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Arsenic exposure to drinking water in the Mekong Delta

R.B. Merola [a], T.T. Hien [b], D.T.T. Quyen [b], A. Vengosh [a,*]

[a] Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, Box 90227, Durham, NC 27708, USA
[b] Faculty of Environmental Science, University of Science, Vietnam National University, Ho Chi Minh City, 227 Nguyen Van Cu Str., Dist. 5, HCMC, Vietnam

HIGHLIGHTS

- Elevated As is found in groundwater used for drinking in the Mekong Delta, Vietnam.
- Arsenic in nails reflects exposure of individuals consuming As-rich groundwater.
- Differential As exposure is observed by the As in nail to As in water ratios.
- Diet and water filtration reduce individual's exposure to As in drinking water.

GRAPHICAL ABSTRACT

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ABSTRACT

Arsenic (As) contamination of groundwater drinking sources was investigated in the Mekong Delta, Vietnam in order to assess the occurrence of As in the groundwater, and the magnitude of As exposure of local residents through measurements of As in toenails of residents consuming groundwater as their major drinking water source. Groundwater ($n = 68$) and toenail ($n = 62$) samples were collected in Dong Thap Province, adjacent to the Mekong River, in southern Vietnam. Fifty-three percent ($n = 36$) of the wells tested had As content above the World Health Organization's (WHO) recommended limit of 10 ppb. Samples were divided into Northern (mean As = 4.0 ppb) and Southern (329.0 ppb) groups; wells from the Southern group were located closer to the Mekong River. Elevated As contents were associated with depth (<200 m), salinity (low salinity), and redox state (reducing conditions) of the study groundwater. In 79% of the wells, As was primarily composed of the reduced As(III) species. Arsenic content in nails collected from local residents was significantly correlated to As in drinking water ($r = 0.49$, $p < 0.001$), and the relationship improved for pairs in which As in drinking water was higher than 1 ppb ($r = 0.56$, $p < 0.001$). Survey data show that the ratio of As in nail to As in water varied among residents, reflecting differential As bioaccumulation in specific exposed sub-populations. The data show that water filtration and diet, particularly increased consumption of animal protein and dairy, and reduced consumption of seafood, were associated with lower ratios of As in nail to As in water and thus could play important roles in mitigating As exposure in areas where As-rich groundwater is the primary drinking water source.

* Corresponding author.
E-mail address: vengosh@duke.edu (A. Vengosh).

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1. Introduction

The Mekong Delta is a biological diverse and water-rich area, and together with the Red River in northern Vietnam, comprises one of the most productive agricultural regions in Southeast Asia (Berg et al., 2001, 2007). Projected hydropower generation and dam construction on the upstream Mekong River pose risks for water availability in the downstream Mekong Delta. Consequently, groundwater is expected to become a pivotal irrigation and drinking water resource in this region. It is estimated that the demand for groundwater will increase by up to 6.5 times by 2020 (510–520 × 10^9 m^3/year) in comparison to the 1990–2000 period (Van, 2004). In addition to water availability, water quality can limit the sustainability of groundwater in the Mekong Delta, and its potential to substitute for declining surface water resources. In particular, previous studies have highlighted the occurrence of high salinity and As (arsenic) in groundwater that could limit agriculture production and pose human health risks (Buschmann and Berg, 2009; Buschmann et al., 2007, 2008). Understanding the geochemical conditions in which contaminants are mobilized to groundwater and the magnitude of exposure of the local residents to these contaminants is important for evaluating the risks of the expected transition from surface water to groundwater utilization in the Mekong Delta.

Arsenic in Vietnam has been measured in groundwater in both the Red River and the Mekong River Deltas (Berg et al., 2001, 2007, 2008; Buschmann et al., 2007, 2008; Nguyen and Itoi, 2009; Winkel et al., 2011). Elevated As (>10 ppb) levels have been reported to typically occur in shallow groundwater from both the Holocene and Pleistocene aquifers. In the Red River Delta, Winkel et al. (2011) have shown that over-pumping of As-free deep groundwater has resulted in the drawdown of the groundwater levels in the deep aquifers. This has induced the downflow of shallow As-rich groundwater to the deep aquifers and caused contamination of deep groundwater, which has been utilized mainly for drinking water.

Arsenic contamination in groundwater from the Mekong Delta is naturally occurring and caused by chemical and microbial induced reductive dissolution of iron-oxides from the alluvial sediments in the delta (Rowland et al., 2008; Quicksall et al., 2008; Fendorf et al., 2010; Winkel et al., 2011). Following river sediment transport and accumulation in the deltaic reducing conditions, As bound to iron-oxides is released (Berg et al., 2001, 2008; Bissen and Frimmel, 2003; Harvey et al., 2002; Nguyen and Itoi, 2009; Nickson et al., 1998; Polizzotto et al., 2005). The World Health Organization (WHO) recommends As concentrations of up to 10 ppb in drinking water (WHO, 2011), but As concentrations in groundwater over 1300 ppb have been reported in the region (Winkel et al., 2011; Stollenwerk et al., 2007; Buschmann et al., 2008). In addition, other inorganic groundwater contaminants with potential health effects, such as Mn and Ba, have been reported (Buschmann et al., 2007, 2008). Buschmann et al. (2008) reported that high As levels occur selectively in low-saline drinking water wells close to the Mekong River, while groundwater located farther away from the Mekong River is characterized by higher salinity and lower As content.

In spite of the extensive literature on the overall toxic effects of As, it is difficult to establish a direct link between health affects and As exposure from drinking water in a given population due to the long latency period between the window of exposure and the development of health outcomes. Keratin, such as in hair and nails, has been shown to be the preferred method to monitor long-term exposure to As in drinking water. While blood and urine are useful biomarkers for smaller exposure windows, the nails reflect an integrated exposure time ranging from 3 months to a year (Schroeder and Balassa, 1966; Slotnick and Nriagu, 2006; Yoshida et al., 2004). Toenails are thought to be better than fingernails at capturing As exposure due to the fact that their slower growth rate provides greater As levels per mass compared to fingernails. Both are thought to be better than hair because an individual's hair growth rates vary more across populations relative to individual's nail growth rates (Karagas et al., 1996, 2000; Slotnick and Nriagu, 2006).

Although elevated As in drinking water sources of the Mekong and Red River Deltas in Vietnam have been identified as a major health concern, no exposure study through the monitoring of As in nails has been conducted in the Mekong Delta Region. Nguyen et al. (2009) found a correlation between As concentrations in groundwater drinking wells from the Red River Delta and As concentrations in women's hair, while Berg et al. (2007) found a correlation between As concentrations in drinking water and As concentrations in hair in the Mekong Delta (in both Vietnam and Cambodia), and also in the Red River Delta. This paper aims to fill the literature gap, focusing on As occurrence and human exposure in the Mekong Delta by measuring As concentrations in drinking water and in nails of local residents that consume groundwater as their major drinking water source.

The objectives of this study are (1) to evaluate As occurrence in the Mekong Delta groundwater; and (2) to assess its bioaccumulation in populations exposed to As in their drinking water. We collected samples measuring As in groundwater and nails from the Dong Thap Province in southern Vietnam and compared the As data to previous studies. By understanding the extent of As distribution in groundwater and its accumulation in the local populations in the Mekong Delta this paper provides the foundation for evaluating the health risks associated with the increased utilization of groundwater, which will likely result from the projected reduction of the Mekong River flow.

2. Methods

2.1. Field sampling

IRB approval was obtained from Duke University and Ho Chi Minh Science University and the Department of Natural Resource and Environment of Dong Thap Province. The study site spans approximately 70 km north to south in the Dong Thap province of Vietnam. Wells were selected based on government approval, as well as consent from individual well owners. In total, 68 groundwater wells were tested as well as 5 surface water samples from the Mekong River.

2.2. Groundwater sampling and analytic techniques

Groundwater from private and monitoring wells, as well as surface waters from the Mekong River were collected following USGS protocols (USGS, 2011). Samples to be analyzed for trace metals were filtered at the site location using 0.45 μm syringe filters, preserved using nitric acid, and then shipped to Duke University for analysis. The samples were analyzed for major elements using an ARL SpectraSpan 7 (Thermo Fisher Scientific, Inc.) direct current plasma optical emission spectrometry (DCP-OES), anions by an ICS 2100 (Dionex) ion chromatography (IC), and trace metals by a VG PlasmaQuad-3 (Thermo Fisher Scientific, Inc.) inductively coupled plasma mass spectrometry (ICP-MS) at Duke University. While more elements were analyzed, for this paper we report only As (detection limit = 0.05 ppb) and Cl (detection limit = 0.2 ppm). Speciation of As was performed in the field and preserved according to methods in Bednar et al. (2002) by using EDTA and anion exchange to isolate the uncharged As(III) species. Parameters collected in the field include pH, temperature, and oxidation–reduction potential (ORP) (YSI pH100A pH/ORP), conductivity (EC) (YSI EC300A), and dissolved oxygen (DO) (YSI DO200A). Meter calibration was performed prior to sampling. More detailed field and laboratory analytical methods can be found in Ruhl et al. (2010).

2.3. Nail sampling and analytic techniques

Toenails were collected from individuals whose water had been sampled. Researchers approached participants, explained the study, and obtained consent. The individuals were then surveyed to collect basic demographic information as well as water consumption patterns and basic health issues. Toenails were then clipped using new clean stainless steal clippers, stored in Ziploc© bags, and shipped to Duke University to be analyzed according to methods described in Merola et al. (2013). In total 62 nail samples were collected.

Toenails were cleaned in the laboratory with successive sonicated rinses of acetone, a 1% Titron-X solution, and another acetone rinse, with water rinses in between. Nails were then dried for at least 24 h at 60 °C and then digested with HNO_3 and H_2O_2. An aliquot of digested solution was then diluted and run on the ICP-MS (Chen et al., 1999; Karagas et al., 2000; Merola et al., 2013; Samanta et al., 2004).

3. Results and discussion

3.1. Arsenic occurrence in groundwater from Dong Thap Province, Vietnam

Groundwater samples from Dong Thap had elevated levels of As. Fifty-three percent (36 out of 68 wells) of the study wells had As levels above the WHO's recommended 10 ppb limit (Table 1). The spatial distribution of the sampling locations, as well as the As concentrations, is shown in Fig. 1a. In general, two sub-groups of groundwater with respect to As content were identified (Fig. 2): (1) groundwater from the northern part of the region near Tan Hong, further from the river with overall lower As concentrations (n = 23; ranging from below limit of detection to 22.2 ppb; median value 2.0 ppb; mean value 4.0 ppb); and (2) groundwater from the southern section of the region, located closer to the Mekong River and containing higher As concentrations near Thanh Binh (n = 45; ranging from 0.1 to 981.4 ppb; median value 271.5 ppb; mean value 329.0 ppb). In contrast, the mean As concentration of samples collected directly from the Mekong River was significantly lower (mean = 1.1 ppb; n = 5; ranging from 0.78–1.35 ppb) but not totally negligible (detection limit = 0.05 ppb), as one would expect to a large river such as the Mekong.

The Mekong Delta region is comprised of alluvial Holocene sediments (depths of 8–40 m) overlying Pleistocene sediments (50–80 m; Fig. 3) (Nguyen and Itoi, 2009). Arsenic above 10 ppb was typically found in relatively shallow wells from both the Holocene and Pleistocene aquifers. Two deep wells (>200 m) of the Lower Pliocene aquifer were exceptional and also showed elevated As. Both deep wells are located in the Northern sub-group.

Groundwater from both the Northern and Southern sub-sets showed large chloride variations with values ranging from 3 to 1527 mg/L, which is consistent with salinity levels reported in Berg et al. (2007). Elevated As concentrations were not found in wells with chloride concentrations above 200 mg/L (with one exception) (Fig. 4). While elevated chloride levels were also found in shallower wells (<100 m depth), chloride and arsenic showed no relationship, indicating different modes of origin. The lack of correlation between As and salinity was also shown in prior work in the region (Buschmann et al., 2008).

Previous studies conducted in the region have suggested that As released from the delta sediments is due to the reductive dissolution of the iron bearing minerals (Berg et al., 2001; Winkel et al., 2011; Nguyen and Itoi, 2009). The As contents of groundwater in our study were consistently associated with low Eh values (approximately −100 mv), which infer reducing conditions (Fig. 5). It has been demonstrated that during sediment transport under oxic conditions, oxyanion As species are bound to Fe-oxides, peat, clay, and other humic substances. Under the delta reducing conditions however, As is mobilized to the ambient groundwater (Berg et al., 2001, 2008; Bissen and Frimmel, 2003; Harvey et al., 2002; Nguyen and Itoi, 2009; Nickson et al., 1998; Polizzotto et al., 2005). Groundwater from the Northern sub-group tends to be less anoxic with higher Eh values and lower pH levels relative to the As-rich Southern sub-group (Fig. 6).

Arsenic in the studied groundwater was composed of a mixture of As(III) and As(V) species, as determined by analytical As speciation. On average, As III) constituted 79% of the total As, while As(V) contributed of only 21% of the total As; no differences in As species distribution were observed between the Northern and Southern sub-areas. This trend is similar to previous reports conducted in the Red River Delta which found that As(III) constituted 90% of the total As (Nguyen et al., 2009).

Table 1
Arsenic, chloride, redox state, and pH data of the wells investigated in this study.

Well ID	As (ppb)	Cl (ppm)	Eh (mv)	pH
DT7	563.9	107.0	−126	6.78
DT6	0.5	56.1	142	6.71
DT5	0.7	46.8	199	7.04
DT3	0.4	345.2	169	6.44
DT4	0.1	500.1	165	6.51
DT2	1.8	632.8	101	6.66
DT1	13.1	19.7	97	7.75
TB11	462.3	9.2	−114	6.92
TB18	155.7	25.9	−72	6.52
TB9	187.6	12.8	−128	6.94
TB2	850.4	10.5	−133	7.14
TB24	370.4	13.9	−90	7.15
TB26	139.9	13.8	−83	7.43
TB27	77.7	5.4	−33	7.24
TB21	842.1	21.1	−105	6.88
TB1	276.8	19.6	−92	6.85
TB10	377.3	8.2	−129	6.79
TB25	272.9	11.9	−104	7.20
TB13	746.0	72.7	−125	7.16
TB22	311.0	13.5	−130	6.63
TB15	937.7	19.3	−110	7.04
TB16	314.5	25.8	−115	6.74
TB20	746.3	6.9	−139	6.61
TB23	270.0	12.7	−110	7.01
TB17	224.2	21.5	−126	6.46
TB3	727.0	10.8	−136	7.14
TB12	931.5	2.9	−125	7.03
TB14	747.7	63.4	−115	7.15
TB5	416.3	bdl[a]	−60	7.69
TB4	360.3	42.9	−130	7.34
TB6	315.5	61.2	−111	7.36
TB7	101.1	42.7	−28	7.30
TB8	237.6	124.4	−98	7.17
TB19	300.3	160.3	−120	6.68
TBE10	700.4	81.4	−108	7.07
TBE8	125.1	18.2	−120	6.96
TBE9	196.2	986.6	−110	6.72
TBE7	166.3	20.0	−84	7.16
TBE4	4.4	1499.6	82	6.09
TBE5	981.4	60.4	−110	6.87
TBE3	6.8	2.7	158	7.17
TBE1	6.6	61.7	126	7.10
TBE11	5.3	12.2	60	7.16
TBE6	3.2	1527.0	149	6.73
TH16	0.4	173.6	157	6.14
TH9	0.2	275.3	253	5.84
TH13	bdl[a]	22.7	194	6.19
TH14	0.3	113.6	184	6.02
TH22	0.1	228.1	226	6.50
TH21	0.3	89.9	169	6.10
TH5	0.8	742.1	251	5.83
TH12	2.3	182.7	127	6.31
TH15	8.4	27.5	60	6.18
TH1	6.0	544.4	210	6.08
TH10	3.2	277.3	231	6.00
TH2	2.0	487.6	130	5.87
TH23	0.2	158.5	175	6.04
TH3	1.5	560.2	261	6.00
TH4	2.6	21.4	80	5.99
TH11	8.9	479.8	158	6.56
TH18	3.6	335.6	181	6.29
TH8	6.0	253.2	235	5.85
TH7	0.7	122.3	162	6.29
TH6	bdl[a]	242.8	200	6.19
TH17	22.2	40.5	−13	7.03
TH19	17.5	57.3	145	7.39
TH20	2.4	bdl[a]	24	6.51

[a] bdl: below detection limit.

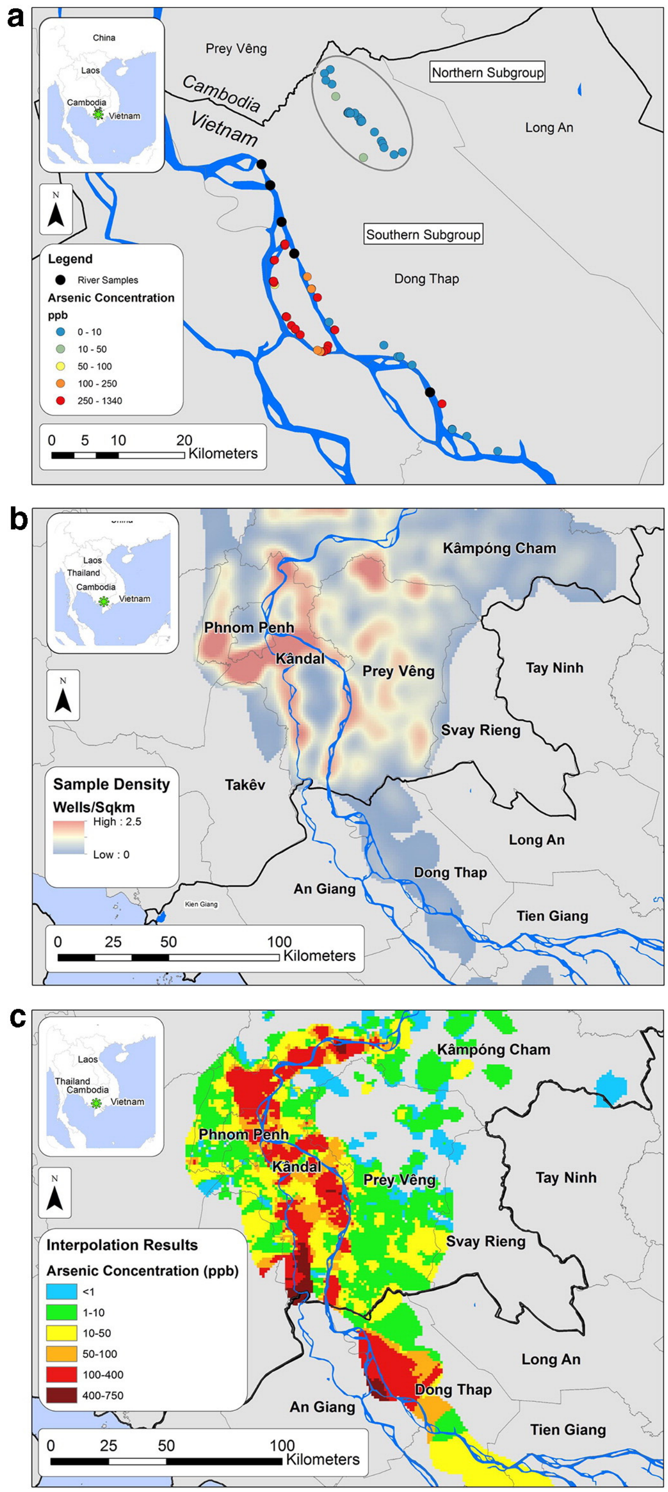

Fig. 1. a) **Arsenic variations in sampling sites of this study**. Samples were divided into two sub-groups: 1) Northern sub-group located away from the Mekong River with lower As concentrations, and (2) Southern sub-group located closer to the Mekong River with much higher As concentrations. b) **Sample density of data points collected from multiple research studies** (Buschmann et al., 2007, 2008; Nguyen and Itoi, 2009; NWD, 2014; Papacostas, et al., 2008; Sthiannopkao et al., 2008) **in the Mekong Delta**. c) **Interpolated As concentrations in groundwater across the Mekong Delta based on this and previous studies**.

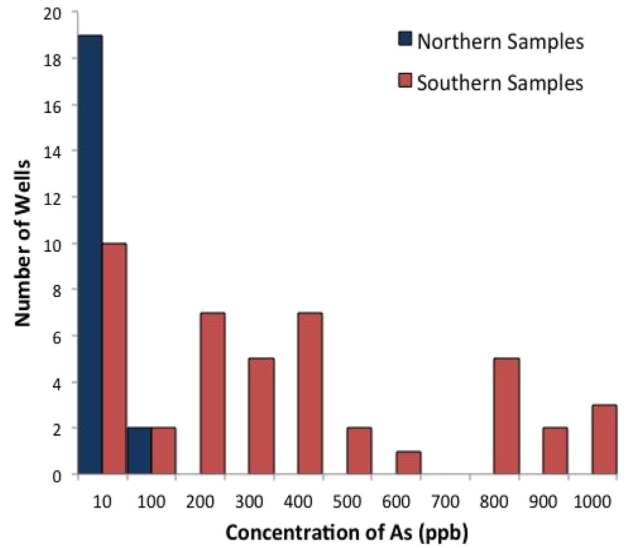

Fig. 2. Histogram of As concentrations in the Northern and Southern groundwater sub-groups. Fifty-three percent of all wells had As content above the WHO's 10 ppb recommend drinking water limit. Most of the higher concentrations were found in the Southern group.

3.2. Arsenic occurrence in groundwater from other areas of the Mekong Delta

A literature review (Buschmann et al., 2007, 2008; Nguyen and Itoi, 2009; NWD, 2014; Papacostas et al., 2008; Sthiannopkao et al., 2008) was used to compile a large water quality database ($n = 7346$) and to integrate the As data distribution in groundwater across Mekong Delta region from Vietnam and Cambodia (Fig. 1b and c). A density map of the distribution of wells shows that more wells have been investigated in Cambodia compared to Vietnam, particularly in the Phnom Penh region (Fig. 1b). Fig. 1c illustrates the distribution of As contents in the groundwater and shows the proximity of the high-As groundwater to the Mekong River.

While the highest As values are found closest to the Mekong River, measureable As levels (>1 ppb) were recorded in almost all the

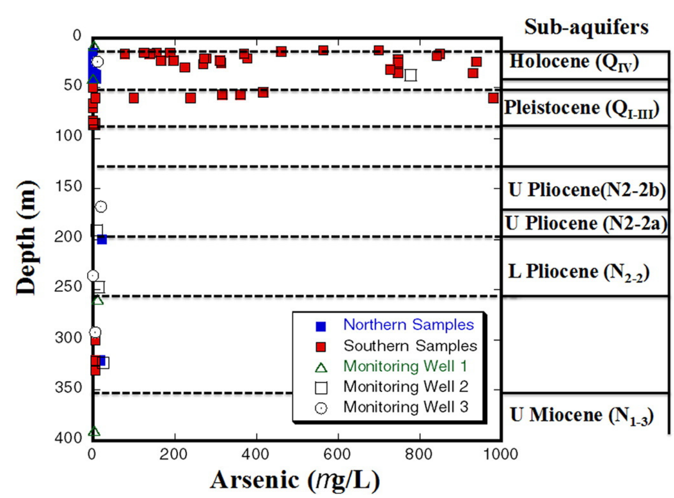

Fig. 3. Depth of wells versus arsenic concentration in groundwater in the study area. Water samples were sorted by the location (Northern and Southern) and type of the wells. The depth of groundwater from the pumping wells from the Northern and Southern sites refers to the overall well depth while the three monitoring wells represent separated piezometers that were drilled into different depths in the aquifer. The water sample depths are compared to the approximate depths of the different sub-aquifers in the Mekong Delta region (DWRPIS, 1992).

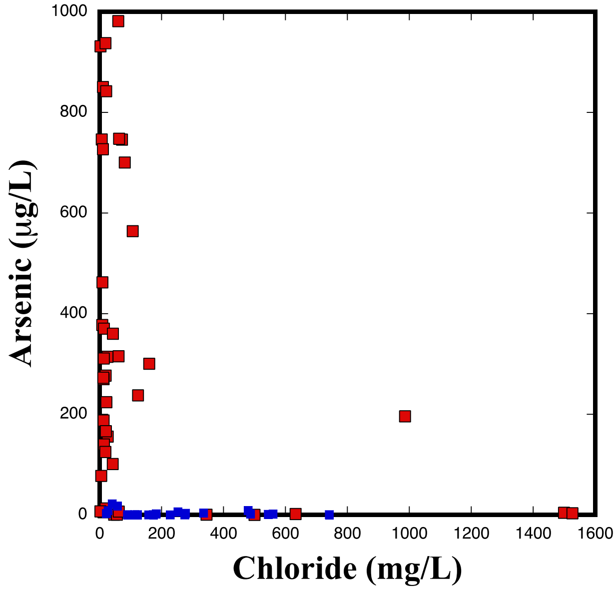

Fig. 4. Arsenic versus chloride concentrations in the study groundwater, sorted by the groundwater location. Groundwater from the southern area (red squares) was characterized by higher arsenic relative to the northern area (blue squares). No correlation between arsenic and salinity was observed although water with high salinity had typically lower As. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

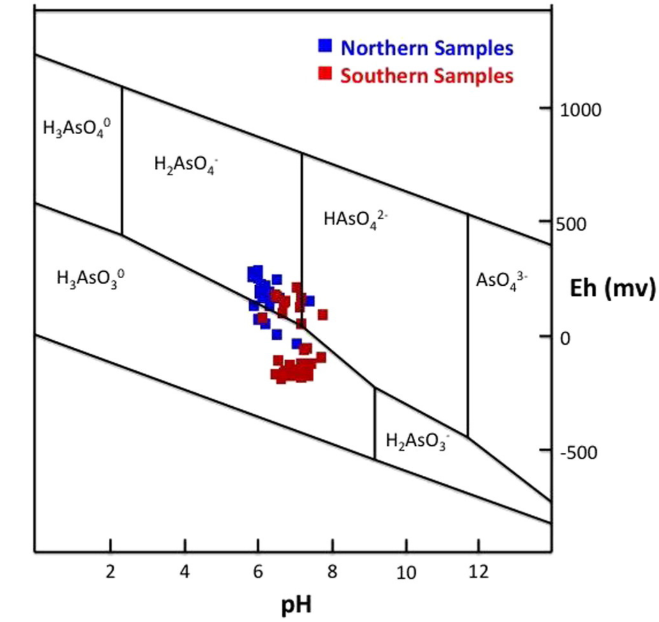

Fig. 6. Redox potential measured by Eh (v) versus pH of groundwater in the study area, sorted by their location. Groundwater from the Northern sub-group (blue squares) was less anoxic (higher Eh values) in contrast to samples from the Southern sub-group (red squares). The Southern sub-group groundwater was more anoxic and had higher As concentration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

groundwater samples in the database. Table 2 shows that the average As value decreases with distance from the Mekong River. Within 1 km from the river the average As concentration is ~133 ppb. On average, groundwater within 10 km of the Mekong River had As contents above the WHO's 10 ppb limit, while groundwater located farther away had lower concentrations.

Combining the interpolated As concentration map with population data (CIESIN, 2014) suggests that approximately 12.7 million people in the region are living in areas with average As-groundwater concentrations above the WHO's 10 ppb level, while an additional 4.12 million people are consuming As concentrations above 1 ppb but below 10 ppb.

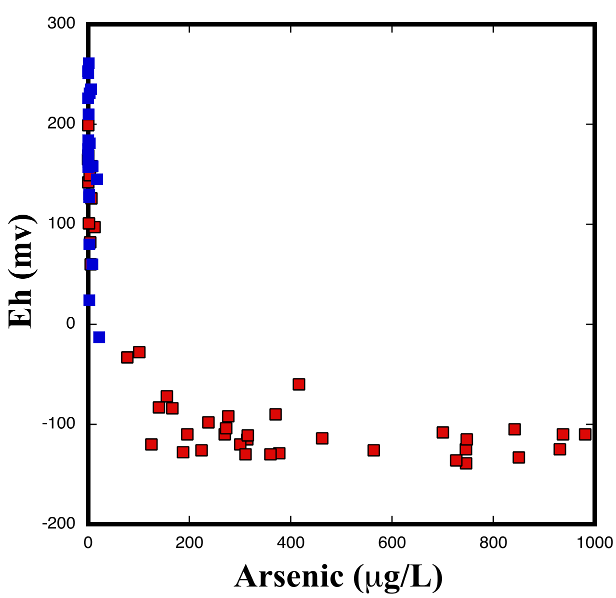

Fig. 5. Redox potential measured by Eh (mv) versus arsenic concentrations in groundwater samples collected in this study, sorted by the groundwater location. Arsenic concentrations were the highest in groundwater with negative Eh values, which reflects anoxic conditions mostly in the southern area (red squares) relative to the northern area (blue squares). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.3. Arsenic in nails from exposed population

A total of 65 individuals donated nails (26 males; 39 females), while only 45 of those completed the accompanying survey. Gender was recorded regardless of survey completion. The average age of all participants was 45 years old ($n = 43$) (mean male age was 51; mean female age was 41). Only 4 minors (defined as participants under 18 years old), 2 males and 2 females, participated in the survey and nail donation. All participants reported living in their current home for at least one year, which negates concerns about capturing exposures from other locations. On average the participants lived in their current home for 20 years with residence times ranging from 1 to 74 years.

Arsenic concentrations in nails were significantly correlated to As concentrations in drinking water ($r = 0.49$, $R^2 = 0.24$, $p < 0.001$; Fig. 7). Previous studies have shown that there may be a threshold level at which As begins accumulating in the nail (Karagas et al., 2000; Merola et al., 2013). Successive linear regressions were preformed to determine if this trend was present in this dataset. Changes in both

Table 2
Average arsenic concentrations in groundwater from different areal segments sorted by the distance from the Mekong River. Data were collected from the literature (Buschmann et al., 2007, 2008; Nguyen and Itoi, 2009; NWD, 2014; Papacostas et al., 2008; Sthiannopkao et al., 2008).

Average As concentration (ppb)	Distance from Mekong River (km)
132.9	0–1 km
128.2	1–2 km
107.6	2–3 km
103.6	3–4 km
84.1	4–5 km
17.3	5–10 km
5.3	10–15 km
3.9	15–20 km
4.4	20+ km

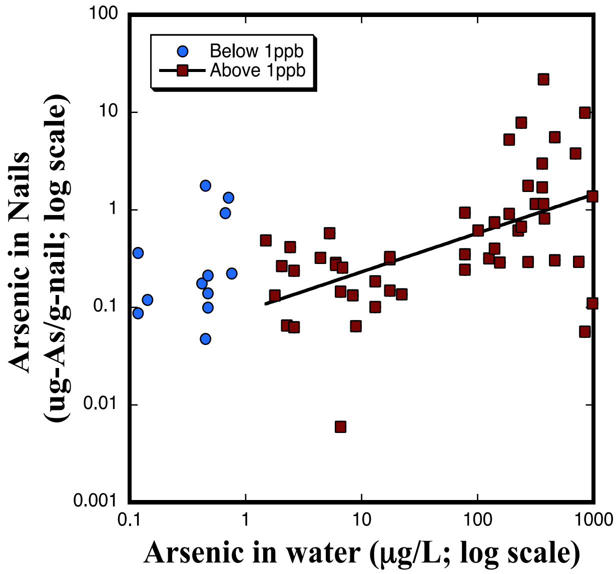

Fig. 7. Nail–As concentrations (μg-As/g-nail, log scale) versus arsenic concentration in drinking water (ppb; log scale). Nail–As values are significantly correlated with arsenic concentrations in drinking water ($r = 0.49$, $p < 0.001$). Dark squares are nail–water pairs measured in groundwater with As content above 1 ppb, while blue circles are pairs in groundwater with As below 1 ppb. The correlation between As-nail and As-water improves when only samples above 1 ppb were considered ($r = 0.56$, $p < 0.001$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the correlation coefficient and slope variable were considered when the samples below certain thresholds were removed from the dataset. The threshold at which the correlation was maximized was 1 ppb ($r = 0.56$, $R^2 = 0.31$, $p < 0.001$), which agrees with Karagas et al. (2000). The data show no nail-As concentration differences based on age or gender, however as there were only 4 minors enrolled in the study, this dataset does not have the power to evaluate differences in nail concentrations as a result of age.

3.4. Water treatment and consumption

Diet, water consumption, filtration systems, and occupational information were collected from the participants to evaluate the effect they might have on As exposure (Table 3). To evaluate the possible differential As bioaccumulation, we normalized the As content in the nail to As level of co-existing groundwater. The differential As bioaccumulation factor (χ) is defined as χ = nail concentrations (μg-As/g-nail) divided by As in groundwater (ppb). Thirty-one participants reported their occupation; these were regrouped into two categories: (1) an outdoor exposure group ($n = 18$); and (2) an indoor exposure group ($n = 10$). Individuals working outdoors may consume more water and have a greater potential for As exposure. The outdoor exposure group included farmers, laborers and livestock tenders, whereas the indoor exposure group included homemakers, teachers and a student. Results indicated that the outdoor exposure group had a high bioaccumulation factor (mean $\chi = 0.47$), while the indoor exposure group had a much lower value (mean $\chi = 0.05$; $p = 0.067$).

Most individuals were not using any treatment for the water they consumed ($n = 28$). Testing sand filtration systems in other parts of Vietnam have found 90% removal of the total As in drinking water (Nguyen et al., 2009; Berg et al., 2006). In our study, 25% of households used some form of treatment ($n = 7$). Treatment methods varied and included: carbon filters, settling and boiling combinations, and sand filters. Considering the treatment availability for the investigated household, the average As bioaccumulation factor for individuals not using any treatment was much higher ($\chi = 0.32$) relative to those with treatment ($\chi = 0.03$; $p = 0.057$). To further investigate this relationship, we

Table 3
Variations of As-nails to As-water ratios (bioaccumulation factor) in residents from the Mekong Delta sorted by different social and behavior factors.

Variable	High exposure population (χ)	Low exposure population (χ)	p level
Occupation	Outdoor exposure group 0.47 $n = 18$	Low exposure group 0.05 $n = 10$	$p = 0.067$
Household Treatment	No treatment 0.32 $n = 28$	Some treatment 0.03 $n = 7$	$p = 0.057$
Personal water consumption habits	High exposure group 0.33 $n = 31$	Low exposure group 0.02 $n = 9$	$p = 0.03$
Seafood consumption	Frequent consumption 0.38 $n = 28$	Limited consumption 0.02 $n = 10$	$p = 0.02$
Meat consumption	Frequent consumption 0.01 $n = 19$	Limited consumption 0.50 $n = 21$	$p = 0.02$
Milk consumption	Frequent consumption 0.02 $n = 8$	Limited consumption 0.31 $n = 34$	$p = 0.03$

evaluated the personal water consumption habits and compared the nail concentrations for individuals who reported only consuming unfiltered well water (exposed group) versus individuals who reported drinking filtered well water, occasional use of city water, or use of bottled water (unexposed group). The difference between these two groups was statistically significant ($p = 0.03$); the average bioaccumulation factor for the exposed group was much higher ($\chi = 0.33$) compared to the unexposed group ($\chi = 0.02$). In sum, our data show that evaluation of As exposure requires a careful examination of the personal drinking habits that could mask the overall correlation between As in nail versus As in drinking water.

3.5. Diet

When conceptualizing As exposure it is important to consider confounding issues that might arbitrarily raise or lower As values in the nails. Important variables include age, gender, race, volume of water consumed, source of water, treated versus untreated water consumption, and dietary factors. Diet is of particular interest when understanding exposure because of the complexity it adds to understanding the effects. Studies have shown that increased consumption of animal proteins, folic acid, calcium, and vitamin A is associated with a decrease in As induced skin lesions (Anetor et al., 2007; Mitra et al., 2004; Pierce et al., 2011; Zablotska et al., 2008). Merola et al. (2013)) showed an inverse trend between As concentration in nails and greater rates of animal protein consumption. It has been suggested that increasing the consumption of these nutrients may increase the rate at which As can be metabolized in the body, eliminating it faster and therefore buffering against negative health effects (Brima et al., 2006; Pierce et al., 2011; Mitra et al., 2004).

The participants were asked to report the frequency of consumption of foods that may affect As metabolism and therefore concentration in nails. In particular, we focused on seafood, meat, and milk consumption. Increased seafood consumption was found to correspond with an increase in nail-As concentration, likely from the organic As in seafood. Twenty-eight participants reported consuming seafood daily, while 10 participants stated less frequent seafood consumption (between 1 and 3 times per week). The mean seafood consumption rate was 5 times per week. The average As bioaccumulation factor for those consuming seafood daily was higher ($\chi = 0.38$) than those with less frequent seafood consumption ($\chi = 0.01$; $p = 0.02$). This artificial increase in As may not have any effect on the health of the participants since the As consumed would predominately be organic As instead of the more toxic inorganic form, but it highlights the sensitivity nails have in monitoring As exposure.

Increased meat consumption has been linked with a decrease in As related health problems, by increasing the amount of glutathione in the body that aides in As removal (Mitra et al., 2004; Pierce et al., 2011; Scott et al., 1993). The participants were categorized into two exposure groups (1) a high meat consumption group that was defined as consuming meat at least 2–3 times per week or more ($n = 19$); and (2) a low meat consumption group defined as consuming meat once per week or less ($n = 21$). On average the participants in our study consumed meat twice per week. The participants who consumed meat more frequently had statistically significant lower As-nail/As-water ratios compared to those who consumed meat less frequently ($p = 0.02$). The average As bioaccumulation factor for those in the high meat consumption group was 0.01 relative to 0.50 in the low-meat consumption group.

Calcium, like animal protein consumption, has been shown to have an inverse correlation with negative health outcomes related to As consumption (Mitra et al., 2004). To evaluate calcium intake we surveyed milk consumption among the participants. On average, the participants in our study reported consuming milk approximately twice per month (median was no milk consumption). Thirty-four participants reported no milk consumption, while 8 participants reported milk consumption rates ranging from daily to less than once per month. Here again, we show the effect on As bioaccumulation; the difference in the As bioaccumulation factor was statistically significant ($p = 0.03$) with higher levels for those not consuming milk (mean $\chi = 0.31$; $n = 34$) relative to those who consumed milk with lower As bioaccumulation (mean $\chi = 0.02$; $n = 8$). These results highlight the important role diet may play on the exposure and regulation of As metabolism.

It is important to note that the bioaccumulation factor values for the specific yet different exposure groups we identified were similar ($\chi \sim 0.3$) and higher by a factor of 10 relative to the non-exposed groups. Since the bioaccumulation factor is the slope of the relationship between As in nails to As in drinking water, we propose that this slope can be used to delineate the selective bioaccumulation of exposed and/or higher risk groups relative to the rest of the populations. Thus As content in nails could represent not only the overall exposure of populations to As in drinking water, but can also detect specific populations with higher bioaccumulation factors and thus higher risks. While the overall slope of As-nail to As-water in the entire population was 0.003, the higher exposed and/or less preferred nutrition groups had a higher slope value of ~0.3.

3.6. Health

As part of our study, the participants were asked to report health issues including the occurrence of skin rashes, upper and lower abdominal pains, changes in hearing or vision, numbness or tingling in the extremities, breathing problems, joint pain, delays in wound healing, speed of hair growth, tiredness, and frequency of diarrhea. In total, 13 health variables were collected; a positive response was defined when participants reported no problem with the health issue in question, while a negative response was defined when the participants reported suffering from the particular health issues. On average, each participant ($n = 41$) reported 2.5 negative health responses; the participants' responses ranged from no negative health issues to up to 6 negative health issues. While the nail-As values have no direct relationship to disease occurrence, the data show a general trend of higher As-nail to As-water ratios in individuals reporting some negative health outcomes (Table 4). We show that As bioaccumulation factor in nails was higher (with varying degrees of statistical significance) among individuals reporting skin changes and rashes, lower abdominal pain, upper abdominal pain, vision changes, numbness, and joint pain. While these responses were not significant at the 95% confidence interval, most were significant at the 70–80% confidence interval or greater (Table 4). In contrast, no correlations were observed between the As bioaccumulation factor and health issues of hearing loss, breathing difficulty, the rate of wound healing, speed of hair growth, tiredness, and diarrhea. A major hindrance was the small number of individuals in each sub-group reporting these health issues, however we believe that this potential relationship is incredibly important, additionally validates the strength of using nails as a biomarker of As exposure, and should be further investigated.

Table 4
Relationship between health outcomes that were self-reported by participants in the survey and As-nail to As-water ratios measured in residents from the Mekong Delta.

	Mean χ	Mean χ	p level
	No effect reported	Effect reported	
Health outcomes with relationship to χ			
Skin changes	No changes 0.196 $n = 33$	Changes 0.826 $n = 5$	$p = 0.234$
Abdominal pain	No pain 0.192 $n = 30$	Pain 0.695 $n = 7$	$p = 0.203$
Upper abdominal pain	No pain 0.285 $n = 26$	Pain 0.354 $n = 9$	$p = 0.429$
Vision	No vision changes 0.199 $n = 26$	Vision loss 0.469 $n = 10$	$p = 0.230$
Numbness	No numbness 0.206 $n = 24$	Numbness 0.514 $n = 11$	$p = 0.183$
Joint pain	No pain 0.295 $n = 28$	Pain 0.463 $n = 5$	$p = 0.306$
Health outcomes with inverse or no relationship to χ			
Wound	Heal normally 0.416 $n = 23$	Delayed healing 0.061 $n = 17$	$p = 0.059$
Hair growth	Normal 0.308 $n = 31$	Slow 0.122 $n = 9$	$p = 0.154$
Tiredness	Normal 0.300 $n = 29$	Unusually tired 0.178 $n = 11$	$p = 0.283$
Diarrhea	None reported 0.332 $n = 31$	Frequent 0.066 $n = 5$	$p = 0.065$
Hearing	No hearing loss 0.307 $n = 32$	Hearing loss 0.014 $n = 4$	$p = 0.036$
Breathing problems	No problems 0.380 $n = 27$	Trouble breathing 0.040 $n = 9$	$p = 0.039$

3.7. Study limitations

There are several important limitations to this study that should be considered. The nail digestion method used provides total-As values and does not allow us to differentiate between organic-As, which is non-toxic and inorganic-As. This challenge is particularly problematic with regard to populations consuming seafood, which can be a significant source of organic-As in the body (Gebel, 2000; Liao et al., 2008; Phan et al., 2013; Spayd et al., 2012). Our study attempted to achieve a precursory understanding of this relationship but more work needs to be done in this area. While we have identified increased As levels in individuals consuming seafood more frequently, this As is likely organic-As and therefore non-toxic. A more detailed food consumption survey of a larger population would solve the potential confounding of seafood and meat as distinct variables. The participants were not required to answer all survey questions; all participants who chose to answer questions regarding seafood ingestion, reported at least some level of consumption. This study only captured the frequency, but not the quantity of food consumption. Therefore an individual consuming seafood for three meals a day, everyday, would be categorized the same as an individual consuming seafood once a day and the ability to quantify As bioaccumulation from seafood consumption is not possible. The same problem exists for meat and milk consumption. This study is an important step in identifying potential relationships but future studies should further investigate the relationships of As bioaccumulation, diet, and health.

Rice is a well-documented contributor of inorganic-As to the diet, and several studies have estimated the percent contribution of As from rice in the diet (Agusa et al., 2009; Hanh et al., 2011; Phan et al., 2013). In the Red River Delta, Agusa et al. (2009) estimated that diet contributes 9% of total As exposure. It should be noted however that in individuals consuming drinking water with low to moderate As concentrations, the percent contribution from rice increases dramatically (Hanh et al., 2011). Rice consumption was ubiquitous in the study population, however rice ingestion rates were not obtained as part of our surveys. While this study assumed rice consumption to be approximately equal across our study participants, future investigations should include also the quantity of rice consumed with respect to As bioaccumulation as measured in the exposed populations.

4. Conclusions

Our study shows that approximately 16 million people living in the Mekong Delta in Vietnam and Cambodia are at risk for elevated levels of As in their drinking water. Most of the As occurs in shallow and reduced groundwater, which is common in many deltaic aquifer environments of southeast Asia (Harvey et al., 2002; Nickson et al., 1998; Polizzotto et al., 2005). Populations living closer to the Mekong River have the greatest risk of exposure to elevated As, yet As levels in groundwater above 1 ppb were found in areas over 20 km away from the Mekong River. The positive correlation between As in nails and As in water ($r = 0.49$, $p < 0.001$; Fig. 7) clearly shows bioaccumulation of As in residents in the area, including those who consume drinking water with As concentrations below the WHO's limit of 10 ppb. Consequently, our data show that bioaccumulation of As is occurring for all populations in the region who consume groundwater, including those who are consuming levels considered safe (the range of 1 ppb to 10 ppb). We use the ratios of As-nail to As-water to evaluate the differential As bioaccumulation in the local population. The data show higher As-nail to As-water ratios (~0.3) in sub-groups with higher potential exposure (i.e.; water use, occupation, diet). We propose that the measurement of As in the nails could be used for delineating specific and vulnerable exposed populations with higher risks for As bioaccumulation relative to the rest of the population. Our results show differential As bioaccumulation on the local population based on occupation, diet (more bioaccumulation for seafood, less accumulation for meat (protein) and milk (calcium)), and water treatment. These observations indicate that the exposure of the local population to As in their drinking water could be reduced through treatment of the groundwater, dietary changes, and targeting specific occupations. A reduction in the As bioaccumulation could help mitigate the negative health issues caused by long-term exposure to As in drinking water in the Mekong Delta.

Conflict of interest

All authors declare no actual or potential conflict of interest including any financial, personal or other relationships with other people or organizations within three years of beginning the submitted work that could inappropriately influence, or be perceived to influence, their work.

Submission declaration

We declare that this work has not been previously published and is not under consideration for publication elsewhere. Its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere including electronically in the same form, in English or any other language, without the written consent of the copyright-holder.

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References

Agusa, T., Kunito, T., Minh, T.B., Trang, P.T.K., Iwata, H., Viet, P.H., et al., 2009. Relationship of urinary arsenic metabolite to intake estimates in residents of the Red River Delta, Vietnam. Environ. Pollut. 157, 396–403.

Anetor, J.I., Wanibuchi, H., Fukushima, S., 2007. Arsenic exposure and its health effects and risk of cancer in developing countries: micronutrients as host defence. Asian Pac. J. Cancer Prev. 8, 13–23.

Bednar, A.J., Garbarino, J.R., Ranville, J.F., Wildeman, T.R., 2002. Preserving the distribution of inorganic arsenic species in groundwater and acid mine drainage samples. Environ. Sci. Technol. 36, 2213–2218.

Berg, M., Tran, H.C., Nguyen, T.C., Pham, H.V., Schertenleib, R., Giger, W., 2001. Arsenic contamination of groundwater and drinking water in Vietnam: a human health threat. Environ. Sci. Technol. 35, 2621–2626.

Berg, M., Luzi, S., Trang, P.T.K., Viet, P.H., Giger, W., Stuben, D., 2006. Arsenic removal from groundwater by household sand filters: comparative field study, model calculations, and health benefits. Environ. Sci. Technol. 40, 5567–5573.

Berg, M., Stengel, C., Trang, P.T.K., Viet, P.H., Sampson, M., Leng, M., et al., 2007. Magnitude of arsenic pollution in the Mekong and Red River Deltas — Cambodia and Vietnam. Sci. Total Environ. 372, 413–425.

Berg, M., Trang, P.T.K., Stengel, C., Buschmann, J., Viet, P.H., Dan, N.V., et al., 2008. Hydrological and sedimentary controls leading to arsenic contamination of groundwater in the Hanoi area, Vietnam: the impact of iron-arsenic ratios, peat, river bank deposits, and excessive groundwater abstraction. Chem. Geol. 249, 91–112.

Bissen, M., Frimmel, F.H., 2003. Arsenic — a review. Part 1. Occurrence, toxicity, speciation, mobility. Acta Hydrochim. Hydrobiol. 31, 9–18.

Brima, E.I., Haris, P.I., Jenkins, R.O., Polya, D.A., Gault, A.G., Harrington, C.F., 2006. Understanding arsenic metabolism through a comparative study of arsenic levels in the urine, hair and fingernails of health volunteers from three unexposed ethnic groups in the United Kingdom. Toxicol. Appl. Pharmacol. 216, 122–130.

Buschmann, J., Berg, M., 2009. Impact of sulfate reduction on the scale of arsenic contamination in groundwater of the Mekong, Bengal and Red River deltas. Appl. Geochem. 24, 1278–1286.

Buschmann, J., Berg, M., Stengel, C., Sampson, M., 2007. Arsenic and manganese contamination of drinking water resources in Cambodia: coincidence of risk areas with low relief topography. Environ. Sci. Technol. 41, 2146–2152.

Buschmann, J., Berg, M., Stengel, C., Winkel, L., Sampson, M., Tran, P.T.K., Viet, P.H., 2008. Contamination of drinking water resources in the Mekong delta floodplains: arsenic and other trace metals pose serious health risks to population. Environ. Int. 34, 756–764.

Center for International Earth Science Information Network (CIESIN), 2014. Columbia University and Centro Internacional de Agricultura Tropical. CIAT 2005. Gridded Population of the World, Version 3 (GPWv3): Population Density Grid. NASA

Socioeconomic Data and Applications Center (SEDAC), Palisades, NY (http://sedac.ciesin.columbia.edu/data/set/gpw-v3-population-density. Accessed 7 January 2014).
Chen, K.L.B., Amarasiriwardena, C.H., Christiani, D.C., 1999. Determination of total arsenic concentrations in nails by inductively coupled plasma mass spectrometry. Biol. Trace Elem. Res. 67, 109–125.
Division for water resources planning and investigation for the south of VietNam (DWRPIS), 1992. Hydrogeological Material.
Fendorf, S., Michael, H., van Geen, A., 2010. Spatial and temporal variations of groundwater arsenic in South and Southeast Asia. Science 328, 1123–1127.
Gebel, T., 2000. Confounding variables in the environmental toxicology of arsenic. Toxicology 144, 155–162.
Hanh, H.T., Kim, K.W., Bang, S., Hoa, N.M., 2011. Community exposure to arsenic in the Mekong River Delta, Southern Vietnam. J. Environ. Monit. 13, 2025–2032.
Harvey, C., Swartz, C., Badruzzaman, A., Keon-Blute, N., Yu, W., Ali, M., et al., 2002. Arsenic mobility and groundwater extraction in Bangladesh. Science 298, 1602–1606.
Karagas, M.R., Morris, J.S., Weiss, J.E., Spate, V., Baskett, C., Greenberg, E.R., 1996. Toenail samples as an indicator of drinking water arsenic exposure. Cancer Epidemiol. Biomarkers Prev. 5, 849–852.
Karagas, M.R., Tosteson, T.D., Blum, J., Klaue, B., Weiss, J., Stannard, V., et al., 2000. Measurement on low levels of arsenic exposure: a comparison of water and toenail concentrations. Am. J. Epidemiol. 152, 84–90.
Liao, C.M., Shen, H.H., Lin, T.L., Chen, S.C., Chen, C.L., Hsu, L.I., et al., 2008. Arsenic cancer risk posed to human health from tilapia consumption in Taiwan. Ecotoxicol. Environ. Saf. 70, 27–37.
Merola, R.B., Kravchenko, J., Rango, T., Vengosh, A., 2013. Arsenic exposure of rural populations from the Rift Valley of Ethiopia as monitored by keratin in toenails. J. Expo. Anal. Environ. Epidemiol. 24, 121–126.
Mitra, S.R., Mazumder, D.N., Basu, A., Block, A., Haque, R., Samanta, S., et al., 2004. Nutritional factors and susceptibility to arsenic-caused skin lesions in West Bengal, India. Environ. Health Perspect. 112, 1104–1109.
(NWD (National Wellmap Database), 2014. Cambodian Ministry of Rural Development. http://www.cambodiawellmap.com/.
Nguyen, K.P., Itoi, R., 2009. Source and release mechanism of arsenic in aquifers of the Mekong Delta, Vietnam. J. Contam. Hydrol. 103, 58–69.
Nguyen, V.A., Bang, S., Viet, P.H., Kim, K.W., 2009. Contamination of groundwater and risk assessment for arsenic exposure in Ha Nam province, Vietnam. Environ. Int. 35, 466–472.
Nickson, R., McArthur, J., Burgess, W., Ahmed, K.M., Ravenscroft, P., Rahman, M., 1998. Arsenic poisoning of Bangladesh groundwater. Nature 395, 338.
Papacostas, N.C., Bostick, B.C., Quicksall, A.N., Landis, J.D., Sampson, M., 2008. Geomorphic controls on groundwater arsenic distribution in the Mekong River Delta, Cambodia. Geology 36, 891–894.
Phan, K., Sthiannopkao, S., Heng, S., Phan, S., Huoy, L., Wong, M.H., et al., 2013. Arsenic contamination in the food chain and its risk assessment of populations residing in the Mekong River basin of Cambodia. J. Hazard. Mater. 262, 1064–1071.
Pierce, B.L., Argos, M., Chen, Y., Melkonian, S., Parvez, F., Islam, T., et al., 2011. Arsenic exposure, dietary patterns and skin lesion risk in Bangladesh: a prospective study. Am. J. Epidemiol. 173, 345–354.
Polizzotto, M., Harvey, C., Sutton, S., Fendorf, S., 2005. Processes conducive to the release and transport of arsenic into aquifers of Bangladesh. PNAS 102, 18819–18823.
Quicksall, A.N., Bostick, B.C., Sampson, M.L., 2008. Linking organic matter deposition and iron mineral transformations to groundwater arsenic levels in the Mekong delta, Cambodia. Appl. Geochem. 23, 3088–3098.
Rowland, H.A.L., Gault, A.G., Lythgoe, P., Polya, D.A., 2008. Geochemistry of aquifer sediments and arsenic-rich groundwaters from Kandal Province, Cambodia. Appl. Geochem. 23, 3029–3046.
Ruhl, L., Vengosh, A., Dwyer, G.S., Hsu-Kim, H., Deonarine, A., 2010. Environmental impacts of the coal ass spill in Kingston, Tennessee: an 18-month survey. Environ. Sci. Technol. 44, 9272–9278.
Samanta, G., Sharma, R., Roychowdhury, T., Chakraborti, D., 2004. Arsenic and other elements in hair, nails, and skin-scales or arsenic victims in West Bengal, India. Sci. Total Environ. 326, 33–47.
Schroeder, H.A., Balassa, J.J., 1966. Abnormal trace metals in man: arsenic. J. Chronic Dis. 19, 85–106.
Scott, N., Hatlelid, K., MacKenzie, N., Carter, D., 1993. Reactions of arsenic(III) and arsenic(V) species with glutathione. Chem. Res. Toxicol. 6, 102–106.
Slotnick, M.J., Nriagu, J.O., 2006. Validity of human nails as a biomarker of arsenic and selenium exposure: a review. Environ. Res. 102, 125–139.
Spayd, S.E., Robson, M.G., Xie, R., Buckley, B.T., 2012. Importance of arsenic speciation in populations exposed to arsenic in drinking water. Hum. Ecol. Risk. Assess. 18, 1271–1291.
Sthiannopkao, S., Kim, K.W., Sotham, S., Choup, S., 2008. Arsenic and manganese in tube well waters of Prey Veng and Kendal Provinces, Cambodia. Appl. Geochem. 23, 1086–1093.
Stollenwerk, K., Breit, G., Welch, A., Yount, J., Witney, J., Foster, A., et al., 2007. Arsenic attenuation by oxidized aquifer sediments in Bangladesh. Sci. Total Environ. 379, 133–150.
US Geological Survey (USGS), 2011. National Field Manual for the Collection of Water Quality Data. US Geological Survey, Washington, DC.
Van, T.V., 2004. Geological survey, utilization and state management of groundwater in Vietnam. Coordinating Committee for Geoscience Programs in Ease and Southeast Asia (CCOP). 41st CCOP Annual Session 15–18 Nov 2004, Tsukuba, Japan.
Winkel, L.F.E., Trang, P.T.K., Lan, V.M., Stengel, C., Amini, M., Ha, N.T., et al., 2011. Arsenic pollution of groundwater in Vietnam exacerbated by deep aquifer exploitation for more than a century. PNAS 108, 1246–1251.
World Health Organization (WHO), 2011. Guideline for Drinking Water Quality. 4th edn. WHO Press, Geneva, Switzerland.
Yoshida, T., Yamauchi, H., Sun, G.F., 2004. Chronic health effects in people exposed to arsenic via the drinking water: dose–response relationships in review. Toxicol. Appl. Pharmacol. 198, 243–252.
Zablotska, L.B., Chen, Y., Graziano, J.H., Parvez, F., van Geen, A., Howe, G.R., et al., 2008. Protective effects of B vitamins and antioxidants on the risk of arsenic-related skin lesions in Bangladesh. Environ. Health Perspect. 116, 1056–1062.