samples from the four piezometers varied between 22–270 μg/L which is a typical range for VP groundwater. The lowest aqueous concentration (22 μg/L) was measured at the redox boundary (9–10 m) where sediment arsenic was 9.8 μg/g. In contrast, the three piezometers 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 μg/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

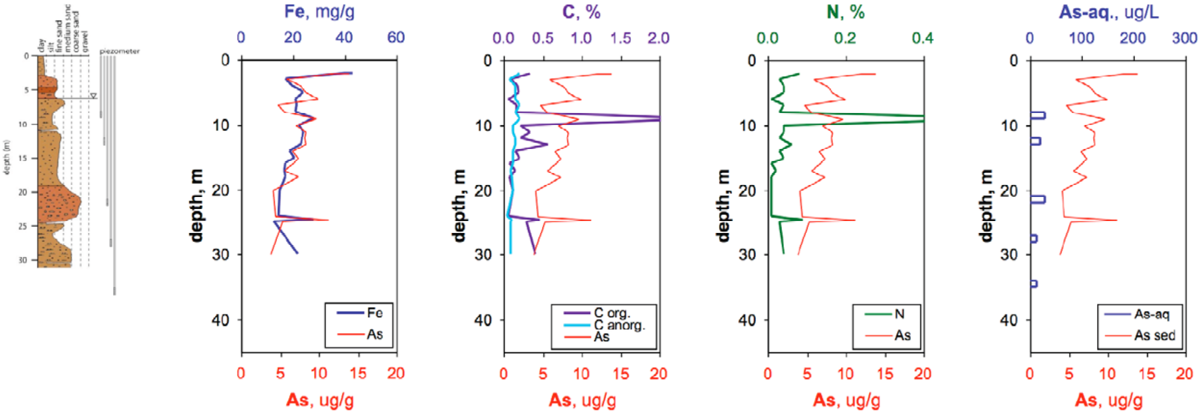
The profile of solid-bound arsenic in TC is less variable than in VP and HL (Figure 14b). The highest concentrations are again found in the top clay layer (1 m, 13.8 μg/g) and in the narrow band of clayey silt at 24.5 m (11.2 μg/g). NOM is mainly present between 9–13 m and 24.5–30 m with a sharp peak 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 material the sediments are made of. Nevertheless, the concentrations are higher in the medium to coarse sand (>20m, average 4.4 μg/g, range 3.8–5.2 μg/g) as compared to VP (>24 m, average 2.7 μg/g, range 1.8–3.8 μg/g). Since these sediments were deposited during the same time period at both locations, they should originally have had the same arsenic levels. The 1.7 μg/g (39%) difference between the average arsenic contents in VP and TC therefore possibly reflect 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.

a) VP



b) TC



c) HL

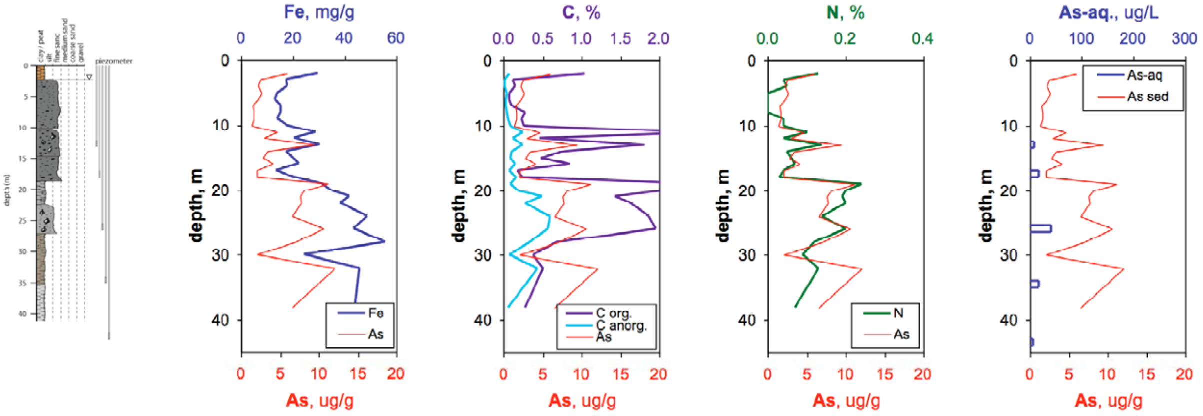


Figure 14. Depth profiles of sediment-bound As, Fe, C, and N, as well as total dissolved arsenic measured in groundwater from the nested piezometers in **a)** Van Phuc, **b)** Thuong Cat, and **c)** Hoang Liet.

The arsenic concentrations in water of the five nested piezometers (14–28 μg/g) match the elevated levels measured in the groundwaters outside the dike (see Figure 7). There is obviously 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 μg/g in the sandy aquifer and >5 μg/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 to iron coatings at former 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 at 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 one of the three latter 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 chapter 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 HCl and oxalate leached fractions were small (11.2% and 8.1%, respectively) and predominantly found in fine grained material, as well as in the more oxic sediments of TC. Arsenic incorporated in crystalline phases (average 24%) are not readily mobilized under reducing conditions (McArthur et al., 2004).

In conclusion, the sequential leaching revealed readily dissolvable arsenic (phosphate leached) in all sediments with a clear prevalence 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. It’s predominantly the reducing conditions combined with a moderate Fe/As ratio that drive arsenic mobilization from the sediments.

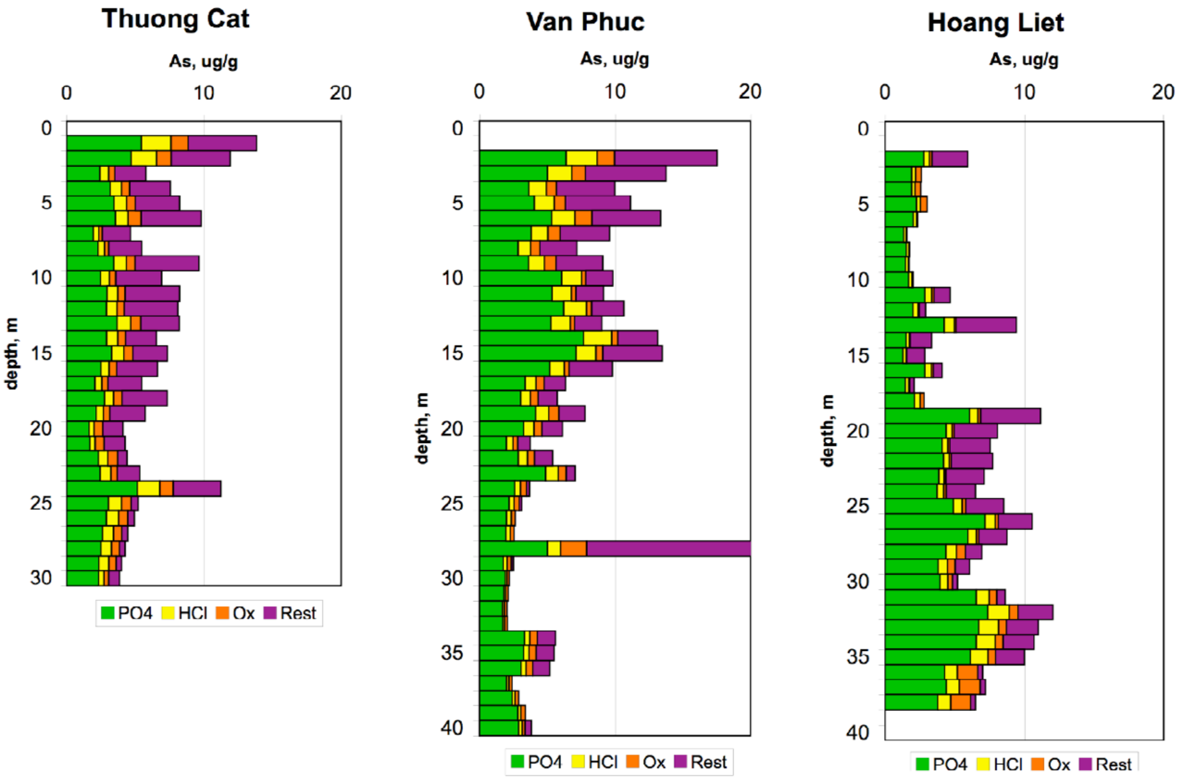


Figure 15. Arsenic leached from the sediments by the sequence of extractants outlined in table 1.

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

extractant	**target phase**	**Thuong Cat (TC)**	**Van Phuc (VP)**	**Hoang Liet (HL)**	**All**
PO4	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

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. Arsenic levels released from the grey (iron-reduced) sediments were significantly higher (max 340 μg/L) than in brown sediments (max 28 μg/L), as demonstrated from the sediment cores of VP and TC. 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, similar levels of TOC (compare 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 one significant difference among the river bank sites. I.e., VP exhibits 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 thus must then be transported to well-depth through the sandy aquifer. Such a scenario is not very likely at our site since the shallow piezometer tapping groundwater from 1–2 m below the redox boundary in VP had a low arsenic level (22 μg/L) while the concentration was >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. (2002) and made responsible for arsenic mobilization in Bangladesh. However, this conclusion of the corresponding publication 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).

DOC migration can only be corroborated if DOC levels are high in the sediment layers above and decrease in the aquifer below. And 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 from the organic-rich clay layer (component 1) with less anoxic groundwater in the aquifer (component 2).

5.2. Arsenic Mobilization and Retention in the Peat Area

Arsenic concentrations in the Holocene aquifer of the peat area were 2 times lower than at the river bank in VP, 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 aquifer sand 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 answer to the question why arsenic levels are higher at the river bank in VP than in the Holocene aquifer of the peat area 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 evolving new sediment phases under iron-reducing conditions that incorporate arsenic and iron from the groundwater. Furthermore, Dixit and Hering provided evidence that the sorption density of As(III) on iron oxide phases is increased at higher Fe(II) concentrations (Dixit and Hering, 2006). The authors observed the absence of competition between As(III) and ferrous iron for sorption sites on goethite. In 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). Correspondingly, 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. This limitation 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 has been shown in this study for the first time.

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

5.3. Impact of Excessive Groundwater Abstraction

Groundwater abstraction from the Pleistocene aquifer for the public Hanoi water supply amounted to 610 000 m^3 per day in 2005 (Cao et al., 2005) and is likely to increase as the population and industry are growing. The authorities are targeting 760 000 m^3/day, but plan to cover 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), and eventually a low contents of arsenic bound to the gravel surfaces. Although the hydraulic conductivity is high in gravel, the excessive pumping is causing massive drawdown in the Pleistocene aquifer (30 m in 2003) and also considerably lowered the groundwater heads of the Holocene (see Figure 2a+b). Despite the sediment core at our location in HL revealed a >20 m aquitard, there is enough evidence that the two aquifers are not well separated as can be seen in the 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 chapter 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.

Based on the manifold data presented in this paper, there is enough indication to conclude that reduced groundwater is vertically seeping into the Pleistocene aquifer, thereby enriching this water 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 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 (see Figure 2). Untreated groundwater collected in 2000 from wells of the Hanoi water works contained 15–430 μg/L arsenic (Berg et al., 2001), yet, it remains unknown to us how these concentrations developed until to date. A trend of increasing arsenic can not be seen in the data of our 14-month monitoring in HL, but the situation must be observed over considerably longer periods.

6. Conclusions

The groundwater arsenic concentrations were neither linked to bulk sediment arsenic (and iron), nor to the phosphate leached fraction of ionic and/or adsorbed arsenic. But the magnitude of arsenic levels in groundwater could 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 of arsenic to sediment phases is enhanced (Dixit and Hering, 2006; Herbel and Fendorf, 2006). To our knowledge, this is the first indication obtained in the field for this arsenic retardation process.

Vertical migration of reduced groundwater was observed in the excessively pumped peat area, but also at the river bank where groundwater pumping has little influence on the natural hydrology. Iron-reducing conditions at the river bank develop in the young clay layer from degradation of NOM, thereby dissolving arsenic, iron, manganese and DOC from the sediments. DOC-burdened water then travels downwards through the clay to reach the aquifer where it establishes (and maintains) reducing conditions. Once these aquifers become reduced, arsenic can be released from the aquifer solids and be additionally derived from the leached groundwater. This behaviour is an important mechanism for groundwater arsenic contamination in aquifers that do not necessarily contain enough organic matter in their sediments (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, and groundwater remains enriched with arsenic and high concentrations of 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 coprecipitaion 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). We therefore strongly recommend the Hanoi water works evaluate alternative water resources for drinking water production, be it groundwater from uncontaminated areas, or surface water.

The groundwater drawdown in the Hanoi area is certainly on the extreme side, but it illustrates what might happen if deep and less anoxic groundwater is not sufficiently replenished. Irrigation in the Red River delta is still mainly established with surface water. However, in the arsenic burdened Bengal delta floodplain, large amounts of groundwater are pumped for irrigation purposes. Its impact on arsenic mobilization is controversial and mainly discussed for irrigation wells tapping arsenic-rich water from ~30 m depth (McArthur et al., 2004; Zheng et al., 2004; Harvey et al., 2006; Klump et al., 2006). What we can learn from the Hanoi situation is 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 stability of redox conditions and arsenic levels should be carefully monitored.

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Annex

to manuscript

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

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Annex (Supplementary Data)

A1. Cross-correlation of As concentrations determined by AFS and ICP-OES.

Annex to chapter 3.3. "Water Analysis, Quality Assurance, and Detection Limits"

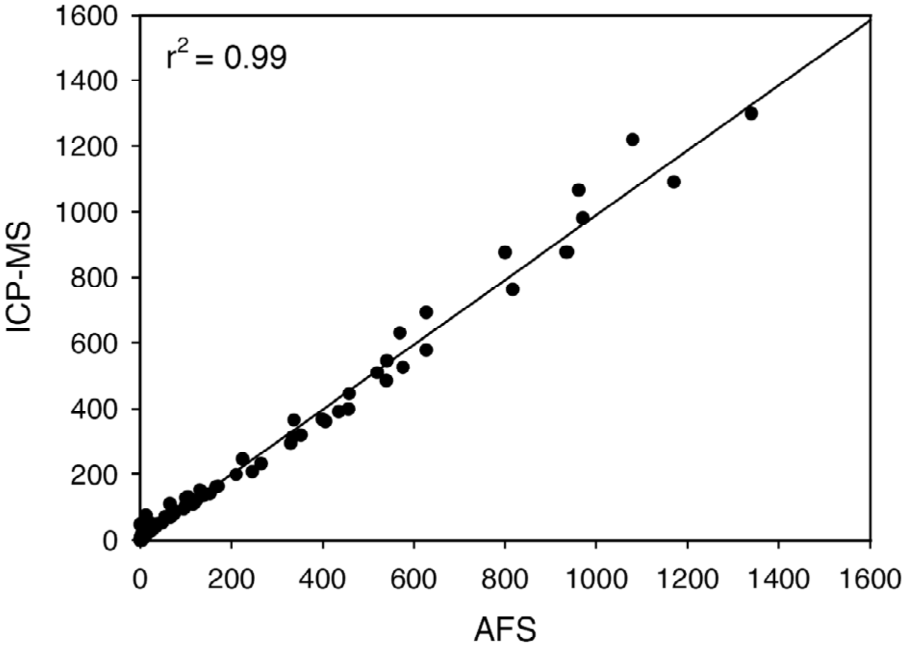


Figure A-1. Arsenic concentrations determined by AFS and by ICP-MS. The cross-correlation exhibited r^2 of 0.99.

A2. Principal Component Analysis (PCA)

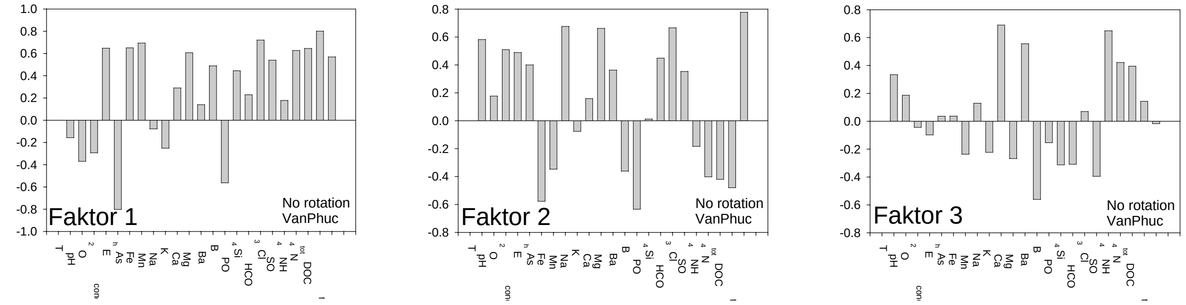
Annex to chapter 3.4 "Statistical Analysis"
and chapter 4.1 "Groundwater"

Identification of parameter associations was performed by principal component analysis (PCA) using Systat 11. Diagrams illustrating the factor loadings of the initial variables on the 3 separated factor axes. High loadings in absolute value on the same axis indicate a close relationship among the respective chemical components. Factor 1 represents the main dissolved load of the waters; Factors 2 and 3 express low and high redox conditions, respectively.

A2. a) Van Phuc

In this village, groundwater is largely replenished by the river (Piper Plot) and there is a pronounced variability of arsenic levels. Factor 1 (27% of the variance) represents two chemically explainable conditions, namely (i) reducing conditions with low E_h and high Fe(II), high DOC and ammonia which is known to be a trigger for As release, and (ii) the composition of major cations and anions such as Ca, bicarbonate and chloride (although bicarbonate rather than chloride is dominant with respect to the Piper diagram in figure 3).
Factor 2 (22% of the variance) clearly depicts an anti-correlation of As and Mn, while high factor loading of Mn is accompanied by high factor loading of T and O_2 - the rest again showing major cations and anions as found in factor loadings of factor 1. MnO_2 reduction occurs at redox potentials that are higher compared to reduction of iron(hydr)oxides. Therefore, As has still an attracting surface to bind to and its concentrations are low. Typically, high Mn concentrations are accompanied with low As concentrations and vice versa. Factor 2 shows, that Mn and oxygen concentrations have similar trends; the higher the oxygen concentrations and the higher the E_h values, the higher the Mn levels. It must be considered, however, that this is only true for suboxic and slightly oxic conditions because otherwise MnO_2 is stable.

Factor 3 shows the rest of the cations such as K, Mg and Ba and the rest of the anions, sulphate. It is noteworthy that Ba is anti-correlating K and Mg (competition), but also anti-correlating sulphate. The more Ba, the less sulphate and vice versa. It seems to be limited by the solubility of $BaSO_4$.



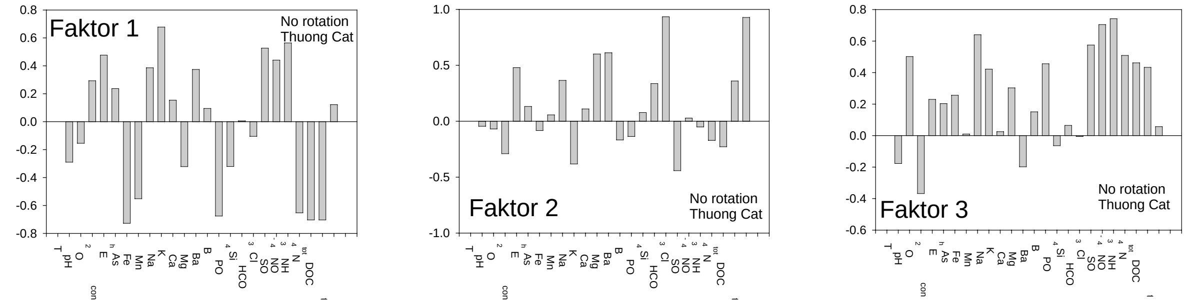
27% of the variance 22% of the variance 11% of the variance

Figure A-2. PCA factor loadings obtained for groundwater of Van Phuc (n=20).

A2. b) Thuong Cat

Like Van Phuc, the groundwater of Thuong Cat is replenished by river water. The major cation and anion composition is similar to the river water, with the exception of some wells exhibiting more Cl instead of HCO_3 and more Na/K instead of Ca. Factor 1 (21% of the variance) clearly depicts the correlation of As, Fe, B, ammonium and DOC. Interestingly, the more Na and Cl are dissolved, the lower the As concentration.

Factors 2 and 3 represent major cations and anions (Ca, Mg and HCO_3) and Mn-reducing conditions, respectively.

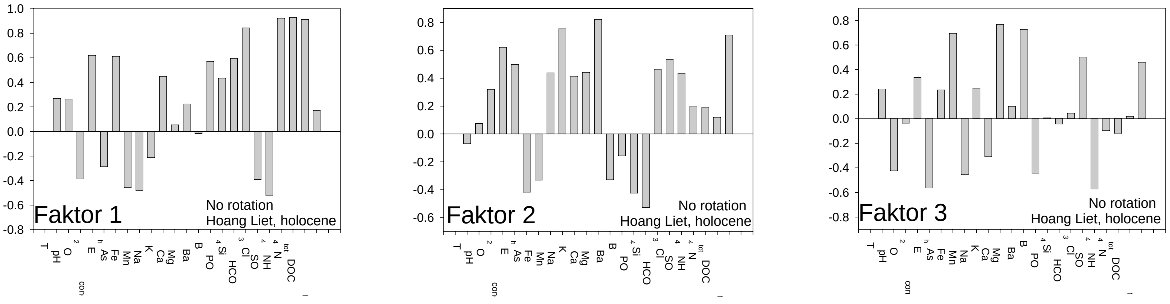


21% of the variance 15% of the variance 15% of the variance

Figure A-3. PCA factor loadings obtained for groundwater of Thuong Cat (n=22).

A2. c) Hoang Liet, Holocene

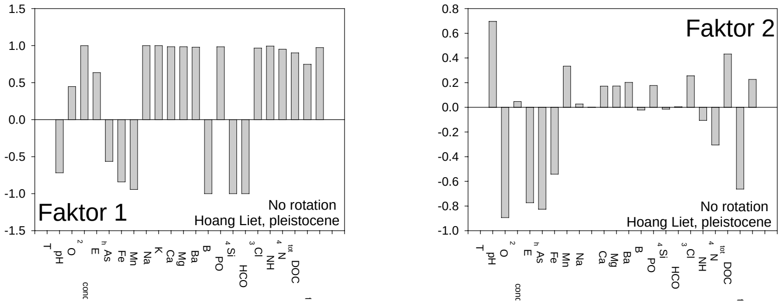
This village is not in the vicinity of the river, which is supported by the Piper plot. The upper aquifer has higher concentrations of Cl than river water. Factor 1 (28% of the variance) represents an anti-correlation of As with respect to Fe and Mn. This is special because in most cases high As levels correspond to high Fe(II) levels. The anti-correlation of As and Mn, however, is plausible due to the fact that under Mn-reducing conditions there are still enough iron oxide surfaces for As to sorb. In this case, however, it seems that high Fe is accompanied by low As and vice versa. Factor 2 (20% of the variance) represents major cations and anions - again, as found in factor 1 at Thuong Cat village with Na/Cl anti-correlating to some extent with As. Factor 3 (16% of the variance) shows two anti-correlations; (i) Fe - Mn and (ii) Ba - sulphate.



28% of the variance 20% of the variance 16% of the variance

Figure A-4. PCA factor loadings obtained for Holocene groundwater of Hoang Liet (n=19).

<u>A2. d) Hoang Liet, Pleistocene</u>: there are not enough data to be analyzed properly in PCA.



82% of the variance 18% of the variance

Figure A-5. PCA factor loadings obtained for Pleistocene groundwater of Hoang Liet (n=7). Data set is too small for meaningful interpretation.

A3. Temporal Fluctuations of Groundwater Composition in Hoang Liet

Annex to chapter 4.1.5 "Variation of Groundwater Composition During the 14-Month Study"

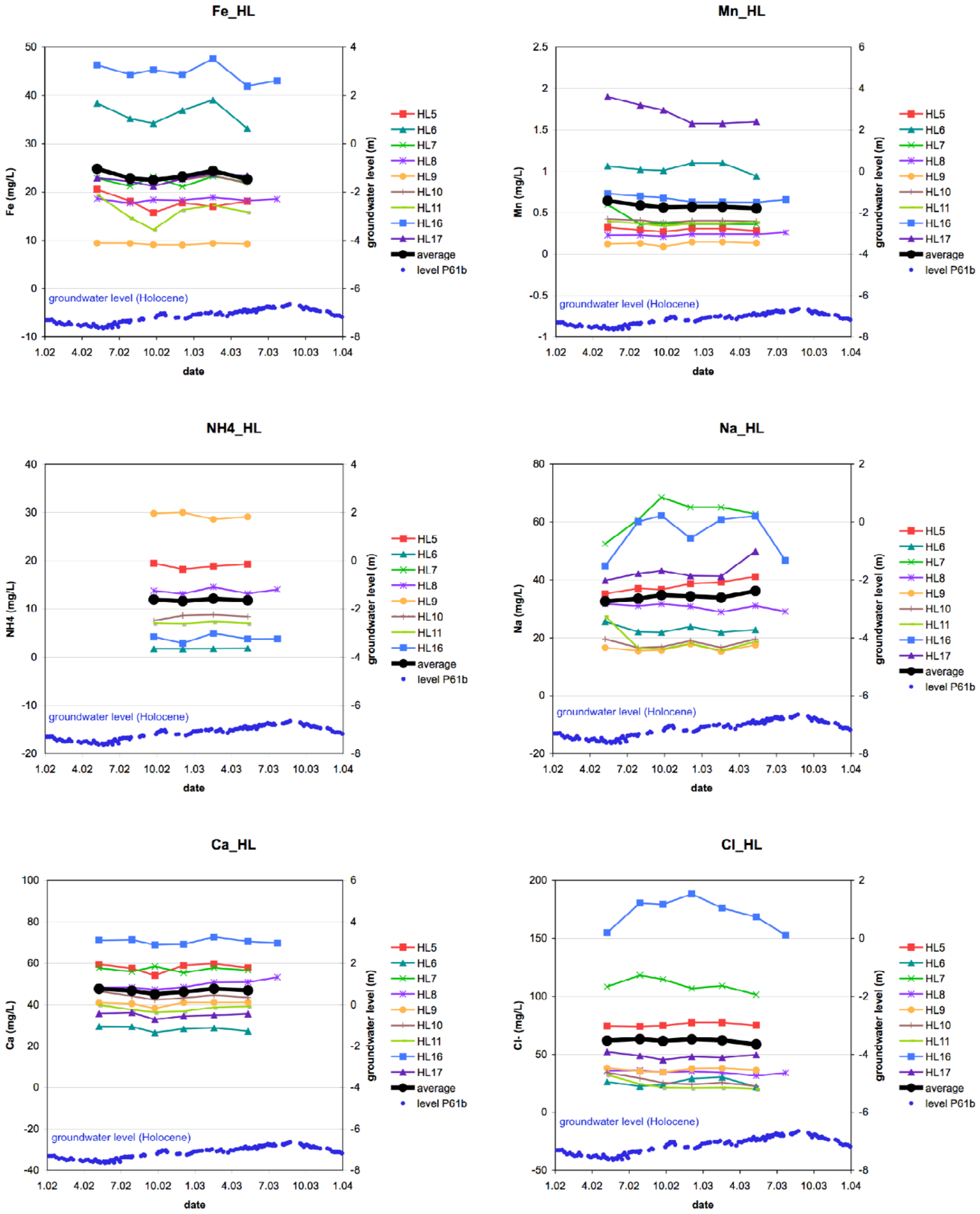


Figure A-6. Holocene groundwater levels and fluctuations of Fe, Mn, NH_4^+, Na, Ca, and chloride in Hoang Liet during this study (2002–2003).

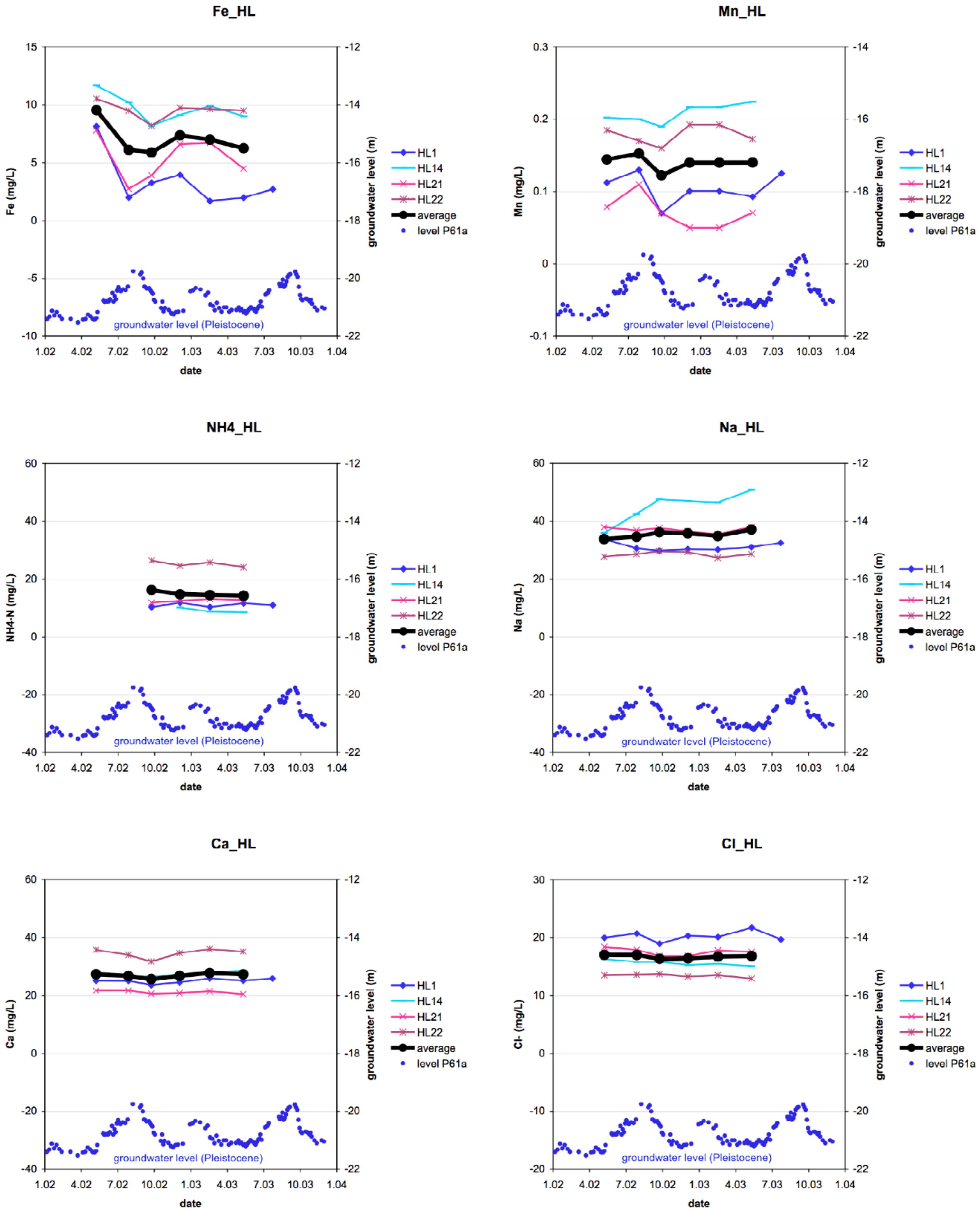


Figure A-7. Pleistocene groundwater levels and fluctuations of Fe, Mn, NH_4^+, Na, Ca, and chloride in Hoang Liet during this study (2002–2003).

A5. Relation of Grain Size with Levels of Arsenic and Other Elements.

Annex to chapter 4.2.4 "Chemical Species in Sediments and Corresponding Groundwater"

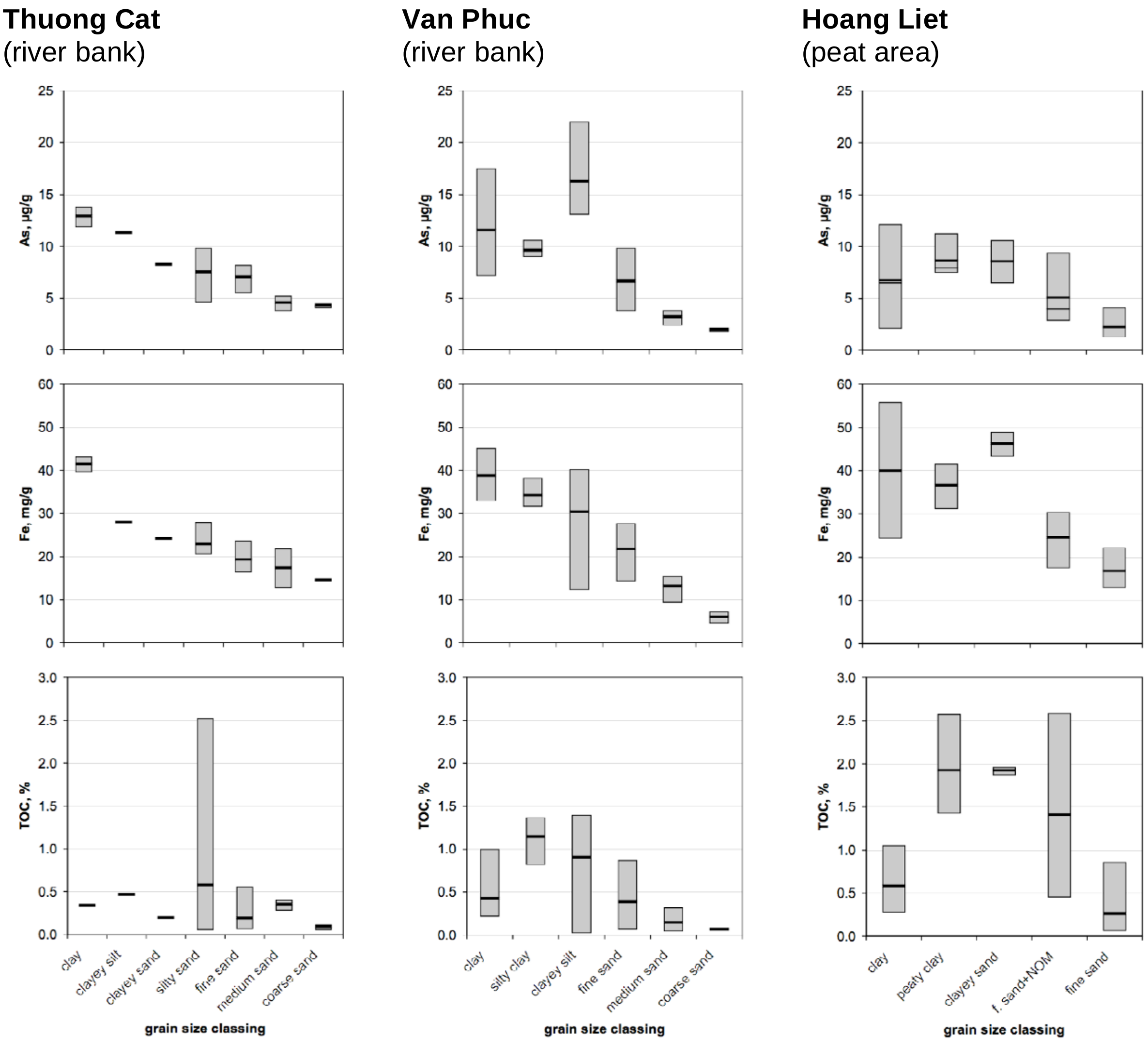
Grain sizes of the various sediment layers were visually classified. The sediments of Hoang Liet containing peat or plant remains were grouped separately to distinguish the fraction associated with organic matter. The ranges and average concentrations measured in digested sediments of corresponding grain size are depicted for As, Fe, and TOC in figure A-8. Since small particles generally exhibit larger surface areas than bigger ones, elements associated with surface coatings (such as e.g. As and Fe) are expected to be most abundant in clay and gradually less concentrated in coarser material.

A5.1 Thuong Cat

Arsenic and iron showed an expected relation with grain size in the river bank sediments of Thuong Cat. Organic carbon is not related since its deposition in sediments is not much depending on the surface size of the buried minerals, but on the amount of plant remains deposited over time.

A5.2 Van Phuc

Levels of iron also gradually increased with smaller grain size in Van Phuc, as did phosphorus (data not shown). But arsenic showed a different trend. It peaked in clayey silt and had smaller levels in clay and silty clay. A decrease of arsenic was only observed for clayey sand and coarser particles. Arsenic was also highest in clayey silt when just the amount of adsorbed arsenic was considered (see phosphate extraction in chapter 4.2.5). Clayey silt further exhibited the highest concentrations of antimony (Sb(tot) data not shown) that forms oxyanions (like arsenic) and might therefore be associated with the same sorption sites as arsenic. Meharg et al. (Environ. Sci. Technol., 2006, 4928–4935) recently postulated that considerable amounts of arsenic are co-deposited with natural organic matter (NOM) where it has absorbed and accumulated on iron coatings of formerly aerated plant roots. In Van Phuc, an association of arsenic and organic carbon can be seen in sandy material. However, the finer grained sediments (i.e. clay and clayey silt) do not follow such a relation.


Thuong Cat (river bank)

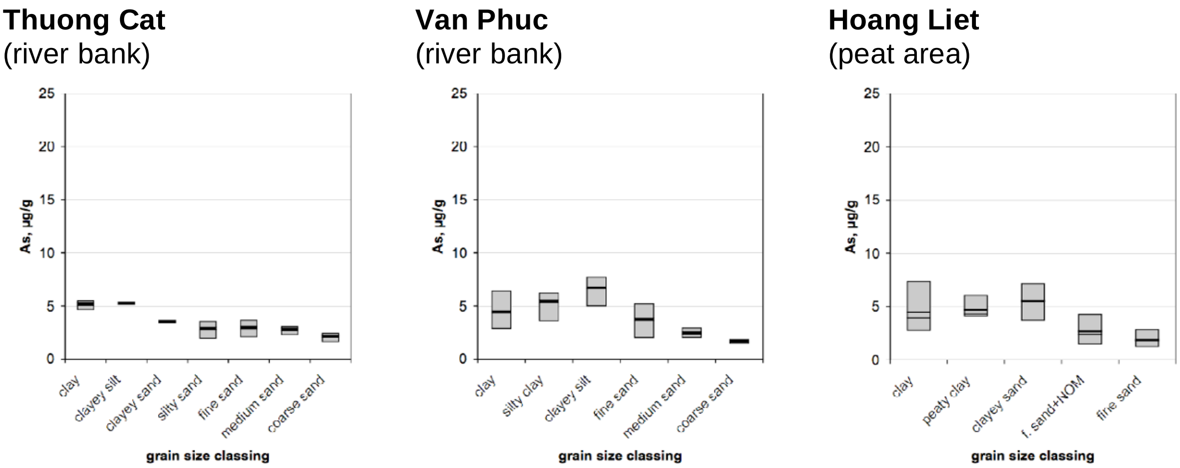
Van Phuc (river bank)

Hoang Liet (peat area)

Figure A-8. Concentration range and average of As, Fe, and TOC plotted against visually classified grain size. The concentration are those measured in sediment digests.

A5.3 Hoang Liet

As can be seen in figure A-8, arsenic was consistently higher in sediments containing elevated TOC levels in Hoang Liet. The same behaviour is found when only the adsorbed fraction of arsenic is considered (see phosphate extraction in chapter 4.2.5). There is also a clear distinction among clay and peaty clay, as well as between fine sand with and without plant remains (NOM, natural organic matter). This result is in agreement with the correlation of arsenic with TOC (r^2 0.71, n=27) and TON (r^2 0.87, n=27). An association of arsenic with organic matter is therefore plausible for the organic-rich sediments of Hoang Liet.



Thuong Cat
(river bank)

Van Phuc
(river bank)

Hoang Liet
(peat area)

Figure A-9. Fraction of adsorbed As (PO4 leached)

Table A-1. Parameters determined in Van Phuc groundwater samples of December 2002.

Place	Sampling	Depth	pH	diss O2	Ec	Eh	As	Fe/As	Fe	Mn	Na	K	Ca	Mg	Ba	B	PO4-P	Si	HCO3-	Cl-	SO4-	NO3-N	NH4-N	N-tot	DOC
ID	Date	m		mg/L	µS/cm	mV	µg/L	(molar)	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Van Phuc																									
VP1	3.12.02	35	7.3	0.02	303	66	<1*		<0.05*	0.52	28.7	2.6	14	19	187	25	<0.2*	11.1	231	4.54	1.6	<0.25*	0.31	<1.5*	<1.5*
VP2	3.12.02	36	7.3	<0.1*	571	75	<1*		<0.05*	0.45	16.2	3.9	41	52	112	14	<0.2*	11.6	428	9.77	1.0	<0.25*	0.41	<1.5*	<1.5*
VP3	3.12.02	36	7.3	<0.1*	752	-130	173	97	12.5	0.12	11.4	4.4	93	42	43	11	<0.2*	8.4	565	8.49	12.5	<0.25*	14.48	14.5	3.1
VP4	3.12.02	45	7.2	2.70	833	58	2		<0.05*	1.24	17.5	3.4	131	35	157	10	<0.2*	16.2	604	18.76	0.1	<0.25*	3.19	2.8	<1.5*
VP5	3.12.02	40	7.2	<0.1*	744	88	9		<0.05*	1.72	14.4	2.5	123	27	125	11	<0.2*	17.1	567	12.04	<0.1*	<0.25*	6.17	5.9	<1.5*
VP6	3.12.02	42	7.3	<0.1*	652	-118	336	49	12.3	0.16	10.4	2.6	88	23	480	14	<0.2*	14.1	450	13.12	<0.1*	<0.25*	12.96	13.0	3.1
VP7	3.12.02	45	7.3	0.46	811	-102	236	68	12.0	0.63	13.9	3.4	119	39	263	9	0.14	14.3	615	8.45	<0.1*	<0.25*	4.03	4.7	2.1
VP8	3.12.02	28	7.4	<0.1*	674	-117	333	42	10.5	0.70	9.1	2.8	106	27	335	11	0.51	12.2	522	6.70	<0.1*	<0.25*	7.93	7.6	2.3
VP9	3.12.02	36	7.3	0.40	697	-95	64	214	10.3	0.20	9.8	1.3	122	25	326	14	0.45	18.0	509	9.86	11.6	<0.25*	1.41	1.5	<1.5*
VP10	3.12.02	50	7.2	<0.1*	753	-97	304	35	8.0	0.22	17.4	4.1	87	26	537	13	<0.2*	17.4	526	13.28	<0.1*	<0.25*	18.29	20.5	3.6
VP11	3.12.02	45	7.3	0.21	865	-74	118	70	6.2	0.64	13.7	3.6	159	32	643	11	0.20	14.6	630	24.18	<0.1*	<0.25*	3.43	3.8	1.8
VP12	3.12.02	45	7.6	3.00	644	73	7	35	0.2	1.09	9.9	3.0	113	27	111	13	<0.2*	15.7	525	10.72	<0.1*	<0.25*	3.34	3.4	<1.5*
VP13	3.12.02	45	7.4	0.21	340	-86	80	56	3.3	0.87	17.1	4.3	95	24	87	10	0.61	21.9	492	8.37	<0.1*	<0.25*	15.92	15.0	2.8
VP14	3.12.02	48	7.3	0.02	815	-48	146	17	1.8	1.36	14.6	5.6	99	44	140	12	0.52	15.3	608	8.07	2.5	<0.25*	12.59	12.0	1.5
VP15	3.12.02	48	7.3	0.37	751	-92	27	631	12.7	1.60	28.8	4.1	94	31	225	10	0.14	17.9	531	12.19	<0.1*	<0.25*	3.68	3.8	2.0
VP16	3.12.02	48	7.3	0.11	745	-77	100	71	5.3	2.61	14.2	5.0	133	40	177	9	0.37	21.5	655	27.49	<0.1*	<0.25*	9.21	8.7	1.6
VP17	3.12.02	38	7.5	0.31	675	127	1		<0.05*	1.29	11.2	3.1	109	25	85	7	<0.2*	16.9	490	<2.5*	<0.1*	<0.25*	5.24	4.4	<1.5*
VP18	3.12.02	42	7.2	0.03	877	-44	76	109	6.1	1.05	18.7	3.4	133	36	219	9	0.15	16.5	642	14.08	0.7	<0.25*	6.71	6.5	1.8
VP19	3.12.02	24	7.3	0.14	892	-80	95	249	17.6	0.22	23.5	2.5	139	26	306	8	0.93	17.5	609	23.32	<0.1*	<0.25*	6.39	6.2	2.7
VP20	3.12.02	40	7.2	<0.1*	754	-128	323	54	13.0	0.48	10.7	3.2	100	26	463	14	0.32	14.2	509	13.94	<0.1*	<0.25*	13.13	12.8	2.9
	Min	24	7.2	<0.1*	303	-130	<1*	17	<0.05*	0.12	9.1	1.3	14	19	43	7	<0.2*	8.4	231	<2.5*	<0.1*	<0.25*	0.31	<1.5*	<1.5*
	Max	50	7.6	3.00	892	127	336	631	17.6	2.61	28.8	5.6	159	52	643	25	0.93	21.9	655	27.49	12.5	<0.25*	18.29	20.5	3.6
	Median	42	7.3	0.07	748	-79	88	68	6.2	0.67	14.3	3.4	108	27	203	11	0.14	16.0	528	11.38	<0.1*	<0.25*	6.28	6.0	1.8
	Average	41	7.31	0.40	707	-40	121	120	6.6	0.86	15.6	3.4	105	31	251	12	0.22	15.6	535	12.37	1.5	<0.25*	7.44	7.4	1.6
River																									
RR-VP	21.7.03	0	8.0		140	2	4		<0.05*	0.02	3.4	1.4	25	4	30	2	4.76	4.7	101	1.37	5.9	0.4	0.16	<1.5	2.7

Table A-2. Parameters determined in Thuong Cat groundwater samples of December 2002.

Place	Sampling	Depth	pH	diss O2	Ec	Eh	As	Fe/As	Fe	Mn	Na	K	Ca	Mg	Ba	B	PO4-P	Si	HCO3-	Cl-	SO4-	NO3-N	NH4-N	N-tot	DOC
ID	Date	m		mg/L	µS/cm	mV	µg/L	(molar)	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Thuong Cat																									
TC1	5.12.02	13	7.1		417	-43	40	60	1.8	0.31	2.5	1.2	60	17	135	6	0.33	8.9	268	5.6	6.6	<0.25*	1.31	1.6	2.2
TC2	5.12.02	13	6.8	0.32	68	98	8	110	0.6	3.19	7.7	1.5	86	30	452	4	<0.2*	14.3	445	3.5	7.7	<0.25*	3.77	4.2	2.6
TC3	5.12.02	17	6.6	0.20	579	130	<1*		<0.05*	4.32	15.4	2.0	69	20	317	6	0.21	14.1	392	3.2	<0.1*	<0.25*	6.15	6.1	3.0
TC4	5.12.02	21	6.6	0.51	503	122	<1*		<0.05*	2.92	17.5	2.9	50	15	285	5	<0.2*	11.3	282	26.8	<0.1*	<0.25*	6.33	6.5	<1.5*
TC5	5.12.02	18	7.3	0.31	528	-46	144	15	1.6	0.56	3.7	2.2	94	12	107	6	<0.2*	8.6	351	3.7	7.9	<0.25*	0.35	<1.5*	<1.5*
TC6	5.12.02	18	6.9	0.17	782	117	<1*		<0.05*	1.31	23.4	11.2	93	28	560	8	<0.2*	7.5	450	32.1	12.2	<0.25*	3.19	3.3	1.8
TC7	5.12.02	18	6.6	0.30	609	119	<1*		<0.05*	5.34	9.0	1.8	72	28	345	6	<0.2*	11.7	382	14.8	1.6	<0.25*	4.12	4.3	2.3
TC8	5.12.02	18	6.2	0.24	724	94	<1*		<0.05*	1.91	53.4	2.7	54	18	319	5	<0.2*	9.6	221	108.1	20.8	0.3	2.05	2.4	<1.5*
TC9	5.12.02	20	7.1	0.27	801	13	<1*		0.3	1.62	5.6	2.1	130	30	217	10	<0.2*	11.1	542	4.1	10.4	<0.25*	0.86	<1.5*	2.0
TC10	5.12.02	20	6.6	0.22	569	111	<1*		<0.05*	1.15	13.7	4.3	61	29	268	5	<0.2*	10.0	370	9.8	3.2	<0.25*	3.73	4.2	<1.5*
TC11	5.12.02	25	6.6	1.69	580	80	<1*		0.1	0.84	24.8	4.2	31	34	252	8	<0.2*	11.1	240	69.9	0.5	<0.25*	2.07	2.1	<1.5*
TC12	5.12.02	33	7.1	0.15	721	53	<1*		<0.05*	3.64	7.3	2.2	124	29	265	7	<0.2*	10.8	543	3.4	<0.1*	<0.25*	1.22	<1.5*	2.1
TC13	5.12.02	16	6.8	0.27	901	103	<1*		<0.05*	8.70	39.5	5.7	63	56	226	6	<0.2*	12.8	420	70.6	27.0	0.4	0.90	<1.5*	2.2
TC14	5.12.02	21	6.5		462	88	<1*		<0.05*	0.37	10.7	4.5	26	41	330	6	<0.2*	7.7	306	10.9	<0.1*	<0.25*	0.06	<1.5*	<1.5*
TC15	5.12.02	26	6.4	1.95	496	55	<1*		<0.05*	0.75	36.8	3.0	21	33	346	4	<0.2*	9.4	323	9.0	1.0	<0.25*	0.56	<1.5*	<1.5*
TC16	5.12.02	33	7.1	0.60	779	63	2		<0.05*	0.57	15.5	7.0	71	81	347	5	0.15	9.4	615	<2.5*	<0.1*	<0.25*	0.50	<1.5*	1.5
TC17	5.12.02	35	6.7	0.28	654	-6	2		1.4	0.39	11.1	5.9	48	60	69	4	<0.2*	12.7	456	<2.5*	<0.1*	<0.25*	0.36	<1.5*	<1.5*
TC18	5.12.02	32	6.3	3.70	466	31	<1*		<0.05*	0.38	9.4	4.4	29	40	358	6	<0.2*	11.4	315	3.7	1.2	<0.25*	<0.1*	<1.5*	<1.5*
TC19	5.12.02	27	7.1	0.68	756	73	<1*		<0.05*	3.12	9.5	4.0	65	72	65	1	<0.2*	15.6	571	<2.5*	<0.1*	<0.25*	0.38	<1.5*	2.3
TC20	5.12.02	32	6.1	0.43	392	202	<1*		0.3	0.63	19.9	3.6	21	26	113	5	<0.2*	15.6	254	6.8	2.8	<0.25*	<0.1*	<1.5*	<1.5*
TC21	5.12.02	44	7.0		670	-100	198	25	3.6	0.49	3.4	4.6	84	24	249	20	<0.2*	11.6	433	3.4	1.3	<0.25*	11.34	12.7	6.9
TC22	5.12.02	21	6.7		458	-80	62	271	12.5	0.34	10.1	3.9	61	34	149	7	0.22	12.6	387	<2.5*	<0.1*	<0.25*	2.07	4.0	6.0
	Min	13	6.1	0.15	68	-100	<1*	15	<0.05*	0.31	2.5	1.2	21	12	65	1	<0.2*	7.5	221	<2.5*	<0.1*	<0.25*	<0.1*	<1.5*	<1.5*
	Max	44	7.3	3.70	901	202	198	271	12.5	8.70	53.4	11.2	130	81	560	20	0.33	15.6	615	108.1	27.0	0.4	11.34	12.7	6.9
	Median	21	6.7	0.31	580	76	<1*	60	<0.05*	0.99	10.9	3.8	62	29	267	6	<0.2*	11.2	384	4.8	1.3	<0.25*	1.26	0.8	1.6
	Average	24	6.7	0.68	587	58	21	96	1.0	1.95	15.9	3.9	64	34	262	6	0.04	11.3	389	17.7	4.7	0.0	2.33	2.3	1.6
River																									
RR-TC	20.7.99	0			124	10	3		<0.05*	0.027	2.9	1.7	26	5	37	4	<0.2*	4.6	96	0.8	10.4	0.5	<0.1*	<1.5	4.2

Table A-3. Parameters determined in Hoang Liet groundwater samples of December 2002, and surface water of July 2006.

Place	Sampling	Depth	Aquifer	pH	diss O2	Ec	Eh	As	Fe/As	Fe	Mn	Na	K	Ca	Mg	Ba	B	PO4-P	Si	HCO3-	Cl-	SO4-	NO3-N	NH4-N	N-tot	DOC
ID	Date	m			mg/L	µS/cm	mV	µg/L	(molar)	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Hoang Liet																										
HL2	4.12.02	25	Holocene	6.4	0.32	847	-106	59	691	30.4	0.48	17.8	3.8	81	22	337	16	1.93	24.0	429	20.8	<0.1*	0.4	14.3	12.6	7.1
HL3	4.12.02	28	Holocene	6.9	0.20	743	-29	55	132	5.4	0.16	16.9	4.0	33	20	237	127	3.89	33.2	440	12.4	<0.1*	<0.25*	49.9	56.4	8.9
HL4	4.12.02	18	Holocene	6.6	0.51	659	-17	87	119	7.7	0.82	17.5	2.8	54	33	58	13	0.41	20.1	325	11.2	<0.1*	<0.25*	11.0	10.3	6.5
HL5	4.12.02	20	Holocene	6.4	0.31	737	-62	116	205	17.8	0.31	38.7	2.1	59	16	258	18	1.91	25.6	307	77.4	<0.1*	<0.25*	18.2	19.0	7.9
HL6	4.12.02	20	Holocene	6.3	0.17	454	-72	26	1869	36.9	1.10	23.9	1.1	28	13	330	20	0.65	19.2	174	29.2	9.6	<0.25*	1.7	1.9	4.5
HL7	4.12.02	24	Holocene	6.4	0.30	806	-67	43	660	21.1	0.36	65.1	2.9	55	16	350	15	1.56	21.3	290	107	<0.1*	<0.25*	11.4	10.9	5.2
HL8	4.12.02	26	Holocene	6.6	0.24	594	-88	103	238	18.3	0.24	30.9	2.5	48	16	289	18	1.75	20.5	310	35.4	<0.1*	<0.25*	13.1	13.4	6.0
HL9	4.12.02	34	Holocene	6.8	0.27	623	-64	94	129	9.0	0.15	17.9	2.6	41	24	252	80	2.66	28.3	337	37.8	<0.1*	<0.25*	30.0	28.7	7.5
HL10	4.12.02	25	Holocene	6.5	0.22	453	-68	86	352	22.5	0.40	19.0	2.5	43	12	463	16	1.01	21.4	242	24.2	<0.1*	<0.25*	8.7	8.4	4.3
HL11	4.12.02	22	Holocene	6.6	1.69	401	-45	73	302	16.3	0.37	18.0	2.0	37	9	246	15	1.04	22.6	214	21.0	<0.1*	<0.25*	6.9	7.0	5.0
HL12	4.12.02	35	Holocene	6.5	0.15	605	-60	76	330	18.7	0.37	31.3	2.7	53	16	343	20	1.27	22.8	309	42.1	<0.1*	<0.25*	13.5	13.0	5.0
HL15	4.12.02	20	Holocene	6.6	1.95	770	-43	33	1003	24.7	0.31	125.6	2.5	75	32	376	12	1.06	17.8	401	220	<0.1*	<0.25*	8.4	8.0	3.1
HL16	4.12.02	24	Holocene	6.6	0.60	910	-69	35	1719	44.3	0.63	54.4	1.3	69	26	392	17	0.48	18.9	204	188	1.4	<0.25*	2.9	3.2	3.3
HL17	4.12.02	18	Holocene	6.6	0.28	502	-52	8	3897	22.7	1.58	41.5	1.2	35	15	96	20	0.42	18.8	218	48.2	7.8	<0.25*	1.4	<1.5*	2.4
HL18	4.12.02	16	Holocene	6.8	3.70	576	-32	1		12.5	0.19	46.8	1.4	41	23	209	17	0.64	16.8	240	77.6	11.0	<0.25*	0.5	<1.5*	1.9
HL19	4.12.02	9	Holocene	6.6	0.68	708	24	1		0.3	3.30	71.8	6.3	52	26	102	22	<0.2*	14.3	315	89.2	26.8	1.7	0.3	1.7	1.7
HL20	4.12.02	10	Holocene	6.6	0.43	702	-70	79	477	28.2	0.57	22.8	3.2	72	19	491	16	1.18	21.8	318	55.7	<0.1*	<0.25*	7.3	9.9	3.8
HL24	4.12.02	33	Holocene	6.6	0.23	1333	-75	90	6	0.4	0.25	59.6	5.0	55	30	222	35	0.15	19.6	809	27.3	<0.1*	<0.25*	101	98.4	20.0
HL26	4.12.02	24	Holocene	7.0	0.35	555	-112	66	415	20.3	0.18	36.4	5.5	29	15	267	21	<0.2*	18.3	353	8.5	<0.1*	<0.25*	22.8	21.9	5.5
	Min	9		6.3	0.15	401	-112	1	6	0.3	0.15	16.9	1.1	28	9	58	12	<0.2*	14.3	174	8.5	<0.1*	<0.25*	0.3	<1.5*	1.7
	Max	35		7.0	3.70	1333	24	116	3897	44.3	3.30	125.6	6.3	81	33	491	127	3.89	33.2	809	220	26.8	1.7	101	98.4	20.0
	Median	24		6.6	0.31	659	-64	66	352	18.7	0.37	31.3	2.6	52	19	267	18	1.04	20.5	310	37.8	<0.1*	<0.25*	11.0	10.3	5.0
	Average	23		6.6	0.66	683	-58	60	738	18.8	0.62	39.8	2.9	51	20	280	27	1.16	21.3	328	59.6	3.0	0.1	17.0	17.1	5.8
HL1	4.12.02	70	Pleistocene	7.1		446	-28	105	51	3.9	0.10	30.3	2.8	25	12	113	22	0.15	18.2	246	20.3	<0.1*	<0.25*	11.8	11.3	4.1
HL13	4.12.02	60	Pleistocene	7.3	0.27	1059	-30	127	115	10.9	0.18	36.9	4.3	26	14	324	16	1.02	21.5	330	27.2	<0.1*	<0.25*	30.3	27.9	14.1
HL14	4.12.02	100	Pleistocene	6.9		466	-45	37	327	9.1	0.22	46.9	3.5	27	13	147	21	0.36	19.5	295	15.3	<0.1*	<0.25*	10.2	8.2	3.8
HL21	4.12.02	70	Pleistocene	7.4		362	-53	82	110	6.7	0.10	35.5	3.5	21	13	152	12	0.34	18.9	232	17.8	<0.1*	<0.25*	13.1	10.8	4.8
HL22	4.12.02	70	Pleistocene	6.4		623	-55	62	210	9.7	0.19	29.3	4.3	35	15	258	21	1.12	23.3	342	13.3	<0.1*	<0.25*	24.6	24.5	5.1
HL23	4.12.02	54	Pleistocene	6.6	0.15	70	-70	78	232	13.5	0.11	33.5	5.0	35	16	333	22	1.09	22.2	399	14.9	<0.1*	<0.25*	28.3	30.0	8.9
HL25	4.12.02	53	Pleistocene	7.2	4.32	1170	-77	25	383	7.0	1.47	77.3	10.8	115	28	179	66	<0.2*	13.7	682	80.0	1.3	<0.25*	33.6	33.5	15.9
	Min	53		6.4	0.15	70	-77	25	51	3.9	0.10	29.3	2.8	21	12	113	12	<0.2*	13.7	232	13.3	<0.1*	<0.25*	10.2	8.2	3.8
	Max	100		7.4	4.32	1170	-28	127	383	13.5	1.47	77.3	10.8	115	28	333	66	1.12	23.3	682	80.0	1.3	<0.25*	33.6	33.5	15.9
	Median	70		7.1	0.27	466	-53	78	210	9.1	0.18	35.5	4.3	27	14	179	21	0.36	19.5	330	17.8	<0.1*	<0.25*	24.6	24.5	5.1
	Average	68		7.0	1.58	599	-51	74	204	8.7	0.34	41.4	4.9	41	16	215	26	0.58	19.6	361	27.0	0.2	<0.25*	21.7	20.9	8.1
									314																	
			surface water																							
HL-SW-1	27.7.06	0.1	oxbow lake	8.04		307		<10*		<0.05*	<0.05*	50.5	11.3	30	12.1	88	43	<0.2*	6.9	184	46.9	15.1	2.6	0.43	2.6	10.1
HL-SW-2	27.7.06	0.1	channel	7.37		423		<10*		0.15	0.30	52.2	10.2	39	17.3	81	41	2.44	19.9	290	48.6	20.6	<0.25*	21.01	10.3	7.3
HL-SW-3	27.7.06	0.1	creek	7.39		470														356	59.5	15.8	<0.25*		12.4	9.6
HL-SW-4	27.7.06	0.1	oxbow lake	7.25		335		<10*		<0.05*	0.08	51.0	12.7	34	11.7	67	40	<0.2*	12.6	215	46.8	5.4	2.6	1.87	2.8	12.7
HL-SW-5	27.7.06	0.1	lake	9.61		262		<10*		<0.05*	<0.05*	46.3	9.7	35	10.4	45	39	0.33	10.2	213	47.1	24.1	1.0	0.17	4.6	11.4
HL-SW-6	27.7.06	0.1	lake	8.97		248		<10*		<0.05*	<0.05*	34.2	8.4	30	8.6	38	28	0.38	5.2	142	27.2	25.6	2.3	0.53	2.4	9.7
HL-SW-7	27.7.06	0.1	lake	7.73		430		<10*		<0.05*	0.14	55.9	11.9	41	15.8	71	48	2.07	17.6	322	55.3	18.0	<0.25*	22.09	12.0	8.9
	Min	0.1		7.25		248				<0.05*	<0.05*	34.2	8.4	30	8.6	37.5	28	<0.2*	5.2	142	27.2	5.4	<0.25*	0.17	2.4	7.3
	Max	0.1		9.61		470				0.15	0.30	55.9	12.7	41	17.3	88	48	2.44	19.9	356	59.5	25.6	2.60	22.1	12.4	12.7
	Median	0.1		7.73		335				<0.05*	0.04	50.8	10.7	35	11.9	69	41	0.35	11.4	215	47.1	18.0	1.0	1.20	4.6	9.7
	Average	0.1		8.05		354				0.02	0.09	48.3	10.7	35	12.7	65	40	0.87	12.1	246	47.4	17.8	1.21	7.68	6.7	9.9

CHAPTER 4

Arsenic Removal from Groundwater by Household Sand Filters: Comparative Field Study, Model Calculations, and Health Benefits

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Arsenic Removal from Groundwater by Household Sand Filters: Comparative Field Study, Model Calculations, and Health Benefits

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Arsenic removal efficiencies of 43 household sand filters were studied in rural areas of the Red River Delta in Vietnam. Simultaneously, raw groundwater from the same households and additional 31 tubewells was sampled to investigate arsenic coprecipitation with hydrous ferric iron from solution, i.e., without contact to sand surfaces. From the groundwaters containing 10−382 μg/L As, <0.1−48 mg/L Fe, <0.01−3.7 mg/L P, and 0.05−3.3 mg/L Mn, similar average removal rates of 80% and 76% were found for the sand filter and coprecipitation experiments, respectively. The filtering process requires only a few minutes. Removal efficiencies of Fe, phosphate, and Mn were >99%, 90%, and 71%, respectively. The concentration of dissolved iron in groundwater was the decisive factor for the removal of arsenic. Residual arsenic levels below 50 μg/L were achieved by 90% of the studied sand filters, and 40% were even below 10 μg/L. Fe/As ratios of ≥50 or ≥250 were required to ensure arsenic removal to levels below 50 or 10 μg/L, respectively. Phosphate concentrations >2.5 mg P/L slightly hampered the sand filter and coprecipitation efficiencies. Interestingly, the overall arsenic elimination was higher than predicted from model calculations based on sorption constants determined from coprecipitation experiments with artificial groundwater. This observation is assumed to result from As(III) oxidation involving Mn, microorganisms, and possibly dissolved organic matter present in the natural groundwaters. Clear evidence of lowered arsenic burden for people consuming sand-filtered water is demonstrated from hair analyses. The investigated sand filters proved to operate fast and robust for a broad range of groundwater composition and are thus also a viable option for mitigation in other arsenic affected regions. An estimation conducted for Bangladesh indicates that a median residual level of 25 μg/L arsenic could be reached in 84% of the polluted groundwater. The easily observable removal of iron from the pumped water makes the effect of a sand filter immediately recognizable even to people who are not aware of the arsenic problem.

Introduction

Arsenic (As) is a worldwide recurring pollutant of natural and anthropogenic origin with serious health effects upon prolonged intake of even low concentrations. Current estimates are that, e.g., 35−50 million people in the West-Bengal and Bangladesh area, over 10 million people in Vietnam, and over 2 million people in China are exposed to harmful As intake through potable water consumption (*1*−*4*). Arsenicosis and visible skin lesions have been diagnosed in thousands persons in West Bengal, Bangladesh, and China (*2*, *5*). A similar situation may be soon emerging in Vietnam, where As is contaminating tubewells of an estimated 13.5% of the Vietnamese households (some 11 million people) (*1*, *6*). Many developing countries comply to a drinking water As limit of 50 μg/L, while the WHO guideline is 10 μg/L.

In 1998, As pollution of groundwater (1 to >1000 μg/L) was detected in the Red River Delta in Vietnam (*1*, *7*), where private tubewells were introduced in the mid-1990s. The first individuals suffering from As poisoning were identified some 10 years later in 2004 by the Vietnam National Institute of Occupational and Environmental Health. There is an urgent need for simple and efficient As removal techniques on the household level.

Ion exchange, activated alumina, reverse osmosis, membrane filtration, modified coagulation/filtration, and enhanced lime softening are water treatment technologies for As removal recommended by the USEPA. However, none of these technologies are currently applied on a broad scale in developing countries because they require sophisticated technical systems and are therefore unpractical in low income regions.

Anoxic conditions in the aquifers of the Red River Delta result in high concentrations of dissolved Fe(II). An increasing number of rural households in this region are using simple sand filters to remove Fe because of its “bad taste.” Several research groups have experimentally investigated As removal by coagulation with ferric chloride (*8*−*10*), coprecipitation enhanced by solar oxidation (*11*), adsorption onto preformed hydrous ferric oxide (HFO) (*9*, *12*, *13*), iron oxide coated sand (*14*, *15*), or zerovalent iron (*16*). Since Fe(II) is the dominant species in reducing groundwater, coprecipitation studies using Fe(II) imitate the situation of freshly pumped anoxic groundwater (*17*−*20*). Oxidation of Fe(II) by atmospheric oxygen can simultaneously enhance the oxidation of As(III) to better adsorbable As(V) (*21*), often supported by Mn (*22*−*24*). Coprecipitation occurs through oxidation of Fe(II) by atmospheric oxygen, oxidation of As(III), and adsorption of As(III) and As(V) to the precipitating and coagulating HFO particles. The oxidation state of As is crucial for As removal as adsorption affinities to HFO differ for As(V) and As(III) by a factor of 100 (*20*). Typically reported values of As(III)/As(tot) ratios in anoxic groundwater of Bangladesh are about 0.55 with a range of 0.1−0.9 (*4*).

A positive correlation of As removal with initial Fe concentrations is generally observed. As(V) removal increases rapidly from 0 to 2 mg/L Fe(II) in solution while much more Fe is needed to achieve comparable removal rates for As(III) (*20*). Two studies found an enhanced As removal if Fe(II) was added in multiple steps rather than in a single initial

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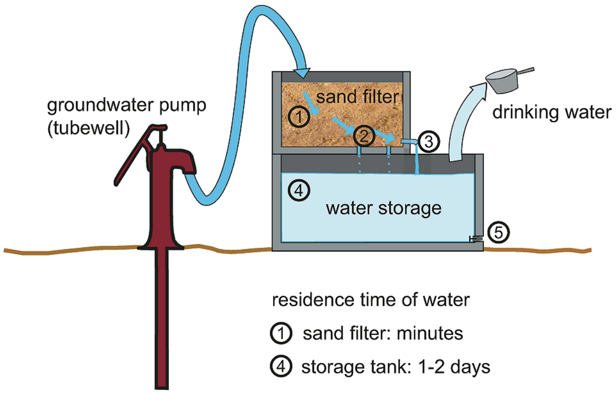

FIGURE 1. Household sand filter consisting of two open containers made of concrete or brick. The upper container (1, 0.05−0.1 m^3) serves as filter and the underlying tank (4, 0.2−0.3 m^3) is used to store treated water. The upper container must have one or a few outlets either at the bottom (2) or in the front wall (3). A simple sieve (e.g., piece of cloth) is used to prevent the sand from flushing out of the filter. The valve (5) serves to empty the storage tank for cleaning.

addition (*16*, *20*). Dissolved anions such as phosphate, silicate, bicarbonate, and sulfate have been reported to decrease the As removal capacity by competing with arsenic oxyanions for adsorption sites (*17*, *25*).

The goal of this study was to investigate the As removal efficiency of simple household sand filters for a broad range of groundwater compositions in Vietnam and assess its applicability for other arsenic burdened regions. Furthermore, this paper presents evidence (based on the results of As measurements in hair) for significantly lowered exposure of people drinking sand-filtered water.

Experimental Section

Study Area. This field study was conducted in three villages located in the Red River Delta, namely Thuong Cat, Hoang Liet, and Van Phuc (see Supporting Information (SI), Figure SI 1a). A total number of 43 sand filters were investigated in households pumping groundwater with elevated As levels. Coprecipitation experiments were conducted with the same 43 groundwaters as well as groundwater collected from 31 additional tubewells. With highly variable concentrations of As (10−382 μg/L), Fe (<0.1−48 mg/L), P (<0.01−3.7 mg/L), and Mn (0.05−3.3 mg/L), the investigated wells represent a broad and representative range of groundwater composition (see SI, Figure SI 1b). Geological and climatic conditions are summarized in refs *1* and *26*.

Sand Filter Design. The tested sand filters comprise two superimposed concrete containers. The upper container is filled with locally available sand and the lower one serves to store the filtered water. A typical design is shown in Figure 1. Some people added gravel, “black sand” (manganese oxide coatings), or charcoal to the sand. The sand needs to run dry between two subsequent filtration periods to prevent microbial activity and maintain oxic conditions. More information on maintenance is provided in the SI and ref *27*. Groundwater is pumped from the tubewell (hand pump or electrical pump) into the filter and trickles through the sand layer into the water storage tank, either through holes at the bottom or an outlet in the front wall of the sand container. The residence time in the sand filter is about 2−3 min for the first flush, with a consecutive water throughput of 0.1−1 L/min. The sand is replaced and the tanks are cleaned with a brush every 1−2 (maximum 6) months (see also ref *27*).

Coprecipitation. For reasons of comparison with sand filter efficiencies, coprecipitation experiments were conducted by filling raw groundwater into 500 mL PET bottles and exposing them to air for 72 or 24 h. The PET bottles were shaken every 6 h and stored in the laboratory without protection from ambient light. Remaining As concentrations were measured after precipitation and filtration (0.45 μm cellulose nitrate, Sartorius, Germany) of HFO particles. These experiments simulate As and Fe removal in an open precipitation tank, where, in contrast to the sand filters, Fe precipitates from solution without contact to sand surfaces.

Water Sampling and Sample Treatment. Two field campaigns were conducted for this study in September 2002 (first campaign) and in December 2002 (second campaign). Groundwater temperature and pH (SensIon1, Hach), dissolved oxygen and redox potential (MX300, Mettler-Toledo), and conductivity (EcoScan con5, EUTECH instruments) were recorded on-site. Samples for lab analysis were taken after stabilization of the oxygen and redox values (typically after 3−5 min of electropumping). Sampling position, description, total number, and treatment of samples, as well as analyzed parameters are summarized in Table SI 1 and further described in the SI. All samples were filtered (0.45 μm cellulose nitrate), filled into pre-washed (HCl and distilled water) PET bottles, and stored at 4 °C in the dark until analysis.

Hair Samples. A study comparing As concentrations in hair and consumed water was conducted in the Hanoi area in 2004 and 2005, two years after the sand filter investigations. Hair samples of about 2 g and water used for drinking were collected in two villages applying sand filters ($n = 102$), and in three villages where groundwater was not treated before consumption ($n = 112$). The procedure applied for hair analysis is described in detail elsewhere (*28*). Briefly, hair samples were probed into clean polyethylene bags, washed tediously with neutral detergent in the laboratory, and microwave digested in a 1:1 mixture of HNO_3 (65%) and H_2O_2 (30%).

Chemical Analysis and Quality Assurance. Concentrations of total Fe, Mn, Na, K, Mg, and Ca were quantified by atomic absorption spectroscopy (Shimadzu AA-6800, Kyoto, Japan). Total As in water and in hair was measured by the same AAS instrument coupled to a hydride generation device (HG-AAS). Silicate and phosphate concentrations were determined photometrically by the molybdate blue method. As(III) was determined in 10 samples acidified after filtration in the field to pH 4, using HG-AFS in the citrate mode as described by Hug and Leupin 2003 (*21*). The full database of measured concentrations and further details on chemical analysis including quality assurance are provided in the SI.

Model Calculations. Theoretical As removal values for coprecipitation were computed assuming partial oxidation of As(III) and competitive adsorption of As(III), As(V), silicate, and phosphate, to freshly precipitated HFO as described by Roberts et al. (*20*). Briefly, the competitive sorption of the anions is described as reversible equilibrium reactions with the sorption sites. The sorption reactions are formulated as overall equations representing several possible reactions for each species (mono- and bidentate binding and different protonation states). The model does not include a pH dependence, and the fitted constants are conditional sorption constants valid at the pH values and solution compositions employed (see Tables SI 2 and 3). Due to the pH dependence of the Fe(II) oxidation rates by oxygen, the calculations are not valid outside the 6.5−8.5 pH range, however, the investigated groundwaters were all in a range of pH 6.5−7.8 (average 7.0). With X representing the oxyanions of As(V), As(III), phosphate (P), and silicate (Si), the following conditions are met:

$$[\mathrm{X}]_{\mathrm{tot}} = [\equiv\mathrm{Fe{-}X}] + [\mathrm{X}]_{\mathrm{d}} \qquad (1)$$

$$[\equiv\mathrm{Fe{-}OH}]_0 = [\equiv\mathrm{Fe{-}OH}] + \sum[\equiv\mathrm{Fe{-}X}] \qquad (2)$$

where $[\equiv\mathrm{Fe{-}OH}]_0$, $[\equiv\mathrm{Fe{-}OH}]$, and $[\equiv\mathrm{Fe{-}X}]$ are the initial,

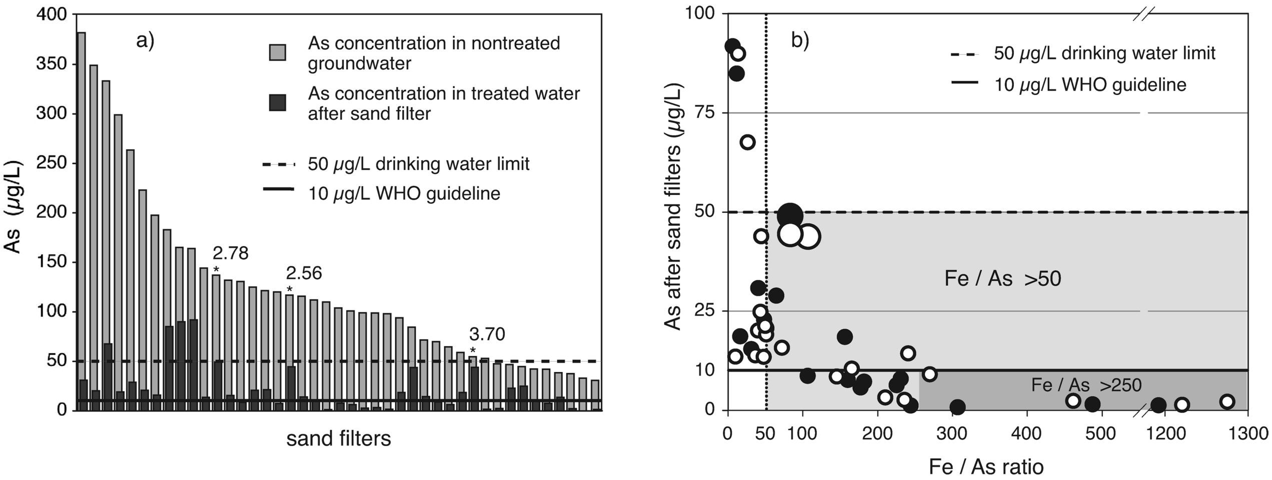

FIGURE 2. (a) Arsenic removal in household sand filters plotted in downward order of groundwater As concentration ($n = 43$). (b) Residual As levels in sand-filtered water as a function of the groundwater Fe/As ratio (mg/mg). Magnified dots indicate samples with phosphate concentrations >2.5 mg P/L. Black dots are results from September 2002; open circles are results from December 2002.

unoccupied, and occupied sorption sites and $[X]_{tot}$, $[\equiv Fe-X]$, and $[X]_d$ are the total, adsorbed, and dissolved concentrations of the oxyanions X. No correction for surface charge was made, as no solids with defined surfaces are formed during the coprecipitation. Oxidation of As(III) to As(V) was modeled by a fast reaction (equilibrium of the anions is reached during the oxidation of Fe(II) and formation of Fe(III) precipitates) following the oxidation of initially present Fe(II) to Fe(III). Equilibrium of dissolved and adsorbed species, $[X]_d$ and $[\equiv Fe-X]$), is hence expressed as follows:

$$[\equiv Fe-X] = [\equiv Fe]_0 \times \frac{(K_x[X]_d)}{(1 + K_{As(III)}[As(III)]_d + K_{As(V)}[As(V)]_d + K_P[P]_d + K_{Si}[Si]_d)} \tag{3}$$

where ≡Fe indicates adsorption sites of Fe(III) precipitates and K_x values are conditional adsorption coefficients. K_x and the calculation of available sorption sites $[\equiv Fe]_0$ from Fe concentrations were adopted from ref *20*. For the computational runs, raw groundwater concentrations of As, Fe, P, and Si measured in each sample were used to calculate theoretical As removal. Numerical modeling was performed three times for different ratios of As(III)/As(V). Roberts et al. (*20*) showed that the fraction of As(III)/As(tot) after coprecipitation is related to the amount of Fe(II) present in the groundwater, reaching values of 0.5 or 0.3 for Fe(II) concentrations of 5 or 20 mg/L, respectively.

Results and Discussion

Arsenic Removal by Sand Filters. Figure 2 depicts the results of sand filter arsenic removal in the studied households. The overall average As removal was 80% (median 89%, $n = 43$). Residual As levels below the WHO guideline of 10 μg/L were reached by 40% of the sand filters, and 90% were below 50 μg/L. The 11 (25%) sand filters removing less than 70% As can be attributed to low Fe (<3.7 mg/L) and/or high phosphate levels (>2.5 mg/L, indicated in Figure 2a) dissolved in groundwater. Iron was very efficiently removed to levels between <0.05 and 0.22 mg/L (data shown in SI).

The proportion at which dissolved Fe and As are present in groundwater is a suitable parameter for estimating the As removal potential (*10*). A common way to describe this parameter is the Fe/As (w/w) ratio, i.e., the Fe concentration in mg/L divided by the As concentration in mg/L. Figure 2b illustrates the residual As concentrations measured in the filtered water as a function of the corresponding Fe/As ratios determined in raw groundwater. It becomes evident that an Fe/As ratio of 50 or more was needed to reduce As concentrations to levels below 50 μg/L. To reach the WHO drinking water guideline of 10 μg/L, Fe/As ratios of >250 were required. The hampered As removal from groundwater containing more than 2.5 mg P/L phosphate is clearly visible in Figure 2b. Another study investigating hypochlorite oxidation of As(III) to As(V) followed by coprecipitation in groundwater of Bangladesh reported an Fe/As ratio of 40 to achieve As below 50 μg/L (*10*). Yet, it must be emphasized that no chemicals were added in our study, neither for the sand filter nor the coprecipitation experiments.

The observed residence time of water in the sand filters is very short (typically 2−3 min for the first flush). In samples taken directly from the outlet of four sand filters after 0, 4, 7, and 10 min (samples F in Table SI 1), As concentrations did not deviate more than 10% from those measured in the outlet of the storage tank. This indicates that As removal in the sand filter is indeed fast and can be considered “complete”, since no indication for further removal in the storage tank was evident. Sand filter effluent concentrations were largely identical after a two month period (December 2002), with an average and median variation of +4% or +3 μg/L (range −31 to +20%).

Comparison of Sand Filter Efficiency with Coprecipitation. Figure 3a shows the As removal efficiencies from coprecipitation experiments averaging 76%. Exposure to air for 72 h did not result in higher As removal than 24 h. It is apparent that the concentration of dissolved Fe is the key parameter governing the extent of As removal from groundwater. In samples with phosphate concentrations >2.5 mg P/L, As removal was hampered to a similar extent as with sand filters. These samples also contained relatively high silicate concentrations (26−32 mg Si/L) and silicate removal was only 2−7%. The overall silica removal averaged 14%, while rates for Fe and phosphate removal amounted to >99% and 90%, respectively. The removal of Mn (71%), Ca (39%), and Mg (4%) was also quantified (data shown in SI). An excellent correlation ($r^2 = 0.84$) between As and phosphate removal was observed (see Figure SI 3), but no correlation with arsenic could be found for any other parameter quantified, such as HCO_3^-, Cl^-, Mg, Ca, Mn, or DOC.

As illustrated in Figure 3b, the As removal rates by coprecipitation were very similar to those of groundwater treated by household sand filters. This indicates that (generally speaking) the same mechanism, namely oxidation of As and coprecipitation with initially dissolved Fe (and possibly

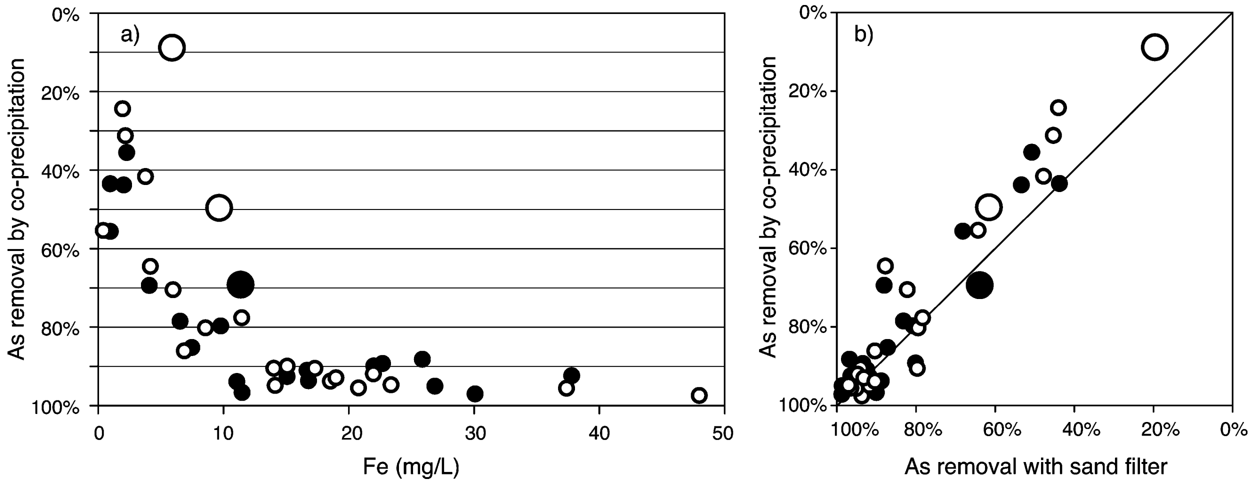

FIGURE 3. (a) Plot depicting As removal rates from coprecipitation experiments in PET bottles as a function of Fe dissolved in freshly pumped groundwater. Magnified symbols indicate phosphate concentrations >2.5 mg P/L. (b) Comparison of As removal of coprecipitation experiments with household sand filter systems. Black dots are results from 72 h air exposure, open circles are results from 24 h air exposure.

Mn), is responsible for the decrease of As concentrations in both systems. Filter specifications seem to play a minor role, since no relationship between As removal and filter volume, water throughput, or materials added to the sand by the owners (gravel, "black sand", or charcoal) was evident. Groundwater composition is thus the key factor determining the As removal capacity, and hence, adsorption to sand surfaces cannot efficiently remove As from groundwater without simultaneous precipitation of iron. However, in the cases where removal efficiencies of coprecipitation were only 10–70%, the sand filters performed somewhat better with 20–88% (+12% in average).

Compared to coprecipitation, the advantages of sand filters do not only arise from a slightly enhanced As removal capacity, but also from their practical benefits for the users to operate and manage them. The process of Fe and As removal is accelerated by the sand surface and completed within a few minutes. This allows treatment of reasonable quantities of water whenever needed, and filtered water can be stored for later use. In comparison, passive coprecipitation and sedimentation in settling tanks require several hours. Furthermore, the water treated by coprecipitation is still turbid after 1 day, resulting in a higher As intake if precipitates are not completely filtered-off.

Another advantage of sand filters is the better disposal possibility of As enriched waste (see considerations in SI). The old sand can be used for construction, or be stored in dedicated areas. Locations to be avoided for sand dumping are ponds which can become anoxic, as well as gardens, vegetable fields, and irrigated fields, because anoxic conditions at the plant roots (*29*) could lead to an accumulation of As in agricultural products.

Model Calculations. The results of the coprecipitation experiments were compared to calculations using the numerical model described above. Computational runs were conducted for various scenarios shown in Figure 4 and explained in the caption. The removal of As(tot) is significantly superior for 100% As(V) abundance in the groundwater than for 100% As(III). Figure 4a depicts this difference averaging at 33% (As(V) 89%, As(III) 56%) which is consistent with the logarithm of the conditional sorption constants log K_d of As(V) and As(III) to Fe(III)-precipitates being 5.7 and 3.7, respectively (*20*). The influence of P and Si shown in Figure 4b accounts for a 5–10% decrease in As removal. Only for the few samples containing high P levels, As removal was hampered by up to 35%. This decrease must almost entirely be attributed to phosphate (log K_d 5.9) since silicate (log K_d 2.8) has a 1000-times lower sorption affinity to Fe(III)-precipitates (*20*).

The model describes the correlation of As removal to Fe concentration well and confirms the hampered As removal if phosphate levels are high. Besides Fe, the abundance of As(V) is another dominating factor determining the extent of As removal. Quantification of As(III) conducted in 10 selected groundwaters revealed As(III)/As(tot) ratios in the range of 0.6–0.9 (av 0.75). Interestingly, the average removal determined in the coprecipitation experiments (76%) was higher than predicted by the model (65%) for an As(III)/As(tot) ratio of 0.75. Figure 4c reveals that the best match for the model and measurements is achieved assuming an initial As(III)/As(tot) ratio between 0.25 and 0.5. This would mean that 50–75% of As(tot) is As(V), but it is rather unlikely that this amount of As(V) is initially present in the anoxic groundwaters studied. Hence, we speculate that factor(s) present in the studied natural groundwaters (but not considered in the synthetic groundwater used to establish the model, see Experimental Section) are responsible for additional As(III) oxidation, such as (i) redox processes involving Mn (either in suspension as birnessite or on surfaces of Mn(IV) oxides) (*22–24*), (ii) the presence of As oxidizing microorganisms (*30*), and (iii) photoinduced As oxidation by dissolved organic matter (*31*). The fact that on average 71% of Mn was removed from the studied groundwaters (see SI) reveals that Mn precipitates must be present in both the sand filter and coprecipitation systems. Additionally, nucleation on colloids existing in natural groundwater might enhance precipitation of mineral phases after aeration.

Benefit for Human Health. Two years after studying the sand filters, a survey evaluating the As exposure of people drinking sand filter treated water or untreated groundwater was conducted. Among several human tissues, hair is widely used as a biomarker of exposure to heavy metals (*32*). Concentrations of As in short hair reflect the mean level in the human body during a previous period of 2–5 months. For people with no elevated As exposure, the levels in hair are generally 0.02–0.2 μg/g while concentrations clearly increase in hair of people consuming As-polluted water. The threshold in hair for an elevated risk to develop pathological skin problems is reported to be 1 μg/g As (*33*).

Raw groundwater, sand-filtered water, and hair of people were thus investigated in 5 Vietnamese villages, representing different levels of As poisoned groundwater. Sand filters were present in only two villages. Figure 5 provides evidence for

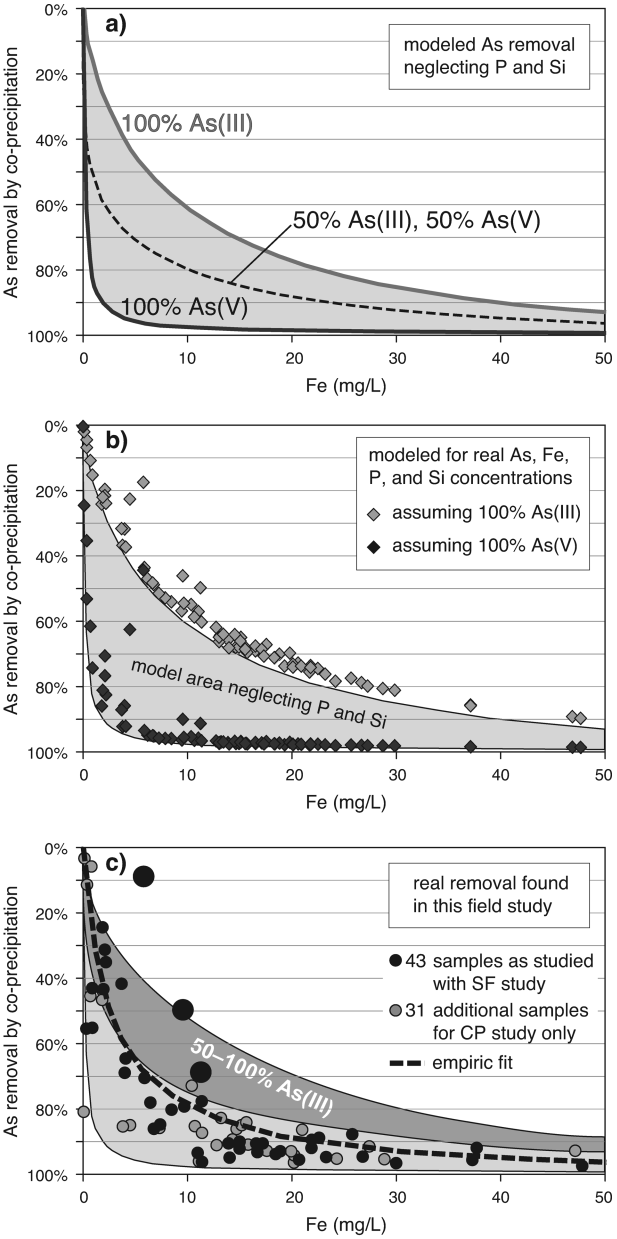

FIGURE 4. Model calculations of As removal and comparison with the results obtained with real coprecipitation experiments. (a) Modeled curves derived from real As(tot) and Fe(tot) concentrations measured in the groundwater samples of this study. Phosphate and silicate were neglected in this run. Assumed initial As(III) and As(V) abundance is indicated for the three scenarios. (b) Theoretical As removal calculated from As(tot), Fe(tot), P, and Si concentrations of the 74 samples used for the coprecipitation experiments. Scenarios were computed assuming 100% initial As(III) or As(V), respectively. The shaded area corresponds to the predicted range of Figure 4a. (c) Overlay of measured coprecipitation removal with the modeled range derived from Figure 4b, considering P and Si. The light and dark shaded areas represent the prediction for the abundance of 0−50% As(III) and 50−100% As(III), respectively. The best fit for measured As removal is indicated by the dotted line. Magnified symbols indicate samples with phosphate levels >2.5 mg P/L.

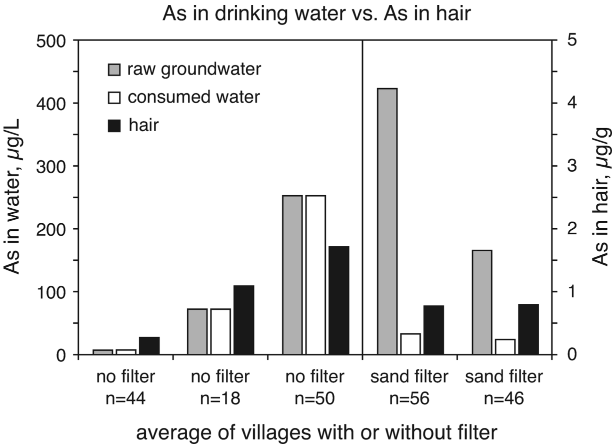

FIGURE 5. Health benefit from using a sand filter expressed by As concentration measured in human hair. Depicted are average levels of As in raw groundwater, consumed water, and hair grouped for people living in the same village.

a significantly lowered body burden in people drinking sand-filtered water. From highly polluted groundwater exhibiting average As levels of 422 ($n = 56$) and 165 μg/L ($n = 46$), the consumed water treated by sand filters contained only 33 and 24 μg/L, respectively. Accordingly, the average concentrations measured in hair of these people (0.8 μg/g) were lower than those in the village consuming untreated water with 72 μg/L As (1.09 μg/g). The demonstration of this health benefit is particularly important to convince local authorities to widely promote sand filters.

Another benefit is the simultaneous removal of Mn which can cause problems of the nervous system if people are chronically exposed to drinking water levels above 0.4 mg/L (WHO guideline). Manganese was removed in the sand filters studied from an initial average of 0.61 mg/L to a safe level of 0.11 mg/L.

Applicability of Sand Filters in Other Arsenic Affected Regions. Sand filters are of great benefit for the people in the studied area. They significantly reduce the level of human As exposure and besides remove Mn to safe levels. Health risks related to As ingestion were eliminated in 40% of the households (residual As <10 μg/L). In 90% of all cases, As levels were reduced to below 50 μg/L, thereby meeting the drinking water limit of many countries. Interpolation of the findings to other As-affected regions must be seen in close relation to the local groundwater composition. High As levels often co-occur with high Fe concentrations in the Red River Delta, which is favorable for As removal.

Based on the best fit for measured As removal shown in Figure 4c, the following empirical equation was derived to estimate the As removal efficiency from concentrations of Fe dissolved in groundwater:

$$\text{As removal (\%)} = 13.6 \times \ln(\text{Fe, mg/L}) + 45 \qquad (4)$$

Average and median As removal and corresponding residual As concentrations calculated with this empirical equation for different scenarios agree well with the measured values obtained in this study for Vietnam as shown in Table 1. The equation is rather conservative for Fe concentrations <1 mg/L which can be seen for the Vietnam scenario As >10 μg/L and Fe 0−1 mg/L. Using the comprehensive database available for groundwater composition in Bangladesh (1493 samples with As >10 μg/L (*34*)), the same calculation was conducted. Although Fe is 2−3 times lower in Bangladesh than in Vietnam, the As removal estimated for Bangladesh is very promising, particularly for the 84% of the samples with Fe levels >1 mg/L. The estimated average residual As concentrations is 39 μg/L with an even lower median of 25 μg/L, corresponding to removal efficiencies of 70 and 66%, respectively. More than 50% of the sand filters potentially applied in Bangladesh might even reach As levels below the estimated average, because corresponding median residual concentrations were always lower. Phosphate levels are somewhat higher in Bangladesh, but 69% of the groundwater samples contain 0−2 mg/L phosphate, a level at which no

TABLE 1. Estimated Sand Filter (SF) Arsenic Removal[a] for Bangladesh[b] as Well as Measured (meas) and Estimated (est) Values for Vietnam (Corresponding Median Concentrations of As, Fe, Mn, and P Are Provided in Table SI 3)

					As removal by SF				residual As after SF			
					average		median		average		median	
scenarios for groundwater composition	n	n %	As[c] av. µg/L	Fe[c] av. mg/L	meas.	est.	meas.	est.	meas. µg/L	est. µg/L	meas. µg/L	est. µg/L
Bangladesh ($n = 1493$)[b]												
As > 10[d], Fe 0−1[e]	235	16%	108	0.5		36%		36%		70		28
As > 10, Fe > 1	1258	84%	132	6.5		70%		66%		39		25
As > 10, PO_4 < 2[e], Fe > 1	1030	69%	127	7.0		71%		67%		36		22
As > 10, PO_4 < 2, Fe > 5	527	35%	134	11.0		78%		75%		30		17
As > 10, PO_4 < 2, Fe > 10	234	16%	110	15.0		82%		81%		20		10
Vietnam ($n = 43$)												
As > 10[d], Fe 0−1[e]	3	7%	87	0.7	59%	40%	65%	44%	41	52	19	33
As > 10, Fe > 1	40	93%	127	15.0	82%	82%	90%	82%	23	23	11	20
As > 10, PO4 < 2[e], Fe > 1	37	86%	129	15.5	85%	82%	91%	81%	19	23	9	19
As > 10, PO_4 < 2, Fe > 5	30	70%	133	18.5	91%	85%	92%	83%	12	20	8	17
As > 10, PO_4 < 2, Fe > 10	24	56%	132	21.3	92%	87%	94%	85%	11	18	6	15

[a] Calculated with eq 4. [b] Samples with As concentrations >10 µg/L from database published in ref *34*. [c] Measured average groundwater concentration. [d] µg/L. [e] mg/L.

significant influence on As removal was obvious in Vietnam. Manganese concentrations are slightly higher in Bangladesh (see Table SI 4).

The results obtained from this calculation indicate that sand filters could be a valuable option to mitigate As exposure and prevent long-term health problems of people living in Bangladesh, or other regions burdened by arsenic contamination from anoxic groundwater. Coprecipitation field trials conducted in Bangladesh by Roberts et al. (*20*) agreed with their model calculation that was also applied in this study, but resulted in lower As removal than predicted by our empiric estimation. These trials were conducted with water containing moderate Fe concentrations (5.5±2 mg/L) and high phosphate levels (1.95±0.27 mg/L P), while the average phosphate levels in Vietnam and Bangladesh are 1.5−2.2 times lower in groundwater containing >1 mg/L Fe. Thus, evaluation and testing of the As removal efficiency under local conditions in potential application areas is compulsory.

Arsenic removal with sand filters is not a technology meeting drinking water standards in all cases. For mitigation actions, short-term health risk reduction and legal constraints must be balanced. As a socially accepted groundwater treatment system in Vietnam, sand filters have advantages in their simplicity, low operation costs, and locally available construction material. They are operated without chemicals, can treat a reasonable amount of groundwater within a short time, and are easily replicated by the affected communities. The easily observable removal of iron from the pumped water makes the effect of a sand filter immediately recognizable even to people who are not aware of the arsenic problem. Thus, sand filters are a good option (at least until better mitigation options become available) for As mitigation in Vietnam with a high potential to be successfully applied in other arsenic affected regions.

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Supporting Information Available

Full database of measured parameters, additional information on the study area (Figure SI 1), experimental and modeling data (Tables SI 1−3), figures depicting correlations of As with P removal and Mn with Ca removal (Figures Si 4 and 5), full table established to estimate the sand filter arsenic removal for Bangladesh (Table SI 4). This material is available free of charge via the Internet at http://pubs.acs.org.

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Arsenic Removal from Groundwater by Household Sand Filters – Comparative Field Study, Model Calculations, and Health Benefits

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Key words
Arsenic removal, manganese removal, drinking water, sand filter, co-precipitation, hydrous ferric iron, exposure mitigation, Vietnam, Bangladesh

Contents

Experimental Section

Text SI 1:

Study Area. This field study was conducted in three villages located in the Red River Delta, namely Thuong Cat, Hoang Liet and Van Phuc (see Figure SI 1a). A total number of 43 SFs were investigated in households pumping groundwater with elevated arsenic levels CP experiments were conducted with the same 43 groundwaters as well as with water collected from 31 additional tubewells. With highly variable concentrations of As (10–382 μg/L), Fe (<0.1–48 mg/L), P (<0.01–3.7 mg/L), and Mn (0.05–3.3 mg/L), the investigated wells represent a broad and representative range of groundwater composition (see Figure SI 1b and database of Supporting Information). Tube well depths at the investigated sites were in a range of 10–100 m (average and median 38 m). Groundwater is predominantly extracted from the quaternary sediment layers that are divided in a Holocene aquifer (10–45 m) with fine clay and sand, and a Pleistocene aquifer (30–70 m) containing coarse material. More information on geology and climate is documented in *(1,2)*.

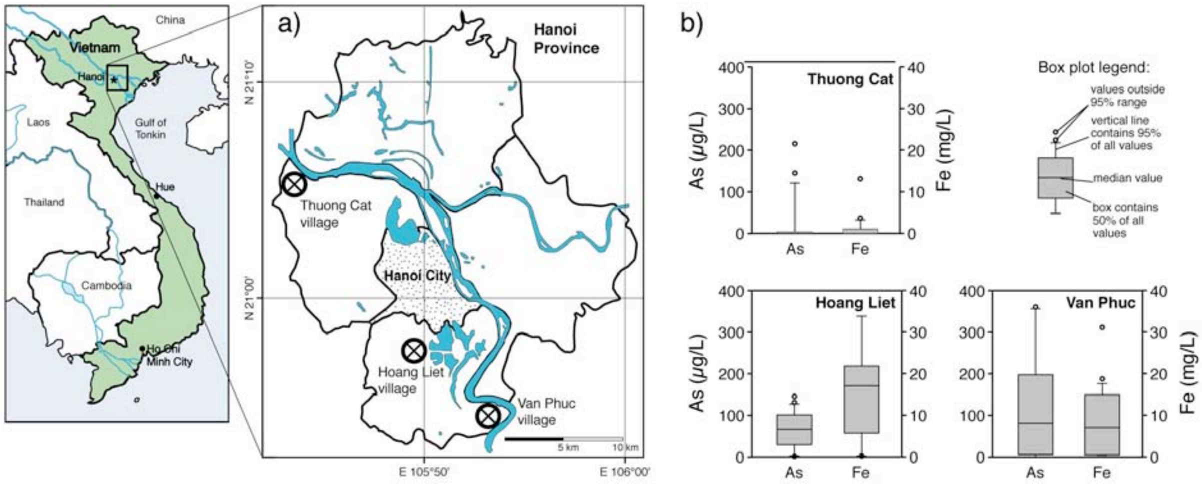

FIGURE SI 1. a) Map of Vietnam and the Hanoi area pinpointing the villages where sand filters were evaluated. **b)** Box plots depicting the broad variability of iron, phosphate, and arsenic concentrations in the groundwaters included in this study.

Text SI 2:

Measures to Prevent Microbial Activity in Sand Filters. Similar to the microbial activity in aquifers, which eventually leads to the release of arsenic into the groundwater, bacteria can also influence the processes of arsenic removal in sand filters. Since bacteria are ubiquitous in the environment, colonisation of a sand filter by microorganisms is only a matter of time if the living conditions are favourable. The organic material, on which bacteria feed, can either get into the filter as dissolved organic matter (DOM) or fall into the tank as dirt, dust, leaves, dead insects, etc. Degradation of organic material by microorganisms depletes the oxygen, thereby hampering the arsenic removal efficiency. Measures to inhibit microbial activity in the sand filter tank are therefore important and include: i) complete drainage of the water from the filter tank after each batch of treatment, which is achieved by placing the water outlet at the very bottom of the filter (see Figure 5); ii) covering the sand compartment with a lid to prevent the influx of solid organic material (e.g., leafs or insects); iii) regular exchange of the filter sand; and iv) removal of microbial colonies by thorough cleaning and brushing of the filter walls every time the sand is exchanged.

Text SI 3:

Water Sampling and Sample Treatment. Two field campaigns were conducted for this study in September (1st campaign) and in December 2002 (2nd campaign). Groundwater temperature and pH (SensIon1, Hach), dissolved oxygen and redox potential (MX300, Mettler-Toledo), and conductivity (EcoScan con5, EUTECH instruments) were recorded on-site. Samples for lab analysis were taken after stabilization of the oxygen and redox values (typically after 3–5 minutes of pumping). Sampling position, description, total number and treatment of samples, as well as analyzed parameters are summarized in Table SI 1. Samples B and C were filtered (0.45 μm cellulose nitrate) on-site before acidification. Samples B, D and E were acidified with 1% HNO_3 to a pH <2 in order to prevent precipitation of solid phases. A subset of samples was acidified to pH 4 for As(III) analysis. Samples D were filled in 500 mL PET bottles for CP experiments, and the open bottles exposed to air for 72 hours (1st campaign) or 24 hours (2nd campaign). The precipitates from samples D were filtered-off (0.45 μm) and the water acidified to pH <2. All samples were filled into pre-washed (HCl and distilled water) PET bottles, and stored at 4 °C in the dark until analysis.

TABLE SI 1. Sampling and treatment of samples

code	sampling position[a]	sample description	volume	treatment	preservation	parameters	no. of samples
A	① tube well	groundwater not acidified	500 mL	no	no	HCO3-, Cl-, SO42-, DOC	74
B	① tube well	groundwater acidified	200 mL	filtration	pH <2	As_{tot}, Fe, Mn, Na, K, Mg, Ca, P, Si	74
C	① tube well	groundwater for As(III) analysis	50 mL	filtration	pH 4	As(III)	10
D	① tube well	groundwater for co-precipitation	200 mL	aeration	no	As_{tot} (Fe, Mn, Mg, Ca, P, Si) [b]	74 (31–52) [b]
E	② storage tank	sand-filtered water	200 mL	no	pH <2	As_{tot}, P, Si	43
F	③ filter outlet	sand-filtered water	200 mL	no	pH <2	As_{tot}, P, Si	16[c]

[a] The positions are indicated Figure 1. [b] Not determined in all CP samples . [c] Four consecutive samples collected from each of four selected filters.

Text SI 4:

Chemical Analysis and Quality Assurance. All chemicals used for sample preservation and analysis were purchased from Fluka (Switzerland) and Merck (Switzerland) in the highest available quality. Concentrations of total Fe, Mn, Na, K, Mg, and Ca were measured by atomic absorption spectroscopy (Shimadzu AA-6800, Kyoto, Japan). Total As in water and in hair was measured by the same AAS instrument coupled to a hydride generation device (HG-AAS). Silicate and phosphate concentrations were determined photometrically by the molybdate blue method. Metals, Si and P in raw groundwater were all analyzed in the acidified water samples. As(III) was determined in 10 samples acidified after filtration (0.45 μm cellulose nitrate) in the field to pH 4, using HG-AFS in the citrate mode as described by

Hug and Leupin 2003 *(3)*. DOC was measured by thermal-catalytic oxidation (highTOCII, Elementar, Germany). Arsenic removal was only determined for households using groundwater with initial As concentrations >10 μg/L. The full database of measured groundwater constituents is also available as Supporting Information.

The quality of chemical and instrumental analysis was assured by parallel measurements at CETASD (Vietnam) and EAWAG (Switzerland). Linear regression of EAWAG and CETASD results produced the following coefficients of determination (r^2, n=74): As (0.95), Fe (0.97), Mn (0.99,), Ca (0.99), Mg (0.98), P (0.97), and, Si (0.96). To further ensure the quality of the measurements, recoveries were determined before every sample series in certified water samples (SPS-SW1, Merck VI standard). Recoveries were in the range of 95-106% (As) and 93-104% (Fe, Mn). As determined in certified reference hair (NCS ZC 81002) was less than 2% deviating from the certified value of 0.59 μg/g. DOC concentrations were only determined at EAWAG.

Text SI 5:

Considerations for Disposal of used Sand. Any arsenic pumped with groundwater eventually ends up in the terrestrial environment, regardless whether it is concentrated on sand or co-precipitation sludge, or consumed with drinking water. The immediate surrounding of an openly running tubewell as well as its sewage must therefore be considered a pollution point source. Sludge from household co-precipitation tanks is usually disposed and discarded in the backyard, posing a threat to vegetation and people. In contrast, sand filters concentrate As over a long time period on sand that is replaced and more mindfully handled than co-precipitation sludge. However, in the worst case assuming that 100 kg of sand is used to treat 30.000 L of groundwater containing 500 μg/L arsenic, the As levels in sand can reach 150 mg/kg. It is therefore important to handle used sand with care. Arsenic does not leach in oxic environments and ambient pH. The old sand can thus be used for construction, or be stored in dedicated areas. The disposal into flowing water of large rivers is also discussed, but the long-term impact of doing so needs to be thoroughly assessed. Locations to be avoided for sand dumping are ponds which can become anoxic, as well as gardens, vegetable fields and irrigated fields, because anoxic conditions at the plant roots *(4)* could lead to an accumulation of As in agricultural products.

Model Calculations.

Table SI 2. Composition of artificial groundwater used for co-precipitation experiments *(5)*

As(V)	500	µg/L
As(III)	500	µg/L
As(III+V)	250 + 250	µg/L
Fe(II)	1–50	mg/L
PO4	0–3	mg/L
SiO4	0–30	mg/L
pH	7.0	

Table SI 3. Fitted sorption constants (K_d's) published in *(5)* and used in this study for the modeling of theoretical arsenic removal by co-precipitation

	log K_d
As(V)	5.7 ± 0.25
As(III)	3.7 ± 0.15
P	5.9 ± 0.15
Si	2.8 ± 0.10

Results and Discussion

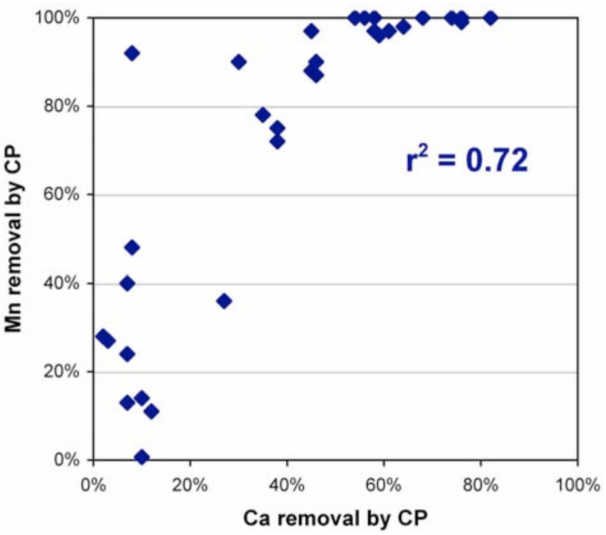

Figure SI 2. Correlation between Mn and Ca removal (r^2=0.72), indicating that Mn might have co-precipitated with Ca carbonate.

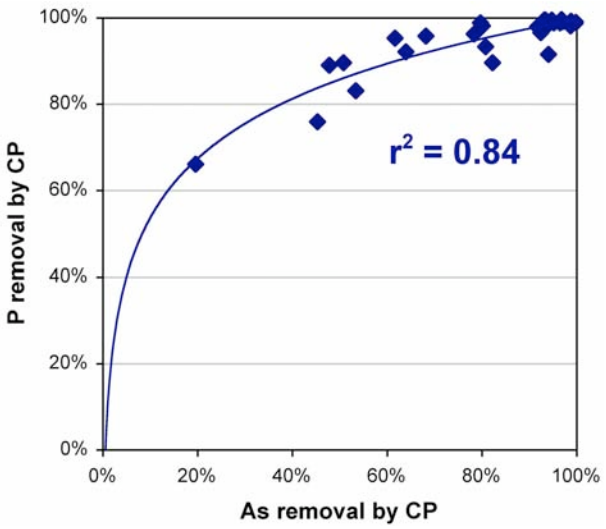

Figure SI 2. Correlation between arsenic and phosphate removal (r^2=0.84, logarithmic). Groundwaters exhibiting less than 0.25 mg phosphate-P per liter were neglected because corresponding concentrations determined after phosphate removal were mostly below detection limit, resulting in high uncertainties of removal rates.

TABLE SI 4. Estimated SF arsenic removal[a] for Bangladesh[b] as well as measured (meas.) and estimated (est.) values for Vietnam, including median and average concentrations of As, Fe, Mn, and P.

scenarios for groundwater composition			As removal by SF (%)				residual As after SF (µg/L)				Fe / As ratio		As (µg/L)		Fe (mg/L)		PO4-P (mg/L)		Mn (mg/L)	
			average		median		average		median											
	n	n %	meas.	*est*[a]	meas.	*est.*[a]	meas.	*est.*[a]	meas.	*est.*[a]	av.	med.	av.	med.	av.	med.	av.	med.	av.	med.
Bangladesh (n=1493)																				
As >10[d], Fe 0–1[e]	235	16%		*36%*		*36%*		*70*		*28*	5	11	108	44	0.5	0.5	1.42	0.50	0.53	0.26
As >10, Fe >1	1258	84%		*70%*		*66%*		*39*		*25*	49	64	132	72	6.5	4.6	1.29	1.00	0.63	0.32
As >10, PO4 <2[e], Fe >1	1030	69%		*71%*		*67%*		*36*		*22*	55	75	127	69	7.0	5.2	0.85	0.80	0.74	0.45
As >10, PO4 <2, Fe >5	527	35%		*78%*		*75%*		*30*		*17*	82	130	134	70	11.0	9.1	0.94	0.90	0.82	0.52
As >10, PO4 <2, Fe >10	234	16%		*82%*		*81%*		*20*		*10*	136	269	110	52	15.0	14.0	0.97	0.90	1.00	0.67
Vietnam (n=43)																				
As >10[d], Fe 0–1[e]	3	7%	59%	*40%*	65%	*44%*	41	*52*	19	*33*	8	15	87	59	0.7	0.9	0.36		0.48	
As >10, Fe >1	40	93%	82%	*82%*	90%	*82%*	23	*23*	11	*20*	118	139	127	107	15.0	14.9	0.86	0.66	0.54	0.37
As >10, PO4 <2[e], Fe >1	37	86%	85%	*82%*	91%	*81%*	19	*23*	9	*19*	120	140	129	104	15.5	14.6	0.68	0.62	0.58	0.40
As >10, PO4 <2, Fe >5	30	70%	91%	*85%*	92%	*83%*	12	*20*	8	*17*	139	162	133	103	18.5	16.7	0.75	0.73	0.57	0.40
As >10, PO4 <2, Fe >10	24	56%	92%	*87%*	94%	*85%*	11	*18*	6	*15*	161	187	132	100	21.3	18.7	0.86	0.92	0.41	0.39

[a] Calculated with equation (4). [b] Samples with As concentrations >10 µg/L from database published in *(6)*. [c] Measured average and median groundwater concentration. [d] µg/L. [e] mg/L.

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