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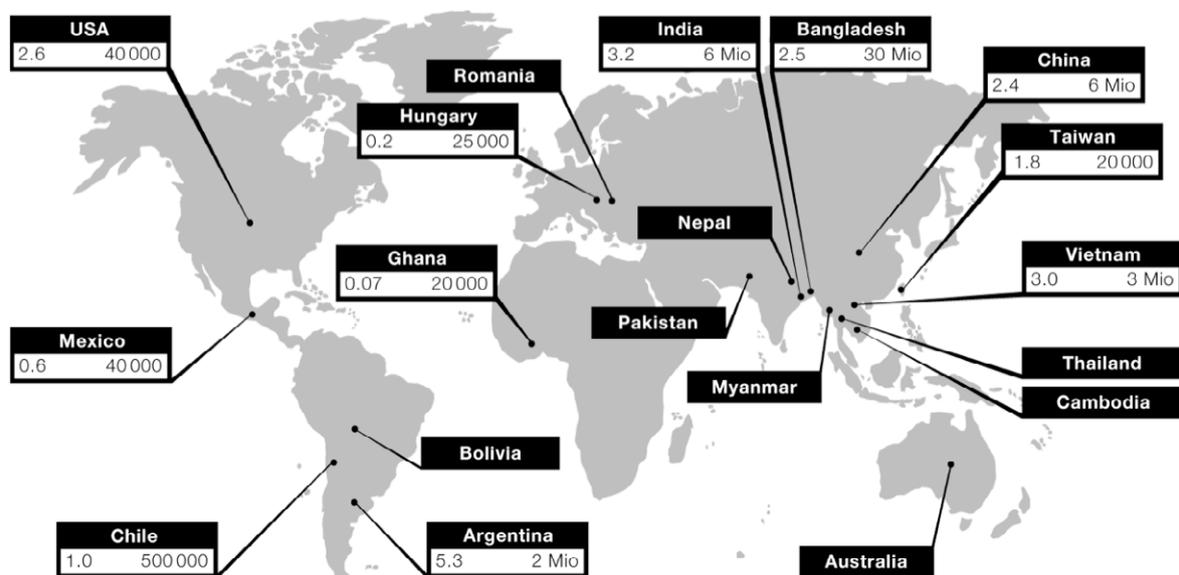
Figure 1. Countries affected by natural (geogenic) arsenic contamination of groundwater. The numbers below the country name list, (left) the highest reported arsenic concentration in mg/L, and (right) the estimated number of affected people (data from SMEDLEY & KINNIBURGH 2002).

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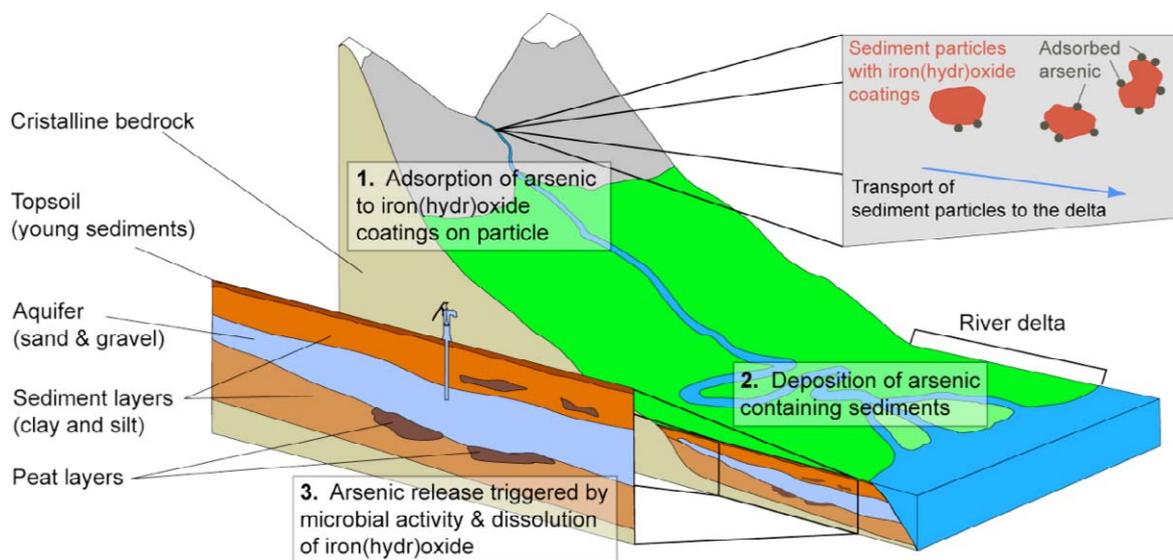
Figure 2. Simplified illustration of the widely accepted theory on the origin of arsenic in groundwater of river deltas.

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$_2$AsO$_4^-$). 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 μg/L levels.
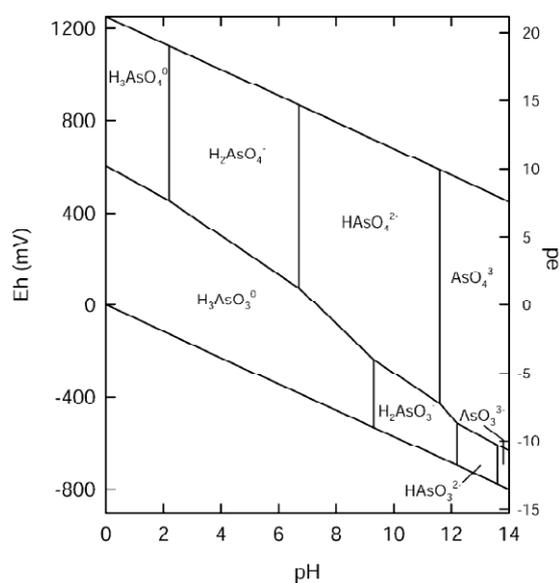
Figure 3. Eh-pH diagram for aqueous arsenic species in the system As–O$_2$–H$_2$O at 25 °C and 1 bar total pressure (SMEDLEY & KINNIBURGH 2002).

Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Under oxidising conditions, the single negatively charged arsenate species H$_2$AsO$_4^-$ 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.

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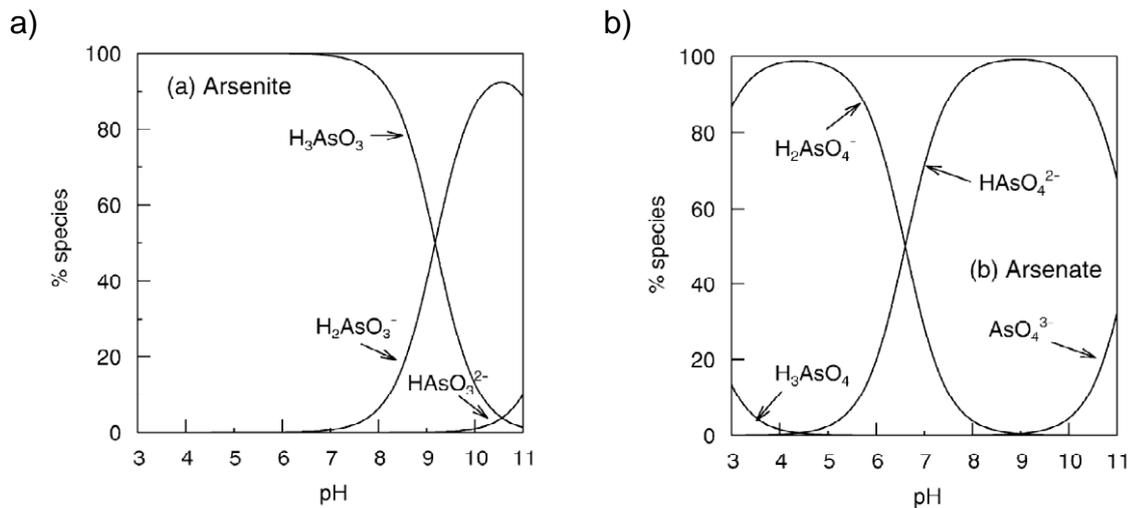
Figure 4. a) Arsenite, and b) arsenate speciation as a function of pH at an ionic strength of about 0.01 M (SMEDLEY & KINNIBURGH 2002).

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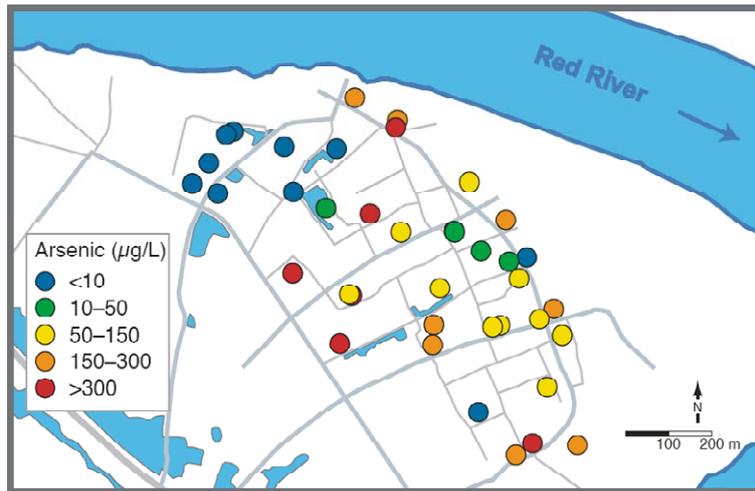
Figure 6. Spatial variability of arsenic concentrations in a small village of the Red River Delta. This example shows that low and high arsenic levels of <10 µg/L and >300 µg /L, respectively, can be just a few meters apart.

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.
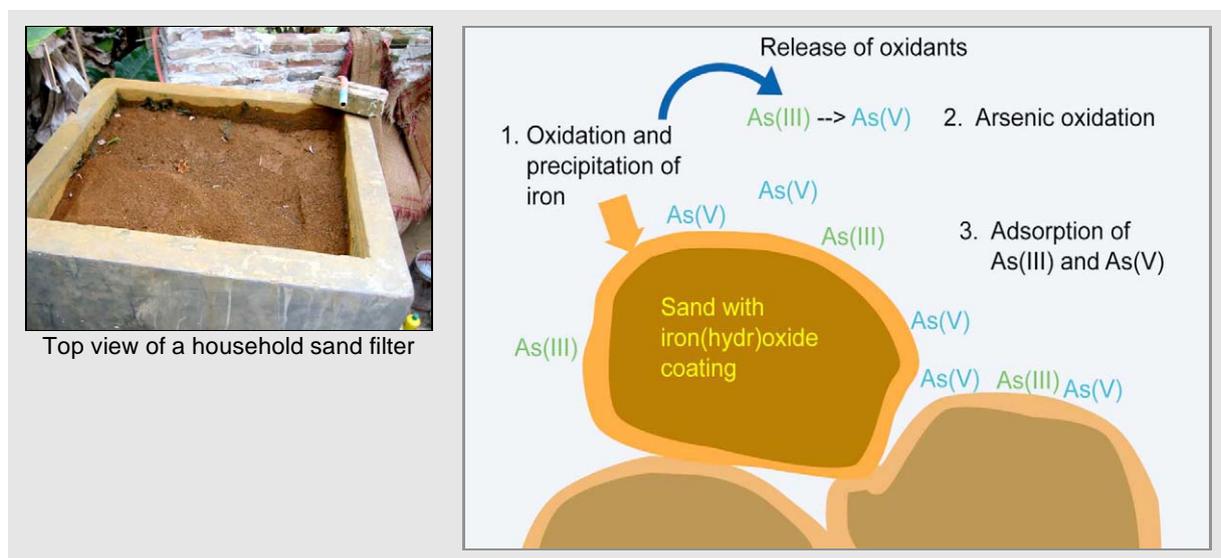

Figure 7. Illustration of arsenic oxidation and adsorption to iron(hydr)oxide coatings on sand grains.

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 $\mu g/g$). 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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