Arsenic contamination in groundwater in the Red river delta, Vietnam - a review

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Abstract:

Arsenic contamination in groundwater and its effect on human health has been a growing concern over recent decades. Some of the most severe incidents occurred in South and Southeast Asia, including the Red river delta, Vietnam. The highest concentration of arsenic found in the Red river delta was 810 µg/L, 16 times higher than the standard guidelines given by WHO for levels of arsenic concentration in groundwater (50 µg/L). However, the contamination levels were not uniform in the whole area. The arsenic levels might be affected by natural factors such as the characteristics of the aquifer, the chemical composition of groundwater and by human activities such as the exploitation of groundwater in the urban and industrial areas or irrigation in rural areas. Due to the complex mobilisation of arsenic in sediment and groundwater, questions remain about arsenic distribution, which are yet to be answered and are in need of further study.

Keywords: ***aquifers, arsenic contamination, arsenic mobilization, arsenic releasing mechanism, Fe oxy-hydroxide, groundwater, Red river delta.***

Classification number: *2.2*

Introduction

The Red river delta is one of the most densely populated regions in Vietnam, with a population of about 17 million people spread over an area of approximately 14,000 km^2. Over the last several decades, groundwater has become a common water source for domestic, manufacturing, breeding and cultivation purposes. However, due to the geochemical structure of the sediments in this delta, the groundwater in the aquifers here contains high arsenic content. Arsenic is a natural element in the sediment and mineral. The release of arsenic into groundwater only occurs under favourable conditions that lead to the contamination of groundwater. In Vietnam, the standard for arsenic concentration in groundwater is 50 µg/L and in drinking water it is 10 µg/L. Because of its high toxicity and adverse effects on human health in even small concentrations, a number of studies have been carried over the past twenty years to assess the arsenic contamination level in groundwater in the Red river delta. The research group at the Research Centre for Environmental Technology and Sustainable Development, VNU University of Science is one of the first groups to study arsenic contamination in groundwater and has the most publications in this field in Vietnam. Approximately 20 publications related to arsenic contamination in groundwater in the Red river delta have been published in Vietnamese and international journals. We have implemented international collaboration projects for a long time, including Vietnam - German cooperation such as VIGERAS, a BMBF/DFG - MOST funded project on arsenic in the food chain, from 2008 till 2011. Recent studies have shown that a strong need exists for the development of methods to control arsenic in rice, that more comprehensive knowledge is needed about arsenic dynamics in the rhizosphere, especially about the behaviour of arsenic within the root plaque, to enhance knowledge of the mechanisms by which arsenic enters plants, that genetic predisposition of human beings and mental impact are not considered by the current threshold values, and this is a health challenge requiring greater attention [1].

Actual state of arsenic contamination in groundwater in the Red river delta, Vietnam

A detailed study on a large scale about the state of arsenic contamination in groundwater was carried out in 2011 by Winkel, et al. [2]. The results showed that about 7 million people in this delta have been using the groundwater contaminated by arsenic and other toxic elements such as manganese, selenium and barium. The authors analysed the chemical composition data from 512 groundwater samples, taken from the wells of private houses, to create the distribution maps for arsenic and other elements. The results showed that the arsenic concentration ranged from <0.1 to 810 µg/L, with 27% of the samples exceeding the value of 10 µg/L that is the WHO standard for arsenic level in drinking water. The wells with the highest concentration of arsenic were located along the two banks of the Red river up to a distance of approximately 20 km from the river. The Southwest area of the delta, which was the position of the ancient Red river, was also high in pollution (Fig. 1). Another finding from the results was that the distribution of arsenic varied from well to well, without any clear tendency.

Apart from the above study, there are some other researches that focused on specific areas on a smaller scale. For example, in 2001 the very first study on arsenic contamination in Vietnam was implemented by Berg, et al. [3]. The study site was Hanoi and its suburban districts. The range of arsenic in the samples was

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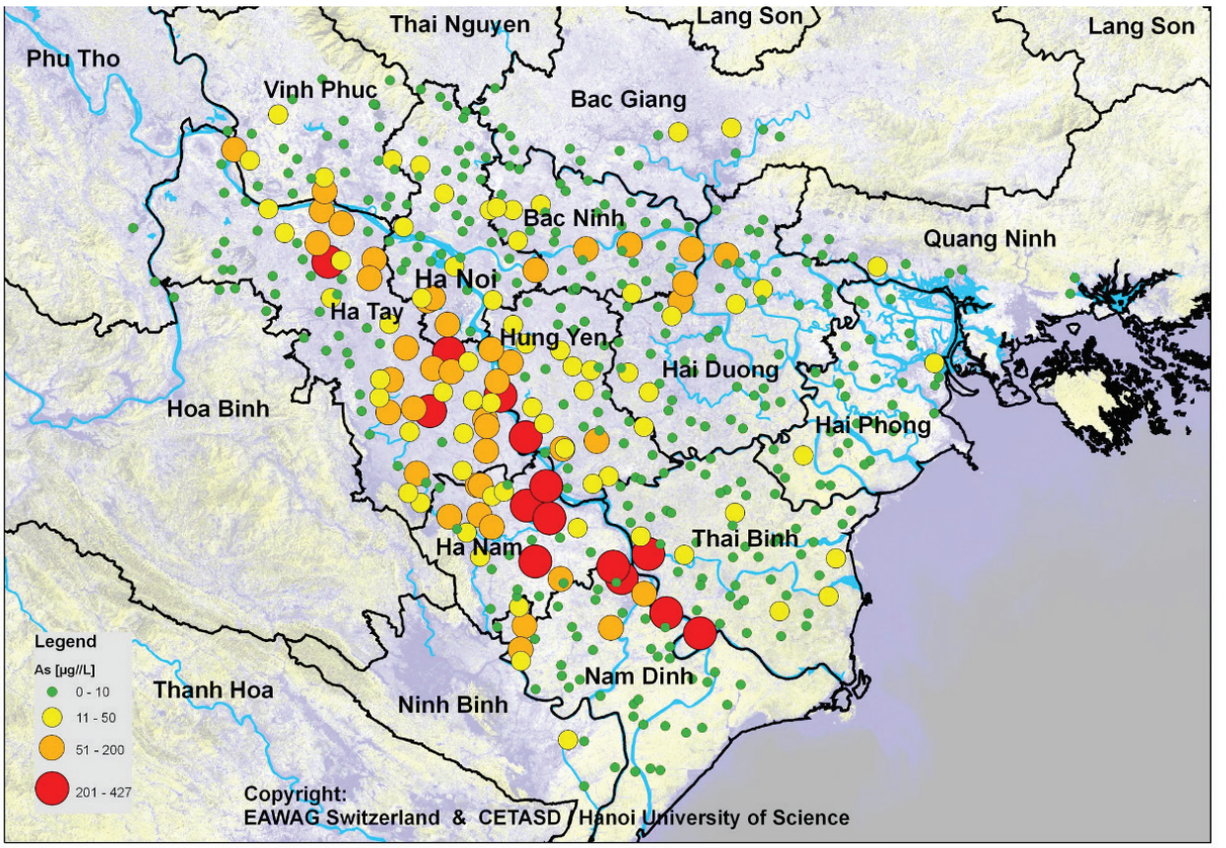

Fig. 1. Arsenic distribution in groundwater in the Red river delta, Vietnam.

from 1 to 3,050 µg/L, with an average of 159 µg/L. By analysing the untreated groundwater samples that were exploited from the deeper aquifer at 8 domestic water supply factories, they found that arsenic concentrations ranged from 240 to 320 µg/L at 3 factories, and from 37-82 µg/L at five other factories. After air bubbling and sand filters were applied at these factories to remove iron, the arsenic concentration decreased to 25-91 µg/L. However, 50% of the samples still contained high arsenic concentration, exceeding the Vietnamese standard at that time (50 µg/L).

Agusa, et al. (2006) studied the arsenic concentration in 25 groundwater samples in Gia Lam and Thanh Tri districts [4]. The variation range of arsenic here was from <0.1 to 330 µg/L, 40% higher than the WHO standard for drinking water (10 µg/L). In addition, 76% and 12% of the samples also exceeded the WHO standard for Mn and Ba, respectively.

Another study of Agusa, et al. (2014) expanded the study site to other areas in the Southwest of the Red river delta thatshowed signals of high contamination, such as Tu Liem, Dan Phuong, Hoai Duc (Hanoi) and Ly Nhan (Ha Nam) [5]. This study compared not only the contamination level in different areas, but also provided the distribution of arsenic concentration in a narrow area of about 1-2 km^2. For instance, in Hoai Duc, Hanoi (formerly Ha Tay), the arsenic concentration in 33 samples ranged from <1-377 µg/L with a mean value of 133 µg/L. 86% of the samples did not meet the standard for drinking water. 51% of the wells contained arsenic concentration higher than 300 µg/L. Compared to other parts of the world, this was a very high contamination level, considered the cause of skin diseases occurring in Western India and Bangladesh. The contamination level was even higher in Ly Nhan (Ha Nam). The arsenic concentration in 15 groundwater samples was from 311-598 µg/L, averaging 420 µg/L. The contamination level in this area was similar for all the wells. If the inhabitants here use the groundwater directly for eating and drinking, there is an obvious risk of arsenic-related diseases. Fortunately, after filtering with sand filters, the mean arsenic concentration in groundwater in Ly Nhan reduced to 23 µg/L. Therefore, the risk of arsenic exposure through filtered drinking water greatly reduced. In contrast, the groundwater in Hoai Duc, even after the sand filters, still contained a high concentration of arsenic (averaged 74 µg/L). Some samples even reached an arsenic concentration of 309 µg/L. Arsenic filtering capacity of the sand filters depend on many factors such as iron, phosphate concentration in groundwater, the sand layer thickness, the temporal changing of sand layer during the period of use, etc. The wells in Dan Phuong contained arsenic concentration from <1-632 µg/L (n=13), average 43 µg/L. In general, the distribution of arsenic in groundwater in the Red river delta was different from area to area. The reason for this difference is still an unanswered question which attracts international and Vietnamese scientists.

Quite different from the above study sites, in the Red river delta, there were areas that were free from arsenic contamination. In their study in 2014, Agusa, et al. found that the arsenic in

groundwater collected at Tu Liem was (n=5) <1 µg/L [5]. The question here was whether arsenic was released into groundwater or not. Was it released into groundwater but then got transferred to other areas due to hydrologic conditions or was it re-absorbed in the sediment? These are hypotheses that are still being studied all over the world.

The arsenic contamination in groundwater in the Red river delta has been assessed systematically with high reliability. The results, which were published in international journals, show that the high arsenic contamination was concentrated in the Southwestern delta and along the Red river banks. The distribution can be quite different in a narrow area, with a non-contaminated area existing alongside a highly contaminated area. However, the finding results are applicable for the respective study sites only, and unsuitable for use in other contiguous areas. At present, arsenic contamination prediction are not capable, because we have not found the exact arsenic forming process and its transportation pathways in the aquifers. Determination of arsenic contamination needs to be done in detail and particularly for each well. However, this is unrealistic due to the limited funding compared to the large number of wells. A solution, which was used earlier, is using the arsenic determination toolkit to determine the arsenic concentrations in all the wells. Yet, the limitation in carrying out the experiment and quality controlling caused the unreliable of the results. Therefore, determination of the study areas and the arsenic contamination levels in groundwater in Vietnam are still in need of implementation.

Arsenic forming process in groundwater in the Red river delta, Vietnam

Studying the actual state of arsenic contamination is an important task in order to determine the range and the pollution levels. This information can be used for warning people living in the contaminated areas. The task therefore is to understand why arsenic is formed in groundwater, and whether the release of arsenic into groundwater is affected by human activities. These questions require the involvement of specialists from fields such as geochemistry, hydrology, water chemistry, soil bacteria, modelling, etc.

The geochemical process related to the arsenic forming and transportation model in an area on a bank of the Red river was studied by Postma, et al. (2007) [6]. The results showed that most the iron minerals here were in the form of goethite and partly hematite. Based on a hypothesis that arsenic exists mainly in iron minerals in sediment, a sediment extraction experiment was carried out by the research group to study the distribution of arsenic in iron minerals. The results showed that while most of the arsenic was linked with iron oxide, the amount of absorbed arsenic in the sediment surface was low. On the surface of iron oxide, As(III) only accounted for about 3% of the surface position; the remaining was carbonate and silicate. Part of the arsenic extracted from iron oxide was absorbed back into the mineral surface, leading to the decrease of arsenic concentration in groundwater.

Studying the groundwater chemical composition showed the reductive condition in the aquifers, which related to the degradation of organic compounds, the reduction of iron oxide and the formation of methane. The specific pressure of CO_2 in groundwater increased due to the dissolution of carbonate in soil. Arsenic concentration showed an increasing trend according to depth and peaked at 550 µg/L, mostly in the form of As(III). Arsenic concentration appeared to correlate with NH_4, which indicated the relationship between the degradation of organic matter and arsenic release from the reducted iron oxide. From the analysis, one can also see that part of the iron (II) re-precipitated in the form of siderite ($FeCO_3$) that was less effective in absorbing arsenic. The extraction experiment with HCl and ascorbic acid (pH 3) showed that with river sediment, most of the iron and arsenic was reductively dissolved by ascorbic acid, while a very small amout of arsenic and iron was extracted by HCl. This indicated the link between arsenic and iron oxide. Moreover, the difference in extracted iron using ascorbic acid and HCl in river sediment indicated the reductive dissolution of Fe(III) caused by ascorbic acid. In spite of this, along with oxidised sediment, iron also was dissolved by ascorbic acid, but there was only a small amount of arsenic absorbed in the sediment. This proved that arsenic was not present in oxidised iron mineral in sediment [7].

In contrast, for sediment in the reductive aquifers, a large amount of Fe(II) and As was extracted using HCl. This might be because of the presence of the mineral that contained Fe(II) linked with origin-unknown. From the data of the ascorbic acid extraction, there were both As(V) and As(III) in river sediment, while the reductive sediment only contained As(III). This indicated that mineral analysis cannot be used to predict the activity of iron oxide related to arsenic release.

Studying the sediment in South and Southeast Hanoi, Berg, et al. (2008) realized that the arsenic content in sediment was in the range of 1.3-22 µg/g [8]. This was the common content of arsenic in natural sediment, and arsenic showed a strong relationship with iron content (r^2>0.8). In the peat area, the content of iron in sediment and water was higher than in other areas. The average mole ratio of Fe/As in water was 350 and in sediment it was 8,700. The high reductive iron in sediment might be the newly formed mineral and this mineral re-absorbed arsenic from groundwater into the sediment. For the water and sediment samples on the bank of the Red river, these ratios were 68 and 4,700, respectively. In this condition, the arsenic reabsorbing process hardly happened, and therefore the arsenic concentration in water was still remarkably high.

In another research in Southeast Hanoi, Eiche, et al. (2008) studied the difference in arsenic concentration at two sites that were approximately 700 m apart. The arsenic concentration at the low site (site L) was <10 µg/L, and at the high site (site H) was 600 µg/L [9]. Sediment extraction experiments were carried out to understand why arsenic was released at site H and not at site L. The results demonstrated that the mineralogy and geochemical properties of the sediments collected at these two sites were not significantly different. The major difference was in sediment colour. At the high arsenic concentration site, most of the arsenic was absorbed on the surface of grey sand that was a mixture of Fe(II)/Fe(III),whereas at the site with low arsenic concentration, arsenic was found to bond in strong links with brownish Fe(III) oxide. High iron concentration (14 mg/L) and low concentration of sulphur (<0.3 mg/L) found at the polluted area indicated the reduction condition. NH_4 concentration was 10 mg/L, HCO_3^- concentration was 500 mg/L and dissolved P concentration was

6 mg/L. These figures indicated that there was Fe oxy-hydroxide reduction process by organisms. The precipitation processes to form siderite and vivianite due to oversaturation and the formation of amorphous Fe(II)/As(III) or iron sulphur might occur at site H. On the other hand, at site L, iron concentration was 1 mg/L and sulphur concentration was 3.8 mg/L. This conflicting phenomenon of the reductive/oxidised conditions at these two sites is yet to be explained.

The studies on the relationship between sediment mineralogy characteristics and the presence of arsenic in groundwater have not thrown up any clear answers. The common finding of most of the authors was that the reductive conditions occurred at the polluted sites, and at the unpolluted sides, the conditions were oxidised.

Arsenic mobilisation in the aquifers

Arsenic, which is released from sediment into groundwater, can be transported to other areas. While being transported, arsenic would take part in other chemical reactions, absorption and desorption processes. That is the reason why simple chemical reactions and tranquil correlation can hardly be used to explain the occurrence of arsenic. One research group has studied the mobilisation of arsenic in aquifers. Can arsenic be transported from a high concentration area to other areas which are free from arsenic?

Alexander van Geen, et al. (2013) initially acknowledged the alteration in hydrology flow and the redox properties of the aquifer due to water exploitation at one district in Southeast Hanoi [10]. The contour lines in figure 2 show that the groundwater level has fallen within the city. The decrease of groundwater level gradient stimulated the mobilisation of arsenic from the shallow aquifers on the riverside to the deeper aquifers. Arsenic infiltrated approximately 120 m from the polluted Holocene to the unpolluted Pleistocene. The results also indicated that arsenic in groundwater was absorbed into the sandy sediment; thereby the transportation rate decreased about 20 times compared to water transportation.

Expanding this research area, Mason O. Stahl, et al. found out that high intensity of groundwater pumping reversed the natural flow of groundwater [11]. In natural conditions, groundwater would pour into the rivers through the apertures along the banks of the rivers. However, in this case, the river water flowed back into the groundwater because of the lower groundwater level due to water pumping. Analysed results showed that the arsenic concentration in the newly alluvial shallow pore holes (<10 years) was remarkably high (about 1,000 µg/L). This amount of arsenic would move down to the deeper aquifers when the water level fell.

Recently, Postma, et al. (2010) used tritium-helium isotope to determine the age of groundwater along the banks of the Red river. The results showed that the age of the deep aquifer (about

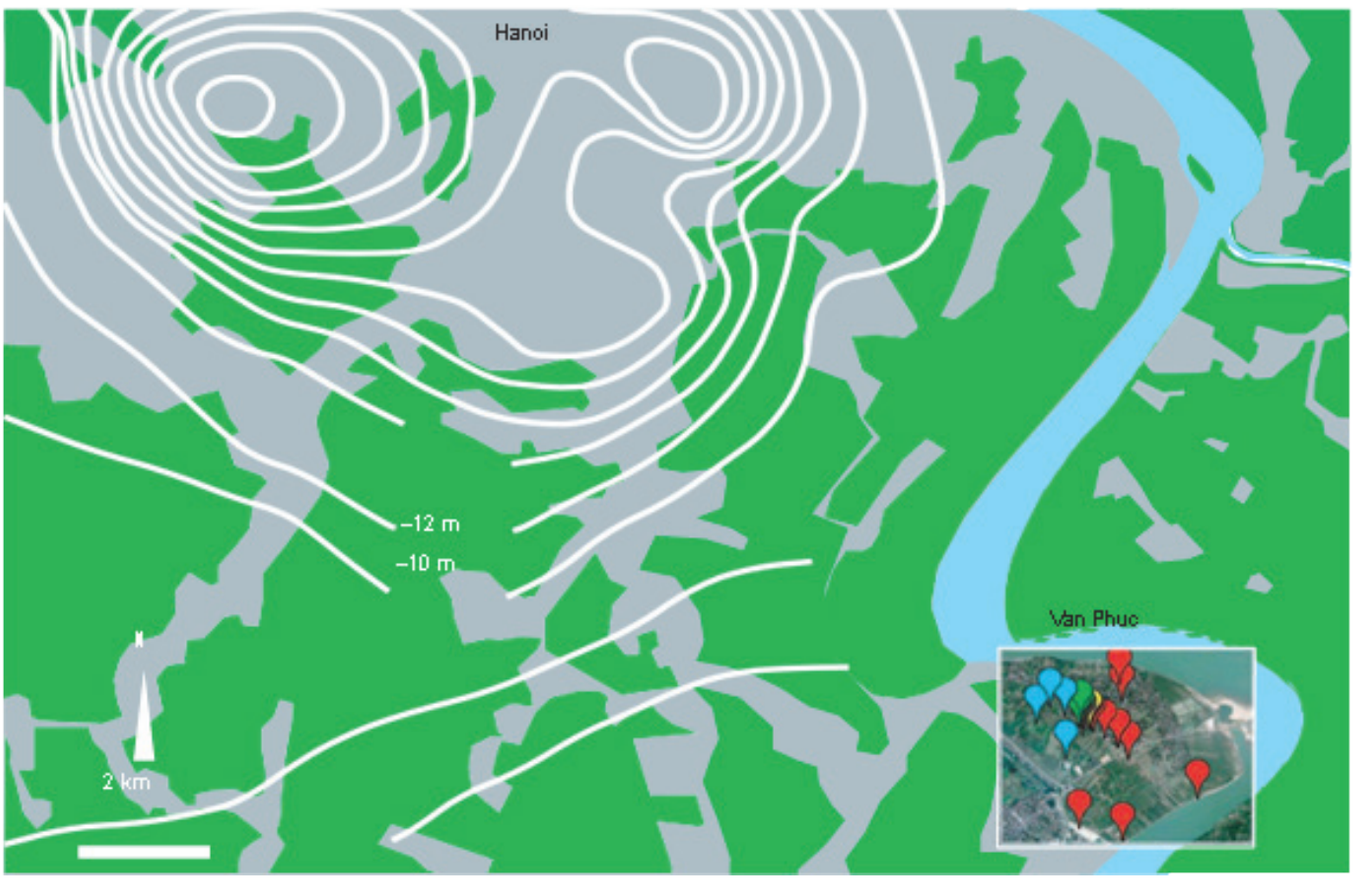

Fig. 2. Relationship between groundwater level and arsenic mobilisation in groundwater on the river banks of the Red river.

40 m deep) next to the river was approximately 1.3±0.8 years [12]. This was equivalent to a vertical transportation rate of about 19 m/year. The conductivity and specific pressure of CO_2 indicated that the water in the sandy Holocene layers and gravelly Pleistocene layers was recharged by river water and this recharged water was also exploited. Dissolved oxygen in the recharged water was consumed in the oxidisation of dissolved organic matter in water and sediment. If these processes continued to happen, the reduction of arsenic-bound iron oxides would occur and release arsenic into groundwater. Arsenic concentration in water was affected by the balance between arsenic being absorbed into sediment and desorption into groundwater.

Conclusions

The actual state of arsenic contamination in groundwater of the Red river delta has been established with the highest contaminated level of 810 µg/L, 16 times higher than the WHO standard for arsenic concentration in groundwater. The South and Southwestern parts of the Red river were much more polluted than other areas. The contamination levels were not uniform in the whole area. The reason for this phenomenon was yet to be determined. In addition, groundwater in this area was polluted by other elements such as manganese, barium, iron and ammonium.

The release of arsenic from sediment into groundwater related to the dissolution redox processes of arsenic-bound iron oxy-hydroxide, demonstrated by the chemical composition of groundwater with a large amount of arsenic, reductive iron, ammonium, bicarbonate and methane. Arsenic released from sediment can be re-absorbed into newly forming minerals or transported to nearby areas.

Hydrological flows in the aquifers of the Red river delta may have changed a lot due to water exploitation in the urban and industrial areas or due to irrigation in rural areas. These changes have caused the penetration of arsenic from the polluted to the unpolluted aquifers. River water exploitation by banks filtration has also increased the risk of moving the reductive conditions from the riverside aquifers to older oxidised aquifers that have not so far been contaminated by arsenic.

Although the whole picture of arsenic contamination in groundwater still has unanswered questions, the above results are warnings about the arsenic pollution levels in groundwater and the effect of human activities on the valuable water resources in the Red river delta. We have recently instituted an international collaboration, namely integrated clean water technologies for rural regions of Vietnam, to face the challenges of arsenic groundwater contamination and decentralised sewage treatment. In the near future, we will continue this potential orientation in order to further improve the ground water quality and safe water supply based on detailed investigations about the biogeochemical aspects related to arsenic contamination and the corresponding health risk assessment in the Red river delta.

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