INVESTIGATION OF ARSENIC CONTAMINATION IN GROUNDWATER IN HANOI AREA

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ABSTRACT

Most of the groundwater from the Red River Delta region contains high concentration of iron, manganese and ammonium indicating conditions similar to those in Bangladesh. This study focuses on arsenic contamination of the Red River alluvial tract in the city of Hanoi and in the surrounding rural districts. Due to naturally occurring organic matter in the sediments, the groundwater are anoxic and rich in iron. The data of arsenic in ground water in qh and qp aquifer in Hanoi and rural areas showed a signal of As contamination.

The relation between total iron and total arsenic in sediments of bore cores in Hanoi and additional parameters such as alkalinity, DO, ORP and ammonia may explain partly of mechanism of arsenic releasing from the reduction of iron oxyhydroxide by microbiological activities in the present of natural organic matters and redox condition. The arsenic in the sediments may be associated with iron oxyhydroxides and released to the groundwater by reductive dissolution of iron.

In a highly affected rural area, the groundwater used directly as drinking water had an average concentration of 430 μg/L. Analysis of raw groundwater pumped from the lower aquifer for the Hanoi water supply yielded arsenic levels of 240-320 μg/L in three of eight treatment plants and 37-82 μg/L in another five plants. Aeration and sand filtration that are applied in the treatment plants for iron removal lowered the arsenic concentrations to levels of 25-91 μg/L, but 50% remained above the Vietnamese Standard of 50 μg/L. The high arsenic concentrations found in the tubewells (48% above 50 μg/L and 20% above 150 μg/L) indicate that several million people consuming untreated groundwater might be at a considerable risk of chronic arsenic poisoning.

Keywords: Arsenic contamination, groundwater, monitoring, hydro-geological condition

Introduction

The Vietnamese capital Hanoi situated in the centre of the 17,000km^2 Red River delta of northern Vietnam is inhabited by 17 million people. Together with the Mekong delta, the Red River delta has become one of the most productive agricultural regions of South East Asia. In the last 5-7 years, a rapidly growing rural population has stopped using surface water or water from shallow dug wells. Instead, it has become popular to pump water by individual private tube wells (small scale pumped wells). The exploitation of groundwater in the city of Hanoi began 90 years ago and has since been expanded several times. Today, eight major well fields are operated by water treatment facilities. Due to naturally anoxic conditions in the aquifers, the groundwater contain large amounts of iron and manganese that is removed in the Hanoi drinking water plants by aeration and sand filtration.

Based on geological analogies to the Ganges delta, we expected elevated arsenic concentrations in the aquifers of the Red River basin. Thus, the scope of our study was to survey arsenic levels in the aquifers of Hanoi and surrounding rural areas. We investigated all major drinking water plants of Hanoi and 68 private tube wells in the adjacent districts, covering an area of approximately 700 km^2. This study was performed within the framework of a project focusing on groundwater contamination by heavy metals. 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 aquifer in 12–45 m depth.

In Vietnam the recent studies of the Research Centre for Environmental Technology and Sustainable Development (CETASD) and the Northern Hydrogeological and Engineering Geological Division (NHEGD), Geology and Mineral Survey of Vietnam under the support by UNICEF in Hanoi in some places of the Red river delta plain showed the signal of the arsenic contamination.

Geological - hydrogeological condition and status of groundwater exploitation

Geological - hydrogeological condition

The study area was in the Hanoi sunken structure. The geological structure have a similar with the geological structure of the BacBo plain, that having thick unconsolidated Quaternary formations. The structure is in vertical rhyme intercalated with coarse and fine grain layers creating alternate aquifers with weak permeable layers.
The characters of the main aquifers and weak permeable layers are described as follows:

Holocene weak permeable sediments

These sediments are in the ThaiBinh formation ($aQ_{IV}^{3}tb_1$), HaiHung formation ($abQ_{IV}^{1-2}hh$) cropping out in the ground surface. They distributed widely in the south of Red river and Duong River is in the Hanoi city. The thickness of soil is 2-8m. The compositions are clay and silt clay. The HaiHung sediments contain vegetable remains alternated with peat and mud-peat layers. There are mud-peat layers in the west strip and in the south of Hanoi area. These sediments are weak permeable.

Holocene inter-granular aquifer (qh)

This aquifer distributes rather widely distribute in the study area except in north area districts of SocSon and DongAnh. Mostly this aquifer is covered by the upper clay layer - ThaiBinh formation ($aQ_{IV}^{3}tb$) and HaiHung formation ($aQ_{IV}^{1-2}hh$). The compositions are sand from fine to medium and sandy. This is unconfined aquifer, in some place it is weak confined. The permeability of soil is in medium to high range. The test-pumping rate of those areas is from 2,08 to 30 l/s and the potential water bearing was also in medium to high level. The water circulating in the aquifer is fresh (TDS = 0.265 g/l) and bicarbonate chloride-calcium- sodium of type and the iron, manganese and ammonia (NH_4^+) contents is relatively high.

The groundwater regime in this aquifer in the south of Hanoi area is affected strongly by groundwater exploitation, in the other hand the lower qp aquifer is abstracted with large amount of water so the water level in this qh aquifer could be lowered too (hydraulic relation). The measured water levels in the PhapVan - TuongMai - ThanhNhan area was from - 6.89m to - 2.83m and the found deepest level of - 9.75m in the Tuong Mai areas. In this aquifer the water is abstracted mainly by the dug wells and UNICEF wells for living activities.

Pleistocene weak permeable sediments
These sediments are in the Vinh Phuc formation ($Q_{III}vp$) distributing widely in the study area. They are cropped out in the north of Red river and Duong River, in the south area they are covered except MaiDich - CauGiay area. In the Red river strip this sediments are absent due to the erosion. The compositions are clay, clayey with motley colour. There is mud-peat layer or vegetable remains in some place. The thickness is 4-20m. They are weak permeable.

Upper-Middle Pleistocene inter-granular aquifer (qp)

This aquifer is in the sediments of the VinhPhuc formation ($aQ_{III}^{2}vp$), Hanoi formation ($aQ_{II-III}hn$; $apQ_{II-III}hn$) distributing widely in the study area except the north area (SocSon) where the cropping out of bed rock. The composition are in two layers: the upper layer composed medium-coarse sand with yellow colour mixed with gravel of the Vinh Phuc formation, the lower layer is cobble, pebble mixed with sand of Hanoi formation. There is clay, clayey layer between these two layers but not continuously.

The aquifer's roof is 12m - 40m and aquifer' bed is 60 - 70m of depth. The thickness is 20-50m. The permeability is high, the test-pumping rate is 10-50l/s. The TDS of groundwater is small 0.2-0.5g/l, and is bicarbonate-chloride-calcium-magnesium of type. The water is neuter, soft but the iron, manganese and some heavy metal content are high, the ammonia content is high (10-50 mg/l). They need to be treated before using.

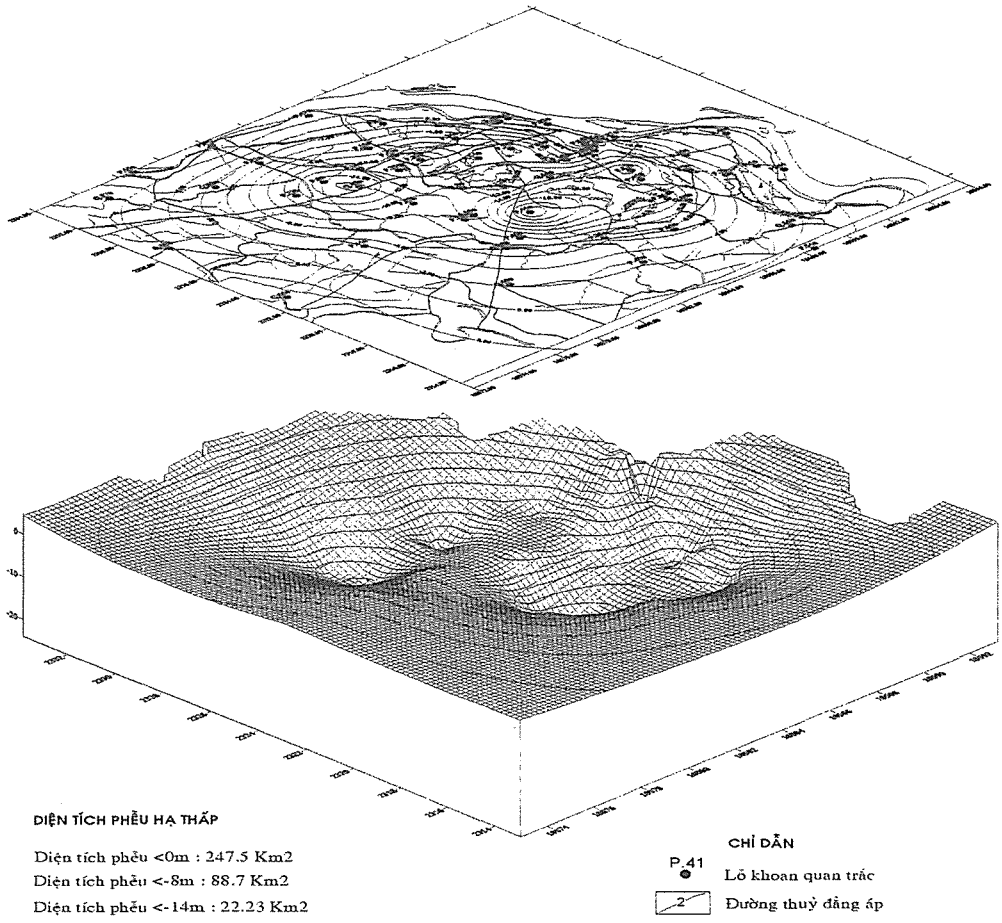

Figure 1. Map of cone of depression in the south of Hanoi area May - 2000

This aquifer is abstracted strongly for domestic. The Clean Water Business Company and other organizations have exploitation wells in this aquifer. Due to the strong exploitation, the cone of depression is created in the south of Hanoi area (figure 1) with 247.5 km^2 area (May 2000) creating flow direction from river and the river recharged to groundwater.

The groundwater regime is affected strongly in the south of Hanoi. The water level is relative low depending on to the rate and schedule of pump of the production wells, the deepest levels were at - 31.05m, - 20.38m, - 23.84m and -15.37m in the HaDinh, Phap Van, Tuong Mai and Luong Yen well fields, respectively.

Status of groundwater exploitation

The French has drilled first production wells since last century for living activities. Nowadays due to the urbanization, the water using demands are increasing. Groundwater is abstracted with huge amount for domestic and industrial demands. There are fewer than three types of exploitation as follows:

Public exploitation wells

These wells are managed by the Hanoi Clean Water Business Company in large diameter and exploited in qp aquifer. There are 8 big well fields and 13 small well fields with 398.000m^3/day of pumping rate.

Private wells

These wells belong to the difference organizations such as enterprises and factories in medium diameter. Some wells in each organization were exploited with medium pumping rate. According to the preliminary investigation there are about 500 private wells in Hanoi area with average 120.000m^3/day of pumping rate in the year 2000.

UNICEF wells

Since sponsorship of the UNICEF, the rural areas and areas which still not yet received public water supply system are used groundwater through UNICEF wells. These wells are in small diameter and using hand pump, each house has one well with capacity of 0.5-3m^3/day. Now this water supply system has improved, in some commune there is public water supply system by one or some big wells. According to the un-detailed data (1997), 4 suburban districts have ten thousand of these wells with 30.000m^3/day of pumping rate.

Analytical Method

Sample collection

500 samples were taken in December of 2000 in dry season in two main aquifers with sampling points as follows:

- 115 boreholes which are operating in long term as monitoring wells of the National Groundwater Regime Monitoring Network and of Hanoi Groundwater Regime Monitoring Network.
- 91 private wells which are investigated in long term of the National Groundwater Regime Monitoring Project.
- 264 UNICEF wells which are distributed evenly in the rural areas.
- 15 surface water points in the rivers, lakes and 15 points of waste water from big factories and in industrial areas.

Freshly drilled bore cores were probed on-site and 20 g wet sediment filled in polypropylene bags which were sealed airtight on the spot. Water and sediment samples were stored at 4 °C.

All the coordinates of sampling points were located by Global Position Systems GPS for mapping of As contamination. Before taking a sample, the water of 2–3 tube well volumes (e.g. 70 L for 20 m depth, tube i.d. 4 cm) was rejected. Each sample was filled in two 500-mL polypropylene flasks and one flask was acidified with 1 mL concentrated nitric acid for storage for heavy metals measurements and the other was kept cool at 4° C for ammonia and alkalinity measurements.

Chemical analysis

The field parameters were directly analyzed by field equipments (HACH) such as pH, temperature, EC, DO, Alkalinity, Ammonia with the following accuracy: pH (0.01 pH), temperature (0.1° C), EC (1μS/cm), DO (0.1 mg/l), Eh 1-3 mV), alkalinity (1mg/l).

Water samples were analysed for total arsenic by atomic absorption spectrometry (AAS/HVG) with MDL of 0.0002 mg/l. For comparison, 50 samples were sent to Switzerland and analysed by an independent contract laboratory with atomic fluorescence spectroscopy (AFS), and at EAWAG with ICP-MS. The

results agreed within an accuracy of 20%. Sediment samples were freeze-dried, digested with concentrated nitric acid and hydrogen peroxide in a microwave oven, and total arsenic and total iron were determined at EAWAG by both AFS and ICP-MS. The sediment analysis was confirmed by semi-quantitative wavelength dispersive X-ray fluorescence (WD-XRF) carried out at the Swiss Federal Laboratories for Material Testing and Research. Total organic carbon was measured with a CHN analyser by thermic oxidation.

Evaluation of ground water contamination

Tested results from UNICEF surveys in 1999

There has been no comprehensive study on arsenic contamination in Viet Nam to date. However, triggered by the tragic events of Bangladesh, CERWASS (MOARD) and UNICEF Hanoi took the initiative to carry out some 1,200 tests for arsenic contamination in drinking water wells located in Hanoi and in other five provinces of the Red River Delta. It is well recognized and understood that the above-mentioned 1,200 tests are not enough to come to a conclusion on the possible magnitude of the arsenic problem in Viet Nam. However, this small test programme showed that there is sufficient evidence that high level of arsenic is present in the Holocene aquifer of the Red River Delta.

Level/Test	Total	Hanoi	Q.Ninh	H.Phong	P.Tho	T.Hoa	T.Binh
<0,01 mg/L (within WHO standard)	106	11	2	0	14	59	20
0.01-0.05 mg/L (within VN standard)	914	336	170	51	62	119	176
0.05-0.10 mg/L	127	105	3	1	2	16	0
0.10-0.30 mg/L	63	56	0	0	0	7	0
0.30-0.60 mg/L	18	17	0	0	1	0	0
>0.6 mg/L	2	1	0	0	1	0	0
Total tests	*1230*	*526*	*175*	*52*	*80*	*201*	*196*

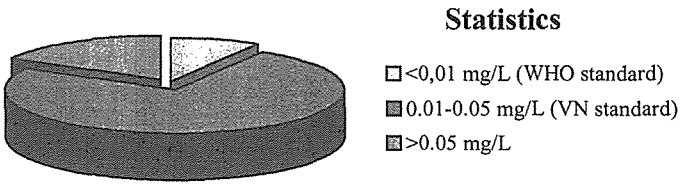

Fig. 2. Evaluation of As concentration in groundwater samples

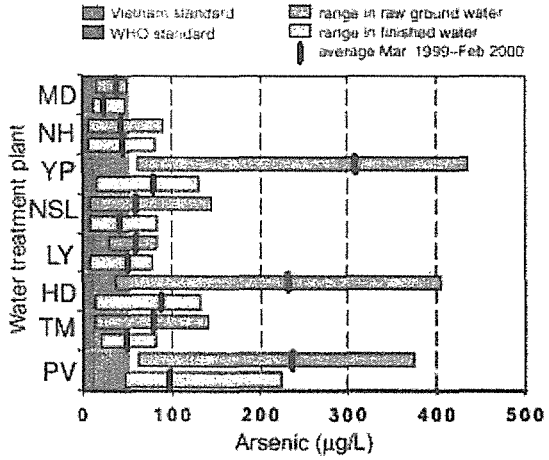

Fig. 3. Arsenic concentration in some main well fields of Hanoi Water Plants (Source: CETASD/EAWAG)

Some 15.5% of the sampled wells (mainly tube wells with handpumps) in and around Hanoi had arsenic concentration exceeding 0.05mg/L (Vietnam standard) and 92.2% exceeds WHO international standard. The most affected province found was Hanoi where 34% of the sampled wells exceeded 0.05 mg/L and 3.4% exceeded 0.30 mg/L. Until now, there had been no attempt to map the available data or to correlate them with available health statistics (epidemiology).

Results of the systematic investigation of CETASD and EAWAG

Parallel to CERWASS (Centre for Rural Water Supply and Environmental Sanitation) and UNICEF efforts to test a number of tubewells for arsenic contamination, the Research Centre of the Environment Technology and Sustainable Development (CETASD) under the supervision of the Swiss Federal Institute for Environmental Science and Technology (EAWAG) carried out a systematic investigation on arsenic in groundwater/drinking water sources in Hanoi and the surrounding rural districts. These efforts were funded by the Swiss Agency for Development and Cooperation (SDC). The high arsenic concentrations measured by CETASD and EAWAG with high quality equipment (HG-AAS) are shown in figures 1 and 2.

Tested results in the surveys in December 2000

The investigated results showed that the groundwater in qh and qp aquifer has signal of arsenic contamination with heavy metal such as arsenic, manganese and ammonia.

- For arsenic: The arsenic contamination area in two aquifers is mainly in the south and southeast area of the Hanoi. As concentrations in groundwater were evaluated in the comparison with Vietnam Standards (<0.05mg/L) and contamination percentage was counted based on samples which have As concentration beyond Vietnam Standards in total 500 samples. The distribution of As contamination in qh and qp aquifers with 31.2% and 26.7% of contamination scale, respectively. Especially, these contamination areas were coinciding with distribution areas of the peat, mud layers as well as high pollution area of ammonia.
- For manganese: the content in both two aquifers is higher than standard limitation. The pollution scale for qh and qp area aquifer 81.5% and 87.6%, respectively. The high contamination area is in the centre and strip along Red river and Duong River.
- For iron: the content in both two aquifers is higher than standard limitation. The pollution scale is 70.8% for qh aquifer and 82.9% for qp aquifer. The high pollution area is in the centre and in south area.
- For ammonia: The pollution area in two aquifers is in the centre and SE area of Hanoi city. The distribution area in two aquifers is coinciding with pollution scale: 33.8% in qh aquifer and 30.3% in qp aquifer. The distribution of pollution area is coinciding with distribution of peat and mud layers. There was only one sample in 15 surface samples detected As which has content higher than Vietnam

Standard For surface water.

Suggestion of arsenic releasing from the soil

Several studies[1,8,12,13] 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. This may used to explain the Kim et al.[14] have invoked the interaction of bicarbonate ions in the leaching of arsenic into groundwater by carbonation of arsenic sulphide minerals. The anoxic conditions in the Red River sediments are driven by natural organic matter (NOM) present in the subsurface[15,16]. In fact, in bore cores we have found peat layers having NOM concentrations of 15% total organic carbon. Dissolved oxygen is rapidly consumed by microbiological mineralisation of NOM, resulting in the formation of bicarbonate and inorganic nitrogen species. This is consistent with the high alkalinity (250–990 mg/L) and high nitrogen concentrations (15–30 mg N/L) measured in the studied groundwater. Inorganic nitrogen was mainly found

in the reduced form of ammonium that reached particularly high levels of up to 25 mg/L (N-tot 30 mg/L) in the most severely arsenic contaminated south-east areas of Hanoi.

The total iron contents and total arsenic contents in sediments showed a good correlation (see Fig. 4.). And the as contamination areas were coinciding with distribution areas of the peat, mud layers as well as high pollution area of ammonia. So this may explain partly the suggested of Nicholson and Mc.Arthur[1] about the reduction of iron oxyhydroxide mechanism as follows:

$$\underbrace{4FeOOH}_{\text{Representative for organic matter}} + CH_2O + H_2CO_3 \xrightarrow{\text{Microbial metabolism}} 4Fe^{2+} + 8HCO_3^- + 6H_2O$$

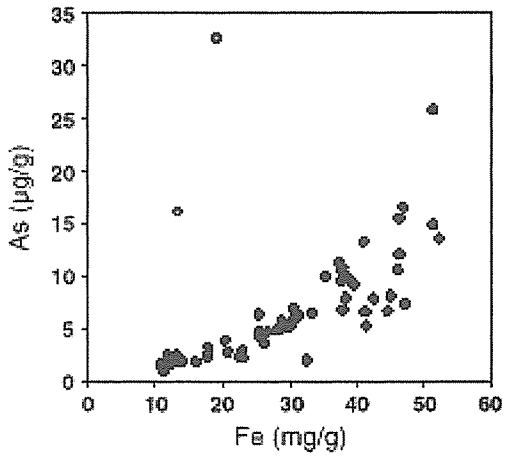

Fig. 4. Correlation between total iron and arsenic contents in sediments

Conclusion

The previous and recent data of arsenic in ground water in qh and qp aquifer in Hanoi and rural areas showed a signal of As contamination. The relation between total iron and total arsenic in sediments of bore cores in Hanoi and additional parameters such as alkalinity, DO, ORP and ammonia may explain partly of mechanism of arsenic releasing from the reduction of iron oxyhydroxide by microbiological activities in the present of natural organic matters and redox condition.

Based on the geological and hydrogeological condition, relationship between factors and analysed results of groundwater samples in Hanoi and rural areas the reasons of As contamination could be caused by:

- Due to man-made factories, enterprises and dwelling places have huge amount of liquid waste and solid waste, mostly they are not treated. The river system, lakes, drains are passing with high density. The waste percolate in to groundwater.
- Due to groundwater exploitation: the water level is lowered due to increasing of percolation and degree of pollution, the chemical- physical process can pollute groundwater resources.
- The content of heavy metals in the soils is rather high, in these arsenic content is 5.10^{-5} - 5.10^{-4}%. During exploitation of groundwater the peat, mud is disintegrated, a large amount of methane is released and they are combined with arsenic creating methylarsen and dissolved into groundwater. Hence
- One can says the reason of arsenic pollution in groundwater in south of Hanoi area is from clay, mud clay mixed with organic matter and peat layer.

The above-mentioned opinions for reasons of groundwater pollution, the detail study, especially origin, forming process, content and distribution in soils should be carried out. Then the available protection and remediation methods can be determined.

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