ARSENIC POLLUTION IN GROUNDWATER IN RED RIVER DELTA, VIETNAM: SITUATION AND HUMAN EXPOSURE

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Abstract

Vietnam is agriculture country with population of above 80 millions, among them some 35 millions inhabitants living at two alluvial deltas namely Red River and Mekong River. Household tube well water extracted from Holocene aquifer is remaining a major drinking source for the farmer there. Arsenic contaminations in tube well water and human burdens were studied at three districts at Red River Delta based on 45 water samples. Among them, Tu Liem district (n=9) appears as non arsenic contaminated area (average 6 μg/L) but nearby, Ly Nhan (n=14), Hoai Duc (n=22) districts are serious arsenic contaminated ones with average concentrations of the toxic element in the tube well water as 435 and 330 μg/L respectively, range from < 1 to 600 μg/L. Total 134 hair and urine samples are collected from residents living at household where the groundwater sampled. The range of arsenic in the hair samples is from < 0.1 to 10.4 mg/kg, with the different average contents according to each district. At none arsenic exposure districts as Tu Liem, the average arsenic concentrations in the human hair are around 0.3 mg/kg. The values of 0.8; 2.5 mg/kg are observed at Ly Nhan and Hoai Duc respectively. The average total arsenic methylates as MMA +DMA recorded at above studied sites are 38, 46 and 99 ng/mg creatinine respectively. The closed relationship between the average concentrations of MMA+DMA in the urine and arsenic in the filtered water is established, $R^2 = 0.997$ but not with raw groundwater $R^2 = 0.1477$.

The positive relation between the arsenic contents in filtered water, hair and total methylated arsenic in urine is observed. Here by, the effect of simple sand filter reducing the arsenic burden in human body is illuminated. The study reveals the need of more intensive screening for arsenic in tube well water at other areas in Vietnam.

Key words: Arsenic; arsenic species; human hair; Red River Delta; removal; sand filter; tube well water; Vietnam.

1. Introduction

Tube wells have been widely used in many developing countries to exploit and supply drinking water for people living far away from the water station. Unfortunately, since the last 10 years, groundwater has been found to be contaminated by arsenic at some areas. The environmental problems from arsenic poisonings were observed in the most populous countries of South Asian region as Bangladesh, India, Vietnam, China, etc. (Berg 2001, Xia 2004, Chowdhury 2000,and Trang 2003). Due to the long-term effects of arsenic to human health even at low-level exposure, the WHO has recommended the arsenic value in drinking water of 10μg/L, Ministry of Health issued the Vietnamese standard for arsenic in drinking water of 10μg/L instead of 50μg/L. Some previous studies on arsenic contamination in groundwater at Vietnam showed a serious situation especially at Red river delta, for example the arsenic average concentration from study of Berg is 159 μg/L (Berg 2001, Trang 2003, Agusa 2006).

In general, human body will excrete a main part of intake arsenic via urine and a small part will be deposed at keratin rich tissue as hair, nail. That is the reason for the using of hair and nail samples as biomarkers for monitoring of arsenic long-term exposure and urine for present exposure. Moreover, arsenic was transformed into derivatives due to the methylation before the elimination from the body. The arsenic methylation patents are different between species and populations. Among the arsenic derivatives found in

human urine, concentrations of inorganic arsenic, monomethylasonic acid (MMA) and dimethylasinic acid (DMA) count in range of 10-30%, 10-20% and 60-70% respectively. The ratio might be changed at different arsenic exposure levels; for instance, Andean female aboriginals in North West Argentina exposure to arsenic with the concentration of 200μg/L in drinking water, but their urine contain inorganic arsenic (25%), DMA (74%) and very little MMA. Whereas, in some studies conducted in several regions in Taiwan, the MMA levels accounted for 20-30% in urine. The nature of inorganic arsenic methylation in body has been a controversial issue and discussed extensively at the present (Vahter 2002, Kitchin 2001, Valenzuela 2005).

Bioactivities of arsenic methylates also have been a concern of scientists (Aposhian 2004, Kitchin 2001). The arsenic methylation has been considered as a detoxification because it changes arsenic from high toxic inorganic forms to low toxic organic ones. However, some recent studies showed that the methylated arsenic might cause cancer as discovered in some experiments on animals (Aposhian 2004, Wanibuchi 2004). In order to provide some eco-toxicology data about arsenic contamination from drinking, a research on distribution of methylated arsenic in urine samples and arsenic accumulation in hair samples was carried out. The study was implemented in some arsenic contaminated areas in Red River Delta, Northern Vietnam.

2. Methods

Sampling procedures

Two arsenic contamination areas are Ly Nhan in Ha Nam province (RU2) and Hoai Duc in Ha Tay province (RU3) were selected. The control site is Tu Liem, Hanoi (RU1). Hair and urine samples were collected simultaneously from the same person. At each family, three to five people are requested to provide bio-samples with consensus. The groundwater from tube wells and drinking water from filtered tank was collected at each family accordingly to the bio-samples. The number of the collected hair and urine samples is 17, 35, and 82 (in RU1-control and RU2 and RU3 - contaminated area respectively). The sampling campaigns were organized at the local health care stations in cooperation with the health workers. The participants are consent to give the sample and the participated percent is about of 85-90% according to the invited number.

Hair and urine samples

Hair behind the scruff and near scalp was cut, stored in tightly closed clean polyethylene bags. Urine samples were stored in new PVC bottles (washed by diluted acid and rinsed by de-ionized Millipore water). Water and hair samples were transferred to the laboratory of Research Center for Environmental Technology and Sustainable Development (CETASD), Hanoi University of Science for analysis. Urine samples were stored at -20oC and analyzed at the laboratory of CMES, Ehime University, Japan.

Water samples

Groundwater from tube well and drinking water from filter tank was collected. The water was filtered by 0.45 μm membrane and stored in new and clean PVC bottles. Concentrated acid HNO_3 was used to acidify the samples to pH <2.

Samples analysis

Analysis of total arsenic in water and hair samples by using HVG-AAS method

Dissolved inorganic arsenic in the water was determined by HVG-AAS method. Arsenic was reduced from As(V) into As(III) by NaI and ascorbic acid solution. As(III) was then converted to vapor AsH_3 by $NaBH_4$ in acidic environment. The generated AsH_3 was quantitatively analyzed by AA-6800 Shimadzu. The calibration curve was established with the concentration range of 1 – 10 μg/L with $R^2 > 0.995$.

The hair samples were soaked with neutral detergent, wash by de-ionized water and dry at 60°C. A portion of 0.3 g the dry hair sample was digested by 3ml HNO_3 65% and 1 ml H_2O_2 30% in microwave oven as referenced at (Flores 2001). The decomposed hair solution was diluted by de-ionized Millipore water, nitro-oxides then eliminated by adding HSO_3NH_2 up to the concentration of 30 mM/L. The further steps will be the same as water samples.

Analysis of arsenic species in urine by using HPLC-ICPMS

The urine samples stored at -20°C were thaw then filtered by 0,25 μm membrane. The urine solutions were diluted 5 times by Millipore water. Arsenic species were analyzed in urine included As(III) (arsenite), MMA (monomethylasonic acid), DMA (dimethylasinic acid), As(V) (arsenate) and AB (arsenobetain). The calibration established by the standard solutions with concentrations of 1, 5, 25, 50, 100 μg/L for the individual arsenic species, correspondingly. Injection volume for the chromatographic analysis is 20 μL. The analysis is carried out by HPLC-ICPMS comprising of LC–10A (Shimadzu) and ICP-MS HP 4500 (Hewlett-Packard). The ion-exchange chromatography column (Hamilton PRP-X100, 25 cm X 4.1 mm id) and the mobile phase of 6.7 mM $NH_4H_2PO_4$ (pH 6.0) with the flow rate of 1.0 ml/m were applied. We also use another ion-exchange chromatography column (Shodex Asahipak ES-502N7C, 10cm X 7.6 mm id) and the mobile phase of 15 mM citric acid (pH 2.0), the flow rate of 1.0 ml/m in order to separate arsenobetaine (AB) from inorganic arsenate (As III). 3 ml urine was sent to other analytical service laboratory in Japan for determination of the creatinine concentrations. The other instrument parameters of HPLC-ICPMS are presented in reference (Kubota 2002).

3. Results and discussion

3.1. Arsenic species in urine and its correlation with arsenic exposure

The chromatographic method separated completely methylated species from the inorganic forms of arsenic and arsenobetaine. Generally, As(V) was found even with low concentration or not detectable by the analytical procedure, thus the total arsenic in urine assumed only included AB, As(III), DMA and MMA. The arsenic concentration in urine is calculated by mg creatinine in order to decrease the dilution impacts of urine that may occur, for example, in case that people have just drunken a lot of water. The calculated total arsenic is comprised of AB, As(III), MMA and DMA, in which AB is mainly originated from arsenic rich food such as fish, other three forms mainly come from inorganic arsenic in drinking water. The organic arsenic existing in fish in form of AB is not toxic and excreted entirely in the urine and does not take part in the metabolism. Meanwhile, new organic arsenic generated by the inorganic arsenic metabolism has high toxicity, thus, the chronic arsenic exposure is caused by a large amount of methylated arsenic accumulated in human body. The biological effects of methylated arsenic have been much concerned so far; we only focused on the determination and assessment of two organic arsenic including MMA and DMA. The frequency of MMA and DMA in the total arsenic in urine as illustrated in Figure 1.

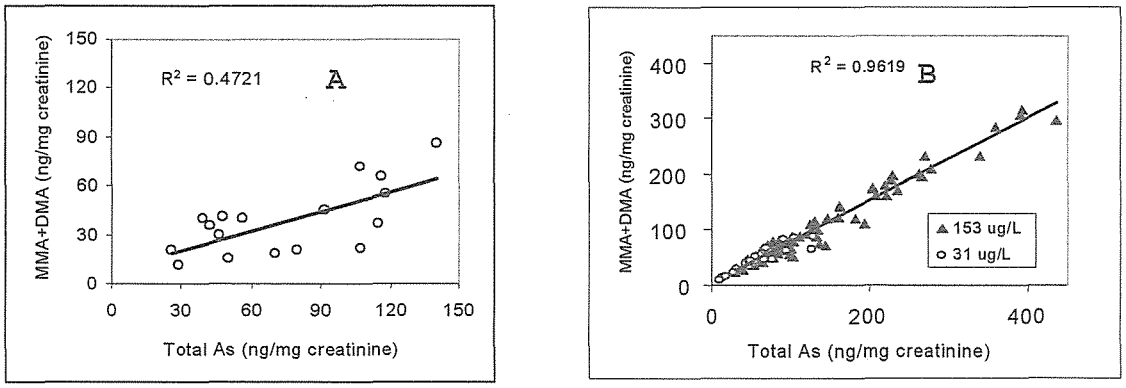

Figure 1. Correlation between concentration of the methylated arsenic species (MMA+DMA) and the total arsenic concentration in urine among various arsenic exposure groups at different levels.

(A)- Reference group RU1- (5 μg/L).

(B)- RU2- 31 μg/L- circle, RU3- 153 μg/L-triangle

It showed that the ratio of the MMA+DMA against the total arsenic excreted by the urine is 55.3% and the correlation between these two quantities is only R^2= 0,472 for the non arsenic exposure individuals (A). Interestingly, the ratio of organic arsenic and the total arsenic in the urine is 81% and the correlation is R^2 =

0,9671 for the individuals in RU2 and RU3 (B), where the arsenic concentration at drinking water are 31 μg/L and 153 μg/L, respectively.

The results suggest that in arsenic exposure communities, the methylated arsenic concentrations increased in comparison with the reference ones, the increasing trend depends on the exposure levels. Particularly, the methylated arsenic increased from 38 ng/mg creatinine in the reference group to 46 ng/mg creatinine in the exposure group by arsenic with the concentration of 31 μg/L, and remarkably increased up to 99 ng/mg creatinine in the exposure group by arsenic with the concentration of 153 μg/L (as illustrated in Figure 1 and the table 1). The increase of the organic arsenic shows not only the specific values but also the occurrence percentage in urine. In the respect of the total arsenic value in urine, the reference samples have a higher total arsenic concentration than RU2 (75 against 58) due to the existence of AB in food such as fish, but the methylated arsenic amount is lower (38 against 46). This suggests that using bio-indicators as the methylated arsenic for assessment of inorganic arsenic exposure levels from drinking water would be more accurate than using the total arsenic concentration in urine. Furthermore, the methylated products are proved to have the toxicity to genes and cause the related cancer (Aposhian 2004, Wanibuchi 2004) as in some experiments on animals. The selection of appropriate biomarkers plays an important role in studying the toxic mechanism of arsenic to human health. The study results in some arsenic exposure communities in Bangladesh, India, Mexico, and China indicated that the main components found in urine included a little inorganic arsenic, mostly monomethylasonic acid and dimethylasinic acid. The measured ratios are 10-30% inorganic arsenic, 10-20% monomethylasonic acid and 60-70% dimethylasinic acid (Tokunaga 2005, Vahter 2002, Valenzuela 2005).

3.2. Arsenic contamination in groundwater and the effectiveness of sand filters illustrated by biomarkers

The average arsenic concentrations in tube well and drinking water (the groundwater filtered or directly used), in hair and in urine in this study are illustrated in the table 1.

Table 1: The arsenic concentrations in tube well, drinking water (the groundwater filtered or directly used), in hair and in urine. Mean *(Min-Max)* values.

Location	No. of samples	As in groundwater (μg/L)	As in filtered water (μg/L)	As in hair samples (mg/kg)	As in urine samples (ng/mg creatinine)	
					MMA + DMA	Total
Reference sample RU1	17	**6** 1-12	**6** Direct use	**0.3** 0.1-0.6	**38** 11-86	**75** 26-140
Ly Nhan RU2	35	**435** 311-598	**31** 1-167	**0.8** 0.2-4.0	**46** 10-88	**58** 10-129
Hoai Duc RU3	82	**330** 184-426	**153** 56-309	**2.5** 0.4-10.4	**99** 23-315	**127** 30-437

The results showed that arsenic in drinking water in reference samples is at average level of 6 μg/L, below the allowed limit. All tested water samples at RU2 contain very high arsenic concentrations (ranging from 311 μg/L to - 598 μg/L). In case people use this water source as drinking water, the risks of being affected by arsenic related diseases would be possible as in Bangladesh or China (Chowdhury 2000, Xia 2004). However, the iron concentration in groundwater in this area was quite high (15mg/L on average based on our statistics), the tube well water is filtered by sand filters before use. The filtration can remove up from 60% to 90% arsenic in groundwater, similar to the results of our previous study (Luzi 2004). Figure 2 presents the correlation of the average methylated arsenic concentrations with the average arsenic concentrations in ground water (R^2= 0,1477) and with filtered water (R^2= 0,997). Based on the obtained R^2 value, we realized that the sand filtered water was the major drinking source or arsenic exposure source at the investigated areas. Thus, the correlation of the exposure level and the biomarkers is very close (R^2= 0,997), which proves the reliability of the methylated arsenic concentration in urine as biomarker. The results showed that if the right exposure source and appropriate biomarkers would not be defined, there will

not an explanation for why people living in RU2 and RU3 have had no symptoms of arsenic related diseases as in Bangladesh, India and China because their arsenic contamination was very high (300-500 μg/L). In fact, thanks to the effectiveness of sand filters, the exposure levels have considerably reduced. The real arsenic exposure level was 31μg/L instead of 435μg/L in RU2 and 153μg/L instead of 330 μg/L in RU3. The role of the sand filters for mitigating the arsenic effects to human health was also proved.

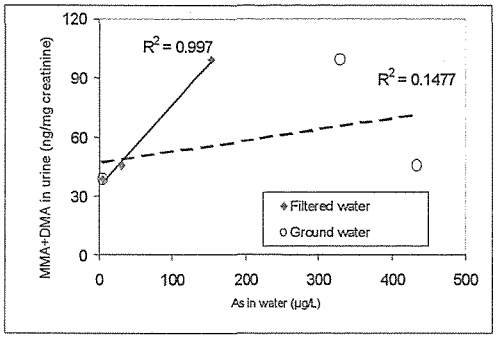

Figure 2. Correlation between MMA+DMA concentrations in urine and As in filter water (lozenge), in ground water (circle). At RU1, ground water directly used.

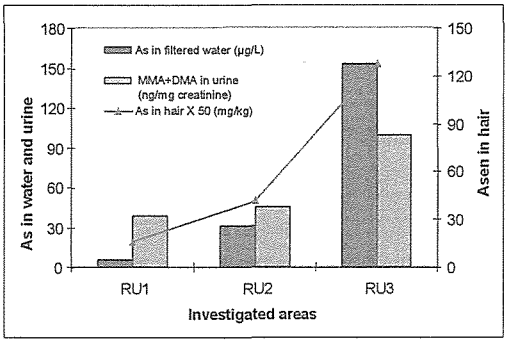

Figure 3. Average arsenic concentration in drinking water (filtered water) and methylated arsenic in urine samples at some investigated areas.

The average results of arsenic concentrations in drinking water and biomarkers such as hair and urine are presented in Figure 3. If the RU3 (arsenic concentration in drinking water of 153 μg/L) is chosen to make a comparison with other studies, the arsenic in hair samples is 2.5 mg/kg in average, similar to the findings in Bangladesh (4.0 mg/kg) and India (1.5mg/kg) reported by Chowdhury. However, the MMA+DMA value in urine was 99-ng/mg creatinine in RU3, lower than that of 193.6 ng/mg creatinine in India reported by Tokunaga. That can be explained that the arsenic concentration in drinking water in the study conducted by Tokunaga was higher what found in RU3. In addition, other reasons such as methylation capabilities among various communities, genetics, and nutrition may cause the differences.

4. Conclusions

The obtained results provide a clear evidence of the chronic arsenic exposure from ground water of the people who are living in RU2 and RU3 at Red River Delta in Vietnam, the arsenic concentrations in tube well water there are in the range of < 1 to 600 μg/L. The arsenic accumulation in hair is 0.8 mg/kg and 2.5 mg/kg, respectively, whereas the normal value is about 0.2 mg/kg. Biomarker as urine showed that the people in Hoai Duc have been continuing exposure by arsenic-rich water sources. The results on the correlation between the methylated arsenic species and the exposure level will contribute to providing a realistic data about the arsenic metabolism and the bad effects to human health. The positive relation between the arsenic contents in filtered water, hair and total methylated arsenic in urine is observed. Here by, the effect of simple sand filter reducing the arsenic burden in human body is illuminated. The study reveals the need of more intensive screening for arsenic in tube well water at other areas in Vietnam.

Acknowledgements

The authors would like to express the sincere thanks to JSPS (Japan), SDC in the frame of the Swiss-Vietnamese Cooperation ESTNV Project, for substantial financial support to this study.

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