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Magnitude of arsenic pollution in the Mekong and Red River Deltas — Cambodia and Vietnam

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Abstract

Large alluvial deltas of the Mekong River in southern Vietnam and Cambodia and the Red River in northern Vietnam have groundwaters that are exploited for drinking water by private tube-wells, which are of increasing demand since the mid-1990s. This paper presents an overview of groundwater arsenic pollution in the Mekong delta: arsenic concentrations ranged from 1–1610 μg/L in Cambodia (average 217 μg/L) and 1–845 μg/L in southern Vietnam (average 39 μg/L), respectively. It also evaluates the situation in Red River delta where groundwater arsenic concentrations vary from 1–3050 μg/L (average 159 μg/L). In addition to rural areas, the drinking water supply of the city of Hanoi has elevated arsenic concentrations. The sediments of 12–40 m deep cores from the Red River delta contain arsenic levels of 2–33 μg/g (average 7 μg/g, dry weight) and show a remarkable correlation with sediment-bound iron. In all three areas, the groundwater arsenic pollution seem to be of natural origin and caused by reductive dissolution of arsenic-bearing iron phases buried in aquifers. The population at risk of chronic arsenic poisoning is estimated to be 10 million in the Red River delta and 0.5–1 million in the Mekong delta. A subset of hair samples collected in Vietnam and Cambodia from residents drinking groundwater with arsenic levels >50 μg/L have a significantly higher arsenic content than control groups (<50 μg/L). Few cases of arsenic related health problems are recognized in the study areas compared to Bangladesh and West Bengal. This difference probably relates to arsenic contaminated tube-well water only being used substantially over the past 7 to 10 years in Vietnam and Cambodia. Because symptoms of chronic arsenic poisoning usually take more than 10 years to develop, the number of future arsenic related ailments in Cambodia and Vietnam is likely to increase. Early mitigation measures should be a high priority.

Keywords: Arsenic groundwater pollution; Phnom Penh; Hanoi; Health risk; Hair; Urine; Reductive dissolution; Iron; Manganese; Ammonium; DOC; Kandal province; An Giang province; Dong Thap province; Bassac River

1. Introduction

In some countries, arsenic is the most important chemical pollutant in groundwater and drinking water. The Bengal delta region is particularly affected as an estimated 35 million people have been drinking arsenic-

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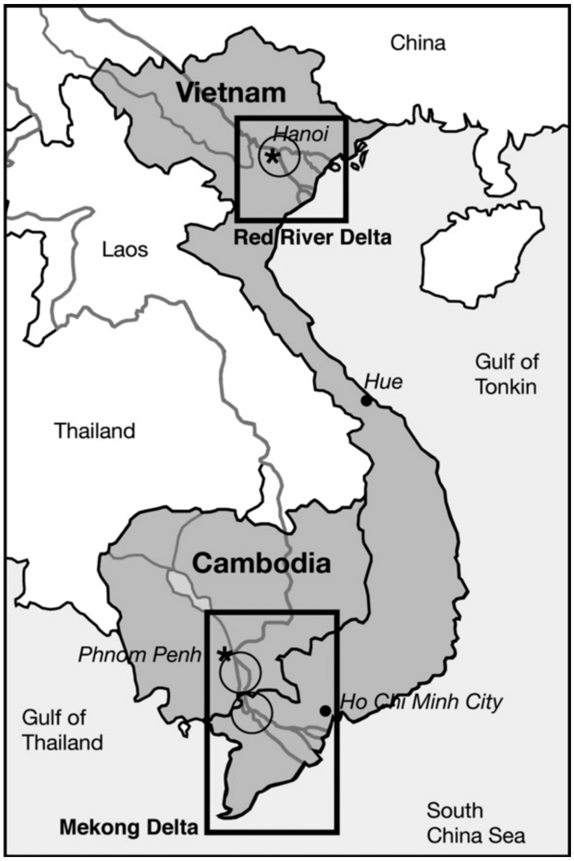

Fig. 1. Map of Cambodia and Vietnam indicating the Mekong and Red River deltas. The studied areas are encircled.

rich water for the past 20–30 years (Smedley and Kinniburgh, 2002). Examination for arsenical dermatologic symptoms in 29 thousand people showed that 15% had skin lesions (Chowdhury et al., 2000). Regions with arsenic-rich drinking water can be found around the globe (Smedley and Kinniburgh, 2002). Natural contamination of groundwater by arsenic is also an emerging issue in some countries of Southeast Asia, including Vietnam, Thailand, Cambodia, and Myanmar (Berg et al., 2001; Buschmann et al., submitted for publication; Polya et al., 2005). Vulnerable areas for arsenic contamination are typically young Quaternary deltaic and alluvial sediments comprising highly reducing aquifers.

Chronic levels of 50 μg arsenic/L can cause health problems after 10–15 years of exposure (Smith et al., 2000). The development of symptoms of chronic arsenic poisoning (arsenicosis) is strongly dependent on exposure time and the resulting accumulation in the body. The various stages of arsenicosis are characterized by skin pigmentation, keratosis, skin cancer, effects on the cardiovascular and nervous system, and increased risk of lung, kidney and bladder cancer. The European Union allows a maximum arsenic concentration of 10 μg/L in drinking water, and the World Health Organisation (WHO) recommends the same value. In contrast, developing countries are struggling to establish and implement measures to reach standards of 50 μg/L in arsenic-affected areas.

Drinking water supplies in Cambodia and Vietnam are dependent on groundwater resources (Berg et al., 2001, 2006; Feldman and Rosenboom, 2001; Fredericks, 2004). The Mekong and the Red River deltas are the most productive agricultural regions of South East Asia (see Fig. 1). Both deltas have young sedimentary deposits of Holocene and Pleistocene age. The groundwaters are usually strongly reducing with high concentrations of iron, manganese, and (in some areas) ammonium. The Mekong and the Red River deltas are currently exploited for drinking water supply using installations of various sizes. In the last 7–10 years a rapidly growing rural population has stopped using surface water or water from shallow dug wells because they are prone to contamination by harmful bacteria. Instead, it has become popular to pump groundwater using individual private tube-wells, which is relatively free of pathogens.

The Vietnamese capital Hanoi is situated in the upper part of the 11,000 km^2 Red River delta, which is inhabited by 11 million people and is one of the most populous areas in the world. The exploitation of groundwater in the city of Hanoi began more than 90 years ago and has since been expanded several times (Berg et al., 2001). Today, ten major well-fields are operated by water treatment facilities, which collectively process 650,000 m^3/day. Due to naturally anoxic conditions in the aquifers, the groundwaters contain large amounts of iron and manganese that are removed in the Hanoi drinking water plants by aeration and sand filtration (Duong et al., 2003). The urban water treatment plants exclusively exploit the lower aquifers in 30–70 m depth, whereas private tube-wells predominantly pump groundwater from the upper aquifers at 12–45 m (Hydrogeological Division II, 2000).

Based on geological analogies to the Ganges delta, elevated arsenic concentrations in the aquifers of the Red River basin were expected (Berg et al., 2001). A first screening by us in 1998 confirmed this assumption and we studied the extent of arsenic contamination in a comprehensive survey from 1999 to 2000. The upper and lower Quaternary aquifers were investigated by analysing groundwaters from small-scale tube-wells and pumped by the Hanoi drinking water plants.

Groundwater arsenic contamination was identified in the Cambodian Mekong delta area in 2000 (Feldman and Rosenboom, 2001), and has since been investigated and addressed through close collaboration of local authorities and NGOs. The first international paper on arsenic groundwater contamination in Cambodia was published by Polya et al. (2005).

In this paper, the arsenic levels in groundwater of the Mekong delta are presented including data for the Vietnamese delta part, which is reported for the first time. In addition to an overview of the magnitude of arsenic poisoning in this region, the limited information available in the international literature on the geology and genesis of the Mekong and Red River delta is summarised.

2. Materials and methods

2.1. Sample collection

Based on a projected density of one sample per 10 km^2, private tube-wells were randomly sampled over areas of 2000 km^2 in Cambodia, 2000 km^2 in Southern Vietnam, and 700 km^2 in the Red River delta. Groundwater was collected at the tube by hand or electrical pumping. Samples were taken after 10 min pumping, when the oxygen concentration in the water reached a stable value, which was measured online by using a dissolved oxygen electrode (PX 3000, Mettler-Toledo). Redox potential, pH, oxygen levels and conductivity were recorded on-site. Water was 0.45 μm filtered and filled in two 500 mL polypropylene bottles. One bottle for the analysis of metals, ammonium and phosphate was acidified with approximately 1 mL of concentrated nitric acid to reach a $pH<2$. Anions and DOC were determined in the non-acidified sample. Freshly-drilled sediment cores were sampled on-site and 20 g wet sediment 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.

2.2. Chemical analysis

Arsenic concentrations in groundwater samples collected in Cambodia and Southern Vietnam were analysed in parallel by atomic fluorescence spectroscopy (AFS) and inductively-coupled-plasma mass spectrometry ICP-MS by the Swiss Federal Institute of Aquatic Science and Technology (Eawag), as well as by atomic absorption spectroscopy (AAS) at the Centre for Environmental Technology and Sustainable Development (CETASD). Iron and manganese concentrations were measured by ICP-MS; ammonium and phosphate by photometry; nitrate, sulphate and chloride by ion chromatography; alkalinity by titration; and dissolved organic carbon (DOC) by a CHN analyser. Groundwaters from the Red River delta were analysed for total arsenic at CETASD using AAS. For quality assurance of these arsenic measurements, 20% of the samples were sent to Switzerland and analysed by Eawag and an independent contract laboratory. The results among the laboratories agreed within 20% deviation.

Sediment samples were freeze-dried, and digested with concentrated nitric acid and hydrogen peroxide in a microwave oven. Subsequently, total arsenic was determined by AFS and metals by ICP-MS. The results obtained from analysis of sediment digests were confirmed by semi-quantitative wavelength dispersive X-ray fluorescence (WD-XRF) carried out at the Swiss Federal Laboratories for Material Testing and Research. Sediment-bound natural organic matter was measured with a CHN analyser by thermal oxidation from groundwater and sediments.

Hair samples of about 2 g were collected from residents living in villages selected for elevated and low groundwater arsenic levels. The hair samples were sealed in polypropylene bags and later tediously washed in the laboratory by neutral detergent and deionised water. The hair was digested with concentrated nitric acid and hydrogen peroxide in a microwave oven (same as for sediments) and analysed by AAS. Certified reference material (hair NCSZC 81002) was used to validate the digestion and analysis procedure. The results from 9 tests (0.58 ± 0.03 mg/kg) were in excellent agreement with the certified value (0.59 ± 0.07 mg/kg).

3. Results and discussion

3.1. Mekong delta: Cambodia and Southern Vietnam

The Mekong delta is located in southern Vietnam and neighbouring Cambodia between 8°30′ to 11°30′ N and 104°40′ to 106°50′ E and is confined by the South China Sea in the southeast, the Gulf of Thailand in the west, the Vamcodong River in the northeast and a well-defined Late Pleistocene terrace to the north (Nguyen et al., 2000). The Mekong River is 4300 km long and has a catchment area of 520,000 km^2. It originates in the Tibetan Plateau, and flows through China, Myanmar, Laos, Thailand, Cambodia and Vietnam. Close to Phnom Penh (Cambodia) the Mekong divides into two branches, the Mekong to the east and the Bassac River to the south. The depositional environment in Phnom Penh is largely limited to a linear trending valley that is fault controlled along the Bassac and limited by Pleistocene uplands adjacent to the Mekong. The Mekong River in Cambodia is a broad, mature river that becomes tidal upstream to the northeast of Phnom Penh, near Kampong Cham (Polya et al., 2005). The delta plain has an area of about 62,000 km^2, with 10,000 km^2 belonging to Cambodia and the rest located in southern

Vietnam. The climate is monsoonal humid and tropical, with average temperatures of 27–30 °C. The rainy season lasts from April to November (Pham et al., 2002). The mean annual precipitation ranges from 2400 mm in the western parts to some 1500 mm in the central and eastern parts. An estimated 2.4 million Cambodians and 17 million Vietnamese live on the delta.

The modern delta formed during the last 6–10,000 years (Holocene) and large areas are tide-dominated areas. The detailed topography of the delta plain indicates two zonal parts of the delta (Nguyen et al., 2000). The Holocene sediment infilled a dissected terrain formed by the 120 m sea level fall and rise at the end of the Pleistocene. The inner part is characterized by river-dominated features, while a well-developed beach ridge system characterizes the outer part of the delta plain along the coast (Nguyen et al., 2000). The mean annual water discharge of the Mekong is 15,000 m^3/s at Phnom Penh and can reach >50,000 m^3/s in the rainy season. Great volumes of sediments (160 million tons/year, mostly composed of silt, clay and sand) are transported to the South China Sea and the delta consists almost entirely of young alluvial soils of marine and fluvial origin (Nguyen et al., 2000). Groundwater varies complexly with depth and is known only in a few areas (Pham et al., 2002). About 60% of the subaerial delta forms low flood plains (<2 m above sea-level) with actual or potential acid sulphate soils (Ollson and Palmgreen, 2001).

3.1.1. Cambodia

3.1.1.1. Reconnaissance studies. The Government of Cambodia, with support from WHO, conducted a survey of drinking water quality of water resources located throughout the country in 2000 (Feldman and Rosenboom, 2001). The survey, which was conducted in 13 of Cambodia's most densely populated provinces, focused on testing the chemical quality of urban and rural water supplies. A total of 88 groundwater samples were collected and sent to an Australian laboratory for the determination of 46 individual pesticides and 21 trace elements including arsenic. Pesticides were very rarely detected, but 9% of the samples contained arsenic contents above 10 μg/L. A follow-up study conducted with 18 groundwater samples originating from the area where the Bassac River branches off the Mekong (Kien Svaay and Ta Khman districts, Kandal province) revealed arsenic concentrations of 100–500 μg/L in hand-pumped tube-wells (Feldman and Rosenboom, 2001).

As a consequence, about 5000 tube-wells were tested by 25 NGOs in 2002 and 2003 using arsenic field-testing kits provided by UNICEF (Halperin, 2003). According to these studies, 20% of the wells located within risk zones had arsenic levels above 50 μg/L and 50% were above 10 μg/L. A large proportion of these test-kit measurements were carried-out by RDIC in the Northern part of the Kandal province, where several readings exceeded 500 μg/L.

UNICEF, at a water and sanitation donors' meeting held in Phnom Penh on June 2003 stated that arsenic concentrations above 50 μg/L have been identified in Cambodian groundwater (Fredericks, 2004). The groundwater studies conducted with field test-kits by UNICEF, RDIC and others in cooperation with Cambodian authorities showed that high concentrations of arsenic are most often associated with the floodplains of the Mekong, Bassac, and Tonle Sap Rivers. Arsenic concentrations in the range of 10–50 μg/L were also found in unconsolidated sediments along the Mekong upstream Phnom Penh.

Fredericks (2004) combined this initial data with geological mapping of unconsolidated sediments to produce an arsenic risk map for Cambodia presented in Fig. 2. This map is based on subsurface geology intersected by 17 deep boreholes. The drilling identified Holocene, Pleistocene, and Plio–Pleistocene sediments overlying basalt. Groundwater concentrations above 50 μg/L were only identified in young (Holocene) lowland alluvial deposits. The increased risk of arsenic polluted groundwater in Holocene alluvial lowland sediments along the Mekong River and its tributaries was verified. The floodplains surrounding the Tonle Sap lake were determined to have low risk in both Pleistocene and Holocene sediments, and, very low risk in basement rocks and basalt (Fig. 2). This risk map was largely confirmed by a survey investigating arsenic levels in groundwater originating from various parts of Cambodia (Polya et al., 2005).

3.1.1.2. Own survey of arsenic and other species in Cambodia groundwater. Between April and December 2004, Eawag and RDI conducted an in-depth groundwater survey covering the Kandal province and bordering areas. This province is largely situated on the floodplain between the Bassac and Mekong Rivers stretching from Phnom Penh to the Vietnam border in the south (see Fig. 2). For this study, a set of more than 200 samples was randomly collected from household tube-wells at a sampling density of approximately 1 sample per 10 km^2. Arsenic concentrations ranged from 1–1610 μg/L (average 217 μg/L, n=207). Arsenic levels are particularly high in the Kandal province (average 250 μg/L, n=175), while provinces bordering Kandal to the east and west are much less affected (average 12 μg/L, n=32). The 14 parameters analysed (see Table 1) indicate

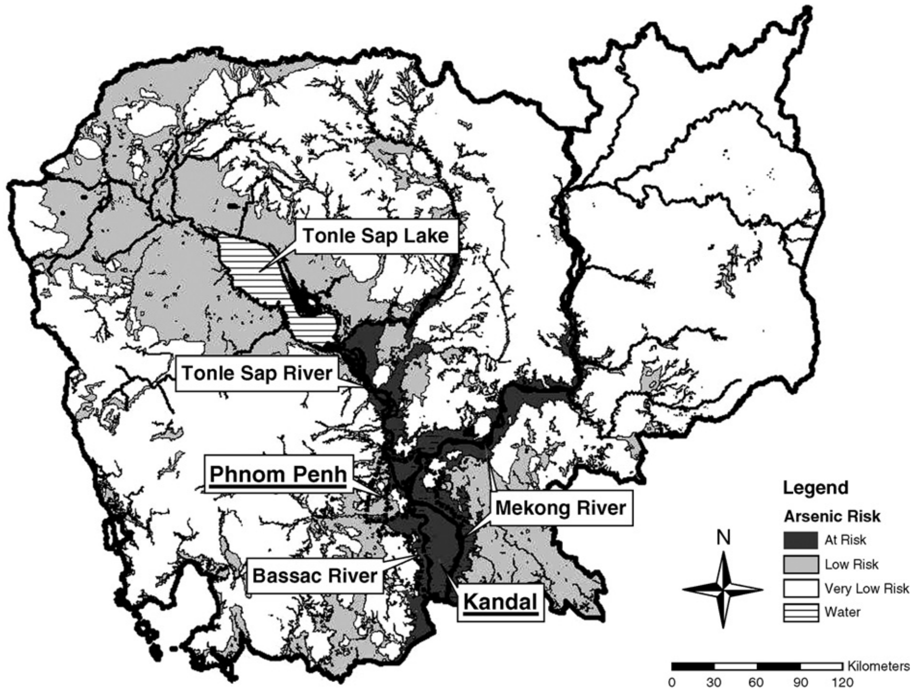

Fig. 2. Risk map for arsenic pollution in groundwater of Cambodia (adapted from Fredericks, 2004). Criteria for "increased risk", low risk", and "very low risk" are described in the text.

that arsenic concentration corresponds to anoxic conditions in the aquifers, leading to reductive dissolution of arsenic-bearing minerals. These values are comparable to concentrations reported for Bangladesh and West Bengal (Smedley and Kinniburgh, 2002; Ahmed et al., 2004; Das et al., 1996). Bivariate plots of arsenic and selected parameters are shown in Fig. 3. The correlations of arsenic with redox potential (Eh), ammonium and DOC are indicative of reductive dissolution of mineral oxides and subsequent arsenic release. The trend of higher arsenic concentrations at pH values > 7 lead to the speculation that arsenic release from sediments might partly be enhanced by alkaline pH, but this needs to be assessed further. A more in-depth report on this survey has been submitted for publication (Buschmann et al., submitted for publication).

3.1.2. Southern Vietnam

There is growing concern about the occurrence of arsenic in groundwater wells of the Vietnamese Mekong delta. Trang et al. (2005) found elevated arsenic concentrations in areas of the Vietnamese Mekong delta, where 40% of the tube-wells had arsenic levels > 100 μg/L. The upper (Quaternary) aquifers of the lower Mekong delta are typically brackish or saline (Pham et al., 2002). The soils and aquifers are chemically reducing and contain natural organic matter of up to 23% in Quaternary deposits (Husson et al., 2000). Groundwater used for public drinking water supply or irrigation is therefore pumped from older (Neogene) aquifers at depth of 150–250 m. According to the Southern Hydrological and Geological Engineering Department (Ho Chi Minh City), these deep aquifers should not be affected by elevated dissolved arsenic concentrations.

Soils rich in iron sulphide (pyrite) are abundant in the tide-dominated area of the Mekong delta (Husson et al., 2000). Weathering of the topsoil layer results in the

Table 1
Cambodia: average concentrations and ranges in samples collected between April and December 2004 ($n = 207$)

		Average	Median	Range
As	μg/L	212	49	<1–1610
Fe	mg/L	2.8	1.3	<0.05–16.2
Mn	mg/L	0.62	0.39	<0.01–3.3
NH_4^+	mg/L	6.0	2.2	<0.1–52
DOC	mg/L	3.9	3.1	<1.3–15.6
HCO_3^-	mg/L	343	337	34–830
NO_3–N	mg/L	0.27	<0.25	<0.25–22
PO_4–P	mg/L	0.59	0.35	<0.2–3.2
Cl^-	mg/L	50	9.0	0.6–1180
Sulphate	mg/L	22	<5	<5–1020
pH		6.94	6.98	5.42–8.01
Eh	mV	−65	−69	−410–190
Dissolved O_2	mg/L	1.21	1.10	0.10–4.9
Conductivity	μS/cm	752	630	78–6150

oxidation of these sulphides, leading to large amounts of sulphuric acid. The resulting acidic conditions can cause pH-values below 3 (Husson et al., 2000). Consequent acidification of the canals and the rivers make the water unsuitable for irrigation and drinking. Oxidation of pyrite results mostly from lowering of the water table (Minh et al., 1998). Gustafsson and Tin (1994) analysed 25 such acid sulphate soils from the Mekong delta. The arsenic contents ranged from 6 to 41 μg/g and were classified 'elevated' by global average values.

The high amount of rainfall during the rainy season combined with high river flow lead to annual flooding of the area. However, in the dry season the levels of the rivers drop significantly due to excessive irrigation demands, which are leading to increased inland flow of seawater through the Mekong and Bassac River channels.

Much of the rural population has limited access to safe drinking water. Tube-wells are therefore installed wherever possible and affordable. With increasing distance from the sea, the groundwater salinity in shallow aquifers decreases, so that the groundwater becomes a suitable source of drinking water that can easily be pumped through small-scale tube-wells. The recognition of arsenic pollution in the Cambodian part of the Mekong delta (see above) strongly suggests that the Vietnamese delta region is also affected. Hence, we have conducted a groundwater survey in the upper part of the Vietnamese Mekong delta where shallow aquifers are not considered saline. This area belongs to the same geological unit as the strongly arsenic affected Kandal province of Cambodia.

3.1.2.1. Concentrations of arsenic and other species in groundwater of Southern Vietnam. In Vietnam, the Bassac and Mekong Rivers (sometimes called Tien Giang and Hau Giang Rivers in Vietnam) flow through the An Giang and Dong Thap provinces before fading-out in the Mekong delta flood plain. Our study focused on these two provinces (see Fig. 1) since the Holocene aquifers of this region are generally unaffected by salt water intrusion. A

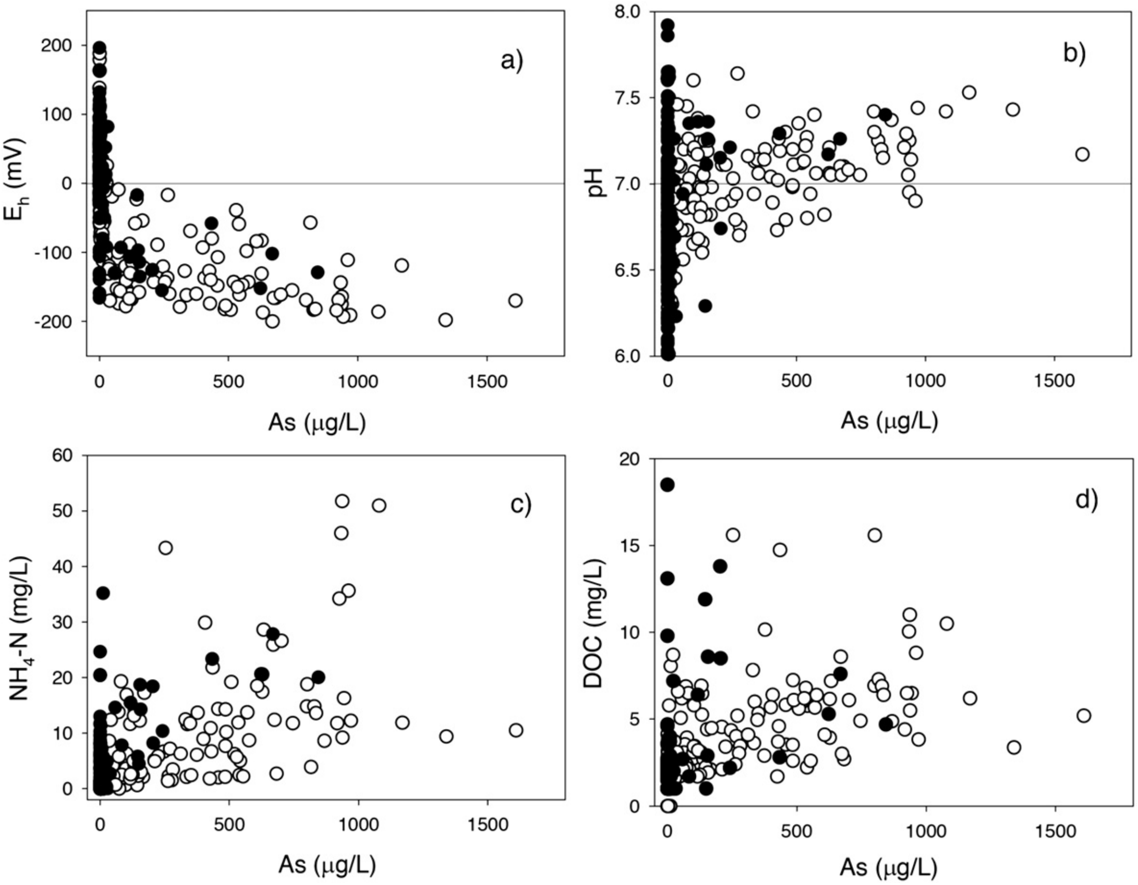

Fig. 3. Bivariate plots of arsenic and selected parameters measured in groundwater samples of the upper Mekong Delta, Cambodia and Vietnam. Open circles (○) are samples from Cambodia (n=207), black dots- (●) from southern Vietnam (n=112). a) redox potential–arsenic, b) pH–arsenic, c) ammonium–arsenic, d) dissolved organic carbon–arsenic.

large portion of the people still use surface water for their daily needs including drinking water. But family-based tube-wells are used increasingly as an alternative.

On July 2004, we randomly collected 112 groundwater samples in this rural area (Trang et al., 2005). Table 2 provides an overview of average concentrations and ranges of parameters measured in this study. Arsenic ranged from <1–845 μg/L (average 39 μg/L). Concentration ranges of other parameters are listed in Table 2. The magnitude of Fe, ammonium, and DOC concentration are similar as the ones in the upstream Kandal province of Cambodia (see Table 1 and Fig. 3).

Although arsenic concentrations reach levels >500 μg/ L, the average is significantly lower than in Cambodia. The chemical groundwater composition summarised in Table 2 and plotted in Fig. 3 further reveals that dissolved manganese and chloride are more abundant. Elevated arsenic levels are often found in samples with pH values>7 where arsenic release from sediments might be enhanced, but the major cause for arsenic pollution seems primarily related to reductive dissolution.

Arsenic concentrations averaged at 64 μg/L within a distance of <10 km from the rivers, while samples in the farther distance (>10 km) had a much lover average of 8 μg/L. This trend is consistent with the finding for Cambodia where the most severe arsenic pollution is found in tube-wells located in the alluvial flood-plain between the Bassac and Mekong Rivers (Kandal province).

3.2. Red River delta, Northern Vietnam

The Red River basin stretches from N 20°00′ to N 25°30′ and E 100°00′ to E 107°10′ and is confined by the Truong Giang and Chau Giang River basins in the north, the Mekong in the west, the Ma River basin in the south and the Gulf of Tonkin in the east. The Red River has a total length of 1150 km and its basin has a catchment area of 170,000 km^2. It is dominated by tropical monsoon climate and is subject to rainy seasons (May–September) and dry seasons (October–April). The average temperature in Hanoi is 23.4 °C and the average rainfall is 1800 mm/year. During the rainy season, the Red River in Hanoi may reach a water discharge of 9500 m^3/s; the long-term average flow is 3740 m^3/s, but the river volume is highly variable throughout the year.

Table 2
Vietnamese Mekong delta: average concentrations and ranges in samples collected on July 2004 ($n=112$)

		Average	Median	Range
As	μg/L	39	<1	<1–845
Fe	mg/L	2.6	<0.05	<0.05–56
Mn	mg/L	3.4	0.97	<0.01–34
NH4$^+$	mg/L	5.0	1.4	<0.1–35
DOC	mg/L	5.3	2.6	1.5–58
HCO3$^-$	mg/L	230	190	19–785
NO3–N	mg/L	<0.25	<0.25	<0.25–4.4
PO4–P	mg/L	0.33	<0.2	<0.2–5.25
Cl$^-$	mg/L	690	374	2.1–8570
Sulphate	mg/L	41	15	<5–360
pH		6.83	6.80	5.00–8.70
Eh	mV	14	24	−303–625
Dissolved O$_2$	mg/L	0.29	0.20	<0.01–3.90
Conductivity	μS/cm	2490	1710	224–17900

The Red River delta is a flat area with a ground level of 5 to 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. The result of these geological processes is a relatively thick Quaternary accumulation (50–90 m in Hanoi) with loose and altering sediment beds, many containing organic material. In general, the Quaternary can be divided into two sequences: the upper part, composed of fine sediment clay, sandy clay and fine sand; and the lower part, containing gravel with cobbles and coarse sand. The Quaternary sediments are underlain by Neogene sedimentary rocks that are composed of conglomerate sandstone, clay and siltstone. In total the Neogene exceed a thickness of 400 m. More detailed information can be found in Berg et al. (2001) and references therein.

A tentative risk map of arsenic being >50 μg/L in groundwater of the Red River delta is presented in Fig. 4. This map was established from geological raster information, climate and land use (geo-referenced raster data was obtained from FAO, www.fao.org/geonetwork). Correlation with measured arsenic values in groundwater was best for recent alluvial sediments of loamy texture (high risk), other Holocene sediments (medium risk) and Pleistocene sediments (low risk). It must be noted that the coastal areas (some 25 km wide) have saline groundwater, which is not used for drinking.

3.2.1. Arsenic pollution in tube-wells of rural areas (upper aquifer)

Fig. 5 shows arsenic concentrations measured in the rural districts on December 1999. The concentrations varied greatly within the studied area, but most tube-wells yielded arsenic concentrations above the WHO guideline of 10 μg/L. In the southern part (district D), most arsenic concentrations exceeded the Vietnamese standard of 50 μg/L.

Our ongoing investigations reveal that the variability of arsenic levels is very pronounced, even within distances of 10–20 m. This is illustrated in Fig. 6 which

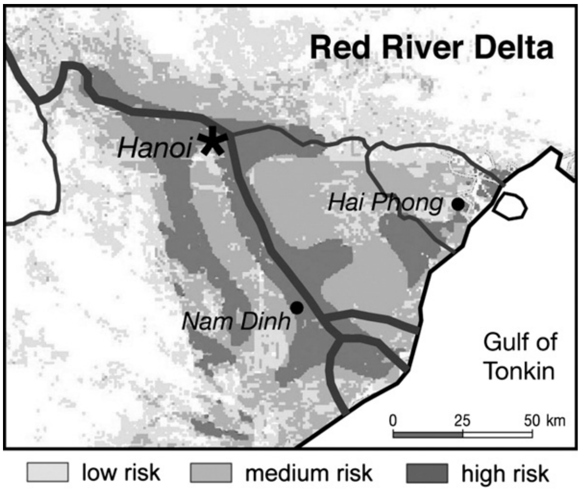

Fig. 4. Tentative risk map for arsenic being >50 μg/L in groundwater of the Red River delta, Vietnam. The criteria for "low risk", "medium risk", and "high risk" are described in the text.

shows high variations of arsenic concentrations in a small village located in district D.

3.2.2. *Public drinking water supply of the city of Hanoi (lower aquifer)*

Raw water (lower aquifer) and treated water from the eight groundwater treatment plants of Hanoi were sampled and analysed seven times between March 1999 and July 2000. The concentrations of December 1999 showed that some raw groundwaters contained greater than 300 μg/L arsenic (Berg et al., 2001). Although arsenic concentrations were substantially lowered by treatment, the levels in finished waters (25–91 μg/L) still exceeded the Vietnamese limit in half of the samples (Dodd et al., 2006). However, most tap-water samples collected at individual homes contained arsenic concentrations below 50 μg/L (range 7– 82 μg/L, average 31 μg/L), suggesting that additional arsenic removal occurs in the distribution system, possibly by adsorption to iron oxide surfaces in the pipes of the distribution system (Berg et al., 2001).

3.2.3. *Origin of arsenic pollution*

Although there is no indication for an anthropogenic origin of arsenic in the subsurface in and around Hanoi, the possibility of pollution through landfill leakage, agricultural fertilizers (McLaughlin et al., 1996) or mining wastes carried by the Red River cannot be excluded. However, the widespread occurrence of arsenic in the investigated aquifers points to natural geogenic sources similar to the situation in the Ganges delta (BGS and DPHE 2001; Das et al., 1996; McArthur et al., 2001; Nickson et al., 2000). Sediment-bound arsenic most probably originates from erosion and weathering processes, which result in the

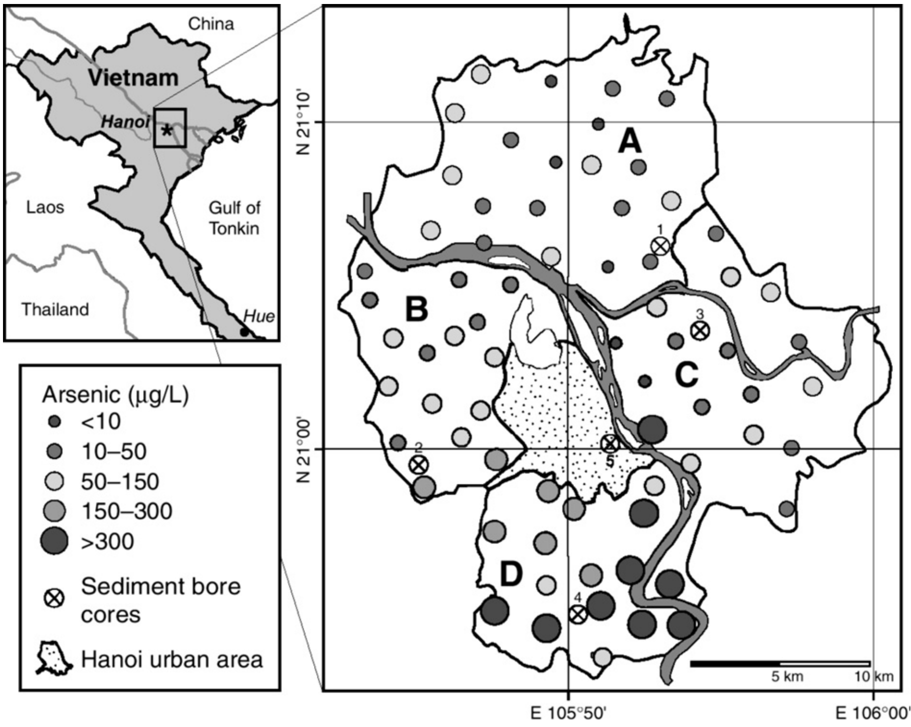

Fig. 5. Arsenic concentrations measured in groundwaters of the larger Hanoi area in samples pumped from the upper aquifer by private tube-wells (December 1999).

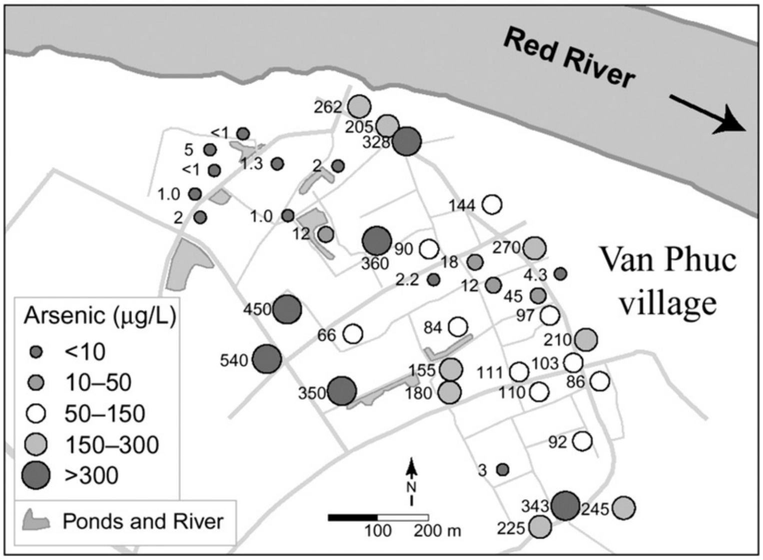

Fig. 6. High variations of arsenic levels are observed over short distances. As an example, this map shows As groundwater concentrations measured on March 2001 in a village. The numbers indicate As concentrations in µg/L.

enrichment of arsenic onto ferric oxyhydroxides followed by fluvial transport and sedimentation (Rodwell, 1994; Welch et al., 1988). Several studies (BGS and DPHE 2001; Korte and Fernando, 1991; McArthur et al., 2001; Nickson et al., 2000) have suggested that elevated arsenic levels in groundwater are caused by reductive dissolution of arsenic-rich iron oxyhydroxides occurring as dispersed phases in the aquifer rocks.

The anoxic conditions in the Red River sediments are driven by natural organic matter (NOM) present in the subsurface (Berg et al., 2001; Trafford et al., 1996): we have found peat layers with NOM concentrations of 15% total organic carbon in sediment cores. Dissolved oxygen is rapidly consumed by microbiological mineralization of NOM, resulting in the formation of bicarbonate and inorganic nitrogen species. This is consistent with the high alkalinity (up to 810 mg/L) and high nitrogen concentrations (10–48 mg N/L) measured in the studied groundwaters. Inorganic nitrogen was mainly found in the reduced form of ammonium that reached particularly high levels of up to 48 mg N/L in the most severely arsenic-contaminated district D (Berg et al., 2001). As a result of the low redox potential, As(V) is reduced to As(III) which contributes 50–100% of total arsenic in the groundwaters.

In order to explain the significantly different arsenic levels of districts A and D (Fig. 5), the different geological settings and actual hydrogeological conditions of these areas must be considered. The geology of the Red River delta is complex, with considerable variation in lithology within short distances. The sediments in district A (predominantly of Pleistocene age) are not as thick as those in the other districts, and form mainly one aquifer 10–25 m in depth. The other districts have sediment layers from both the Pleistocene and Holocene ages, with the latter being partly derived from postglacial marine transgressions (Trafford et al., 1996). Of the 2–3 present aquifers, the first (10–30 m) and the second (30–70 m) are exploited for drinking water. Due to frequent riverbed migrations, the aquifers are not fully separated and are in some locations connected through sand lenses. Even without the pumping of groundwater, recharge in the upper two (Quaternary) aquifers can partly originate from Red River bank filtration. However, Hanoi's high demand of water is causing a significant drawdown of the groundwater table. This is particularly severe in districts B and D where cones of depression reach 30 m deep. Under these conditions, bank filtrates from the Red River must be of major importance and strongly influence the groundwater recharge in the Hanoi area. More detailed information can be found in Berg et al. (2001) and references therein.

3.2.4. Sediment arsenic concentrations

Total arsenic concentrations vary with depth in stratigraphically different sediment layers of five sediment cores (12–40 m depth, mainly upper aquifer). The locations of the sediment drilling sites are marked in Fig. 5 and concentration depth profiles are shown in Fig. 7. The cores were drilled next to groundwater monitoring wells, and water of these wells was sampled concurrently. In the upper 10 m of two cores, distinct peat layers were present. Peak arsenic concentrations of 6–33 μg/g were primarily associated with brown to black–brown clay layers, followed by grey clay (2–12 μg/g) and brown-to-grey sand (0.6–5 μg/g). The arsenic content was highly correlated with the iron content, indicating that arsenic could be adsorbed with iron phases (Fig. 7). No correlation was observed for sediment-bound arsenic with dissolved arsenic concentrations measured in groundwater of the adjacent monitoring wells.

3.2.5. People at risk of chronic arsenic poisoning

The results of this survey reveal that several million people of the Red River delta are exposed to a risk of chronic arsenic poisoning. Yet, to the best of our knowledge, only few disease symptoms have been diagnosed so far. This could possibly be attributed to the fact that in Vietnam, arsenic contaminated groundwater has only been used as drinking water for the past 7–10 years. Furthermore, the early manifestations of arsenicosis are difficult to diagnose and depend largely on the awareness of the local doctors (Saha et al., 1999). The frequencies of the concentration ranges reveal that 25–90% (average = 48%, $n=196$) or 50–98% (average = 72%, $n=196$) of the investigated groundwaters exceed the arsenic limit of 50 μg/L or 10 μg/L, respectively. This means that the Hanoi area and possibly larger areas of the Red River delta are as strongly affected as Bangladesh (27% above 50 μg/L, $n=3534$) (BGS and DPHE, 2001). The very high concentrations in district D raise the question why no arsenicosis has been detected to date. Experience shows that it can take ten or more years before the first arsenic poisoning symptoms to become apparent. Compared to Bangladesh, one might further speculate that the general nutrition of the Vietnamese population is better and that this could have a retarding influence on the manifestation of the disease. Hence, the number of people affected in the future by arsenic-related health problems should not be underestimated.

3.3. Indicators for human arsenic exposure

3.3.1. Cambodia (Mekong delta)

Arsenic concentrations were measured in some 20 hair and urine samples from residents of a farming village exposed to high groundwater As levels. These values were compared with control sites (Agusa et al., 2002). Arsenic levels found in human hair at the exposed village (average 2.0 mg/kg) were significantly higher ($p=0.05$) than at the control site (average 0.3 mg/kg). On the other hand, no regional difference in urinary As concentrations (median values 53–81 μg/L) was observed. However, in this study the highest As concentration in urine (490 μg/L) was detected in the sample of a resident living in the As-contaminated area. At this concentration, symptoms of arsenicosis can be expected to develop (Fredericks, 2004). As depicted in Fig. 8a, the exposure to high arsenic concentrations of people living in the Kandal province is clearly reflected in the hair arsenic levels reported by Agusa et al. (2002).

Like in Vietnam, most of Cambodia's 40,000 tubewells were built in the past decade (Kyne, 2000), indicating that serious As related health problems might not yet have emerged. Nevertheless, cases of skin problems in children that may be traceable to As have been identified in a few cases (Sine, 2002).

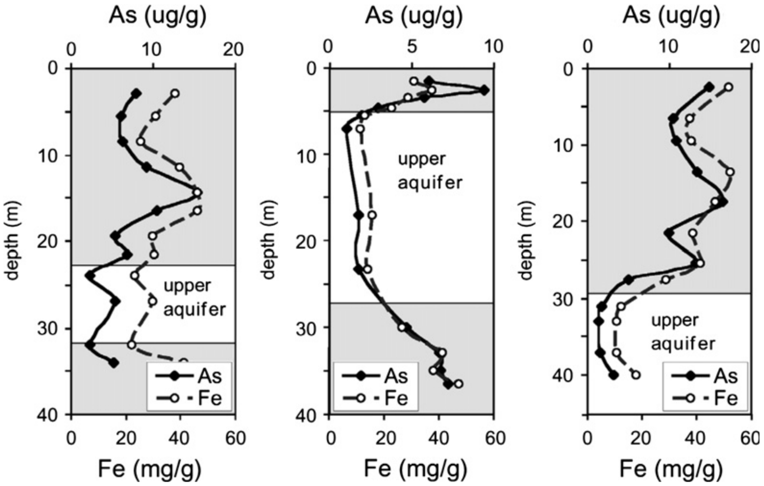

Fig. 7. Vertical depth profiles of sediment-bound total arsenic and total iron depicted for three of the five sediment cores drilled on July 2000. Notes: grey background indicates confining sediment layers (e.g. clay and silt). The layers of the white area consisted mainly of sand and gravel.

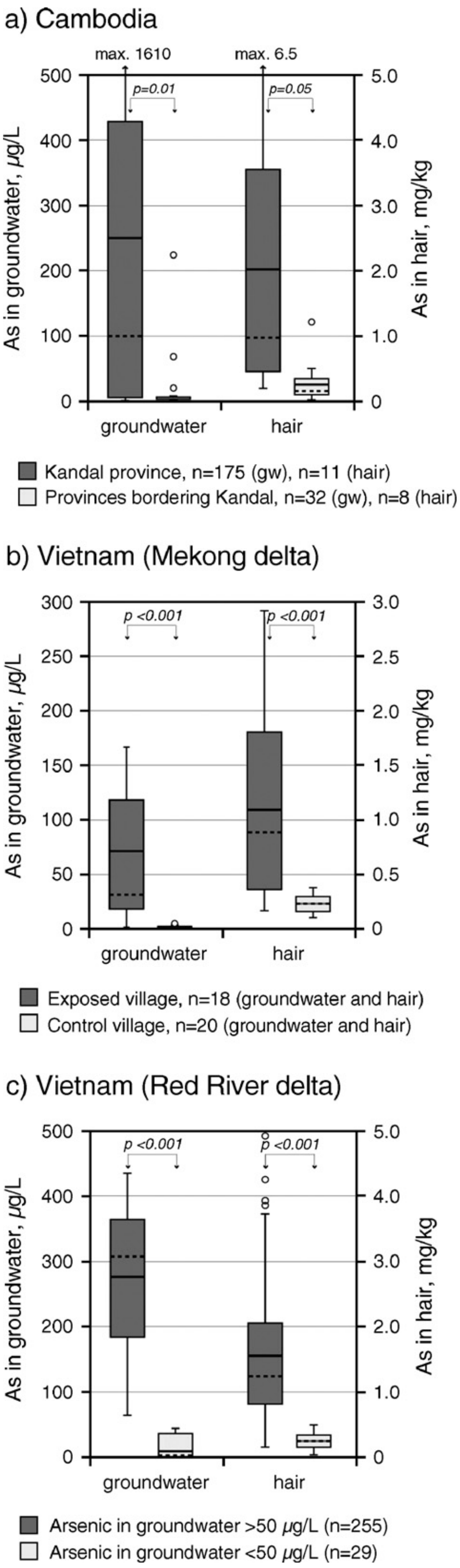

Fig. 8. Box plots of arsenic concentrations in groundwater and hair of residents living in rural areas. a) Kandal province and bordering provinces in Cambodia. b) Upper Vietnamese Mekong delta. c) Red River delta, Vietnam. Average values are indicated by solid lines (—), medians by dashed lines (- - -). The columns contain 50% of the data, the vertical lines 95%. Open circles are data points outside the 95% range. The *p*-values are derived from a paired *t*-test.

Table 3
Arsenic concentrations (µg/L) in groundwaters of rural districts (upper aquifer, Red River delta)

District[a]	*n*[b]	Average	Range
A	48	32	1–220
B	48	67	1–230
C	55	140	2–3050
D	45	430	2–3010
All districts	196	159	1–3050

Notes: three sample series: September 1999, December 1999, May 2000. (a) Districts A to D are as shown in Fig. 7. (b) number of analysed samples.

3.3.2. Southern Vietnam (Mekong Delta)

The As exposure of people living in the Vietnamese part of the Mekong delta was investigated in a survey conducted in 2004 (Trang et al., 2005). Hair samples were randomly collected in two villages, one being exposed to groundwater arsenic pollution and the other having arsenic levels <50 µg/L. These hair samples were analysed together with groundwater sampled from tube-wells, from which these people are pumping drinking water. The As levels found in hair ranged from 0.11–2.92 mg/kg and from 1–167 µg/L in groundwater. As can be seen in Fig. 8b, remarkably higher As concentrations were measured in hair from people living in the village exposed to arsenic groundwater pollution than in the control village using safe water. The difference of the two groups is statistically significant with *p*-values<0.001 for both, hair and groundwater. No conclusions regarding health symptoms can be inferred from these findings, however, they clearly indicate that people of the upper Mekong River delta are chronically exposed to elevated As levels in their drinking water.

3.3.3. Red River delta

In 2001 we have examined the human arsenic exposure in the Red River delta. Hair probes from 51 randomly selected residents were sampled in rural areas and the arsenic levels compared with groundwater collected from their tube-wells. The As concentrations ranged from 0.20–2.75 mg/kg in hair and from 1– 310 µg/L in groundwater. Arsenic in hair of people drinking groundwater with arsenic levels >50 µg/L were evidently higher than of people belonging to the group <50 µg/L (see Fig. 8c). The difference of the two groups is statistically significant with p-values of <0.001 for both, hair and groundwater. This data is demonstrating that people of the Red River delta are chronically exposed to elevated arsenic levels in their drinking water (Table 3). Similar arsenic concentrations found in human hair (0.09–2.8 mg/kg) of people living in the rural Hanoi area were reported by Agusa et al. (2002).

4. Conclusions and outlook

Based on the data presented here, arsenic groundwater pollution in Cambodia and Vietnam is evident and its impact to humans clearly reflected in the high arsenic levels measured in hair of people consuming such groundwater. We currently estimate that 10 million people in the Red River delta and 0.5–1 million people in the Mekong delta are at risk of chronic arsenic poisoning. Considering the magnitude of arsenic pollution, early mitigation measures are urgently needed to protect the people from serious health problems. Household sand filters capable of removing in average 80% arsenic have recently been shown to be particularly efficient and socially accepted in the Red River delta (Berg et al., 2006; Luzi et al., 2004). Options for arsenic removal have also been suggested for communal supply water (Pham et al., 2003; Dodd et al., 2006). Investigations on the occurrence and magnitude of As contamination in Vietnamese groundwaters have so far focused on the Red River delta of northern Vietnam (Berg et al., 2001) and the Mekong delta in the south (Trang et al., 2005). However, other potential areas for As-rich groundwater including the Ma, Ca, Gianh, Huong, and Da Rang river deltas have not yet been assessed. Likewise, besides the Kandal province and neighbouring areas, there is an urgent need to investigate further regions in Cambodia as indicated in the risk map presented in Fig. 2. Obviously the extent of the arsenic problem must more closely be assessed in Cambodia and Vietnam.

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References

Ahmed KM, Bhattacharya P, Hasan MA, Akhter SH, Alam SMM, Bhuyian MAH, et al. Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview. Appl Geochem 2004;19(2):181–200.

Agusa T, Kunito T, Kubota R, Monirith I, Tanabe S, Tana TS. Article in Japanese. Biomed Res Trace Elem 2002;13:254–5.

Berg M, Tran HC, Nguyen TC, Pham HV, Schertenleib R, Giger W. Arsenic contamination of groundwater and drinking water in Vietnam: a human health threat. Environ Sci Technol 2001;35:2621–6.

Berg M, Luzi S, Trang PKT, Viet PH, Giger W, Stuben D. Arsenic removal from groundwater by household sand filters — comparative field study, model calculations, and health benefits. Environ Sci Technol 2006;40:5567–73.

BGS [British Geological Survey] & DPHE [Department of Public Health Engineering, Bangladesh]. Arsenic contamination of groundwater in Bangladesh. In: Kinniburgh DG, Smedley PL, editors. BGS technical report WC/00/19. Keyworth, UK: BGS; 2001.

Buschmann J, Berg M, Stengel C, Sampson ML. Arsenic and manganese pollution in the upper Mekong delta, Cambodia: comprehensive groundwater survey. Environ Sci Technol, submitted for publication.

Chowdhury UK, Biswas BK, Chowdhury TR, Samanta G, Mandal BK, Basu CG, et al. Groundwater arsenic contamination in Bangladesh and West Bengal, India. Environ Health Perspect 2000;108(5):393–7.

Das D, Samanta G, Mandal BK, Chowdhury TR, Chanda CR, Chowdhury PP, et al. Arsenic in groundwater in six districts of West Bengal, India. Environ Geochem Health 1996;18:5-15.

Dodd MC, Vu ND, Ammann A, Chieu LV, Kissener R, Pham HV, Cao TH, Berg M, von Gunten U. Kinetics and Mechanistic Aspects of As(III) Oxidation by Aqueous Chlorine, Chloramines, and Ozone: Relevance to Drinking Water Treatment. Environ Sci Technol 2006;40:3285–92.

Duong HA, Berg M, Hoang MH, Pham HV, Gallard H, Giger W, et al. Trihalomethane formation by chlorination of ammonium- and bromide-containing groundwaters in water supplies of Hanoi, Vietnam. Water Res 2003;37:3242–52.

Feldman PR, Rosenboom JW. Cambodia drinking water quality assessment. Phnom Penh, Cambodia: World Health Organisation of the UN [WHO] in cooperation with Cambodian Ministry of Rural Development and the Ministry of Industry, Mines and Energy; 2001.

Fredericks D. Situation analysis: arsenic contamination of groundwater in Cambodia. Report, January 2004. Phnom Penh, Cambodia: UNICEF; 2004.

Gustafsson JP, Tin NT. Arsenic and selenium in some Vietnamese acid sulfate soils. Sci Total Environ 1994;151:153–8.

Halperin A. Arsenic found in rural Mekong river wells. The Cambodian Daily, June 25, 2003, Phnom Penh, Cambodia, vol. 11; 2003.

Husson O, Verburg PH, Phung MT, Van Mensvoort MEF. Spatial variability of acid sulphate soils in the Plain of Reeds, Mekong delta, Vietnam. Geoderma 2000;97:1-19.

Hydrogeological Division II. Annual Report 1999. Hanoi, Vietnam: Vietnam Geological Survey; 2000.

Korte NE, Fernando Q. A review of arsenic (III) in groundwater. Crit Rev Environ Control 1991;21:1-39.

Kyne P. Arsenic threat found in groundwater survey. Phnom Penh Post. Cambodia: Phnom Penh; 2000. p. 1–2. August 18–31.

Luzi S, Berg M, Pham TKT, Pham HV, Schertenleib R. Household sand filters for arsenic removal — technical report. Swiss Federal Institute for Environmental Science and Technology (Eawag); 2004. Electronic copies of this report can be downloaded through the Internet: www.arsenic.eawag.ch/publications.

McArthur JM, Ravenscroft P, Safiulla S, Thirlwall MF. Arsenic in groundwater: testing pollution mechanisms for sedimentary aquifers in Bangladesh. Water Resour Res 2001;37:109–17.

McLaughlin MJ, Tiller KG, Naidu R, Stevens DP. The behaviour and environmental impact of contaminants in fertilizers. Aust J Soil Res 1996;34:1-54.

Minh LQ, Tuong TP, Van Mensvoort MEF, Bouma J. Soil and water table management effects on aluminum dynamics in an acid sulphate soil in Vietnam. Agric Ecosyst Environ 1998;68:255–62.

Nguyen VL, Ta TKO, Tateishi M. Late Holocene depositional environments and coastal evolution of the Mekong River Delta, Southern Vietnam. J Asian Earth Sci 2000;18:427–39.

Nickson RT, McArthur JM, Ravenscroft P, Burgess WG, Ahmed KM. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. Appl Geochem 2000;15:403–13.

Ollson T, Palmgreen S. Geochemical behavior of arsenic in the soil–shallow groundwater system in a part of the Mekong Delta — a minor field study in Vietnam. Stockholm, Sweden: Department of Civil and Environmental Engineering, Royal Institute of Technology; 2001.

Pham VN, Boyer D, Le Mouel JL, Nguyen TKT. Hydrogeological investigation in the Mekong Delta around Ho-Chi-Minh City (South Vietnam) by electric tomography. Comptes Rendus Geosci 2002;334:733–40.

Pham HV, Tran HC, Cao TH, Hoang VH, Berg M, Giger W, et al. Investigation of arsenic removal technologies for drinking water in Vietnam. In: Chappell WR, Abernathy CO, Calderon RL, editors. Arsenic exposure and health effects V. Elsevier Science; 2003. p. 459–69.

Polya DA, Gault AG, Diebe N, Feldman P, Rosenboom JW, Gilligan E, et al. Arsenic hazard in shallow Cambodian groundwaters. Mineral Mag 2005;69(5):807–23.

Rodwell RJ. Sorption of arsenic by iron oxides and oxyhydroxides in soils. Appl Geochem 1994;9:279–86.

Saha JC, Dikshit AK, Bandyopadhyay M, Saha KC. A review of arsenic poisoning and its effects on human health. Crit Rev Environ Sci Technol 1999;29:281–313.

Sine R. Arsenic emerges a new threat in well water, vol. 15. Phnom Penh, Cambodia: The Cambodian Daily; 2002. June 25.

Smedley PL, Kinniburgh DG. A review of the source, behaviour and distribution of arsenic in natural waters. Appl Geochem 2002;17:517–68.

Smith AH, Lingas EO, Rahman M. Bull World Health Organ 2000;78:1093–102.

Trafford JM, Lawrence AR, Macdonald DMJ, Nguyen VD, Tran DN, Nguyen TH. The effect of urbanisation on the groundwater quality beneath the city of Hanoi, Vietnam. BGS technical report WC/96/22. Keyworth, UK: British Geological Survey; 1996.

Trang PTK, Berg M, Viet PH, Van Mui N, van der Meer JR. Bacterial bioassay for rapid and accurate analysis of arsenic in highly variable groundwater samples. Environ Sci Technol 2005;39:7625–30.

Welch AH, Lico MS, Hughes JL. Arsenic in ground water of the Western United States. Ground Water 1988;26:333–47.