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# INVESTIGATION OF ARSENIC RELEASE FROM SEDIMENT MINERALS TO WATER PHASES – MOTIVATION FOR ARSENIC MITIGATION TECHNOLOGY

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## Abstract

Severe and widespread contamination by arsenic in groundwater and drinking water has been recently revealed in rural and sub-urban area of Vietnamese capital of Hanoi with similar magnitude observed in Bangladesh and West Bengal, India. This fact has prompted the need to investigate the possible mechanisms for such widespread contamination and develop suitable techniques for lowering arsenic concentrations in supplied water. In the present study, laboratory-scale experiments were performed to assess the possible release of arsenic from solid phase into water phase under both anaerobic and aerobic conditions. Various chemical equilibrations governing the speciation of different ions in water phase and alluvial sediment are discussed. Under anaerobic conditions, the release of arsenic seemed to be closely related to the content of MnO<sub>2</sub> in sediments, the reduction of Fe(III) to Fe(II) and the formed sulfur content. Elevated MnO<sub>2</sub> content may inhibit the release of arsenic to groundwater. The reduction of arsenic concentrations in water phases could be due to the formation of Fe<sub>2</sub>AsS or AsH<sub>3</sub>. In aerobic conditions, the hydrothermal oxidation process was proposed as a plausible mechanism of release of arsenic from arsenic-rich mineral surfaces to water phases. In acidic conditions, arsenic concentrations increased due to the more effective release from mineral surfaces. Under neutral medium (pH ≈ 7), the arsenic releasing was less efficacious, which could be due to the co-precipitation onto ferric hydroxide. The possible mechanisms suggested in this study may be useful to explain the elevated contamination of arsenic in surface waters of upstream rivers of mountain areas in northern Vietnam and in underground water of Rivers delta, and critical for moving to the next stage in developing suitable techniques for lowering arsenic concentrations in groundwater and drinking water in Vietnam.

**Keywords:** Arsenic release, aerobic, anaerobic, arsenic-rich mineral surfaces, sorption, groundwater, surface water.

## Introduction

In recent years, the natural occurring contamination by arsenic in groundwater in Asian countries has received particular attention. The concern over serious health effects caused by arsenic poisoning has been observed in Bangladesh and West Bengal, India [1]. In Vietnam, due to the similar composition of groundwater in Bangladesh, elevated contamination by arsenic has been anticipated. Public media have also voiced concern that arsenic contamination in groundwater may become a key environmental problem in Asian developing countries in the 21<sup>st</sup> century [2].

To address this issue, our laboratory has recently conducted comprehensive monitoring survey of the status of arsenic contamination in groundwater and drinking water in Hanoi, the capital of Vietnam and its surrounding areas. Our results clearly demonstrated widespread and elevated contamination by arsenic in groundwater and supplied water in sub-urban and rural areas of Hanoi [3]. The magnitude of pollution were similar to that observed in Bangladesh, with a large number of well waters contained the arsenic concentrations exceeded the Vietnam standard of 0.05 mg/L. This severe situation lead us to continue to conduct further researches towards understanding of possible mechanism of widespread arsenic contamination in groundwater and development of suitable techniques for lowering arsenic concentrations. In 1992, D. V. Can [4] observed extraordinary high arsenic concentrations in water of some streams during his field investigation in highland area of upstream of Ma River, North Vietnam. Subsequent surveys showed that various arsenic-rich minerals, such as arsenopyrite, occurred widely in this area. The possible mechanism of arsenic contamination in water of streams in a mountain area may be due to the weathering

of arsenic-rich minerals [5]. In Vietnam, there is a relatively large pyrite mine located about 60 km far from Hanoi city. In addition, a number of gold mining sites with arsenopyrite are located over a large area of northern Vietnam. The gold mining activities in northern Vietnam have been extensive in recent years and arsenic-rich minerals have been distributed to the land surfaces during gold mining. If the hypothesis that weathering process may be a source of arsenic in surface waters, the contamination by arsenic in surface water would be a serious concern in the near future for a large area of northern Vietnam. In fact, we have tested surface water from Read River, and found that arsenic concentrations in some locations reached a level of 0.09 mg/L, which was exceeded the Vietnam standard level (0.05 mg/L). This fact has prompted us to examine the mechanism of arsenic releasing to surface water from mineral surfaces.

In this study, we proposed the possible mechanisms of arsenic contamination in groundwater, based on our observations in well waters in upper and lower aquifers of Read River delta [3]. The mechanisms of release of arsenic from various solid phases were investigated under anaerobic and aerobic conditions. These experimental investigations may be useful for understanding of mechanism of arsenic contamination in water sources and may be critical steps for developing suitable techniques for lowering arsenic concentrations in supply water and drinking water in Vietnam.

## Methodology

### *Experimental setup for investigation of mechanism of arsenic releasing to groundwater under anaerobic conditions*

A batch experiment was performed to investigate the release of arsenic in groundwater. The experimental setup is described in Fig. 1. The main composition consists of anaerobic column, supplied pump and the deoxygenation apparatus. The anaerobic column with the height of 700 mm, diameter 45 mm and were constructed as 3 layers. The first layer consists of humus collected from earth surface. The second layer is a coarse gravel (2 - 5 mm diameter) and the third layers containing clean sand spiked with 0.001 % As (relative to mass of dry sand layers) in the form of  $\text{AsO}_4^{3-}$  and 0.005 %  $\text{MnO}_2$  co-precipitation with 0.1% Fe(III) in the form of  $\text{Fe}(\text{OH})_3$ . Water phase is prepared as similar to natural water with the composition as shown in Tab. 1. To maintain the anaerobic condition throughout the system, water was pumped from tank (1) to the anaerobic column (2) from the lower end of the column through the layers and finally the water was pumped back to the tank (1).

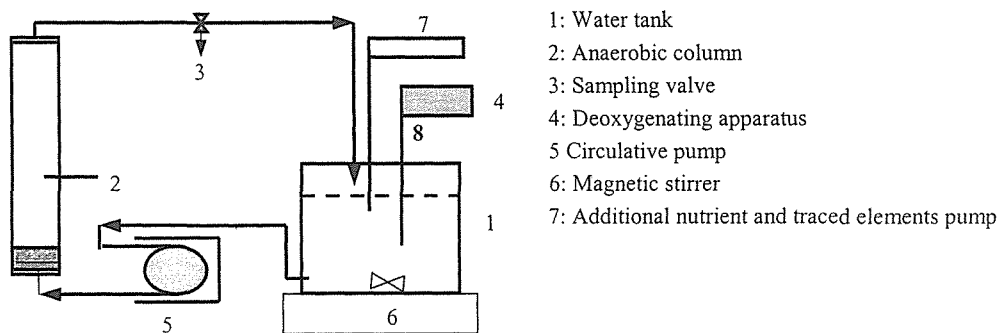


Figure 1. Schematic diagram of the experimental setup for the investigation of arsenic release from alluvial surfaces under anaerobic conditions.

The experiment was run for 56 days continuously. Water samples were collected every 24 hours at the upper end of the anaerobic column by a three-way valve and were analyzed for various parameters such as totals arsenic, iron, manganese, nitrate, phosphate, ammonium, sulfate, sulfur and dissolved oxygen.

Table 1. Composition of water phase in anaerobic experiment.

Composition	Conc. (M)
Ca <sup>2+</sup>	1.0 × 10 <sup>-3</sup>
HCO <sub>3</sub> <sup>-</sup>	2.4 × 10 <sup>-3</sup>
NO <sub>3</sub> <sup>-</sup>	3.0 × 10 <sup>-4</sup>
SO <sub>4</sub> <sup>2-</sup>	5.2 × 10 <sup>-3</sup>
Na-glutamate	1.2 × 10 <sup>-3</sup>
PO <sub>4</sub> <sup>3-</sup>	6.0 × 10 <sup>-7</sup>
Mg <sup>2+</sup>	6.0 × 10 <sup>-5</sup>

Table 2. Analytical methods for determination of various parameters in anaerobic and aerobic experiments.

Composition	Analytical method
Arsenic	HVG - AAS
Fe, Mn	AAS
NO <sub>3</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , NH <sub>4</sub> <sup>+</sup>	Colorimetry
SO <sub>4</sub> <sup>2-</sup>	Conductimetry
S <sup>2-</sup>	Colorimetry (Methylene blue)
Oxygen	Iodometry

Chemical analysis of these ions in water samples was followed the methods reported in Standard Methods for Examination of Water and Waste Water [6] (Tab. 2).

**Experimental setup for investigation of mechanism of arsenic releasing to groundwater under aerobic conditions**

The experimental apparatus is described in Fig. 2. The main component is an aerobic column. The column has 45 mm diameter, 700 mm length and were packed to 2 layers: the lower layer was the minerals derived from weathering process. This mineral was taken from Soc Son district, about 40 km north from Hanoi. The upper layer was the sand phase and spiked with arsenopyrite with an amount of about 0.2 % of the weight of sand. Rainwater was used as water phase. The water was continuously saturated by oxygen throughout the experiment. The temperature was kept constantly at 25 or 38°C by temperature-regulation apparatus (4). Water phase was pumped into the aerobic column from the lower end and then back to the reservoir tank (1). The composition of the rainwater is given in Tab. 3.

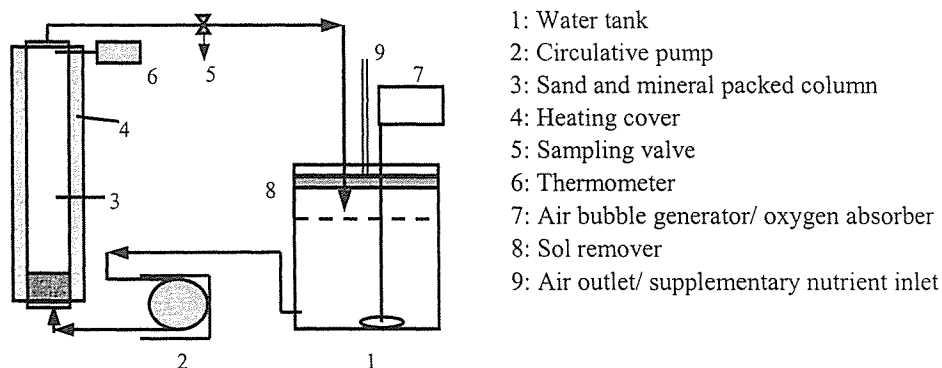


Figure 2. Schematic diagram of the experimental setup for the investigation of arsenic release from mineral surfaces under aerobic conditions.

Table 3. Composition of water phase (rain water) in aerobic experiment

Parameters	As (ppb)	SO <sub>4</sub> (ppm)	NO <sub>3</sub> (ppm)	Fe (ppm)	NH <sub>4</sub> (ppm)	HCO <sub>3</sub> <sup>-</sup> (ppm)
Concentration	0.8	11.6	8.2	0.087	2.4	13.6

## Results and Discussions

### Release of arsenic from mineral surfaces to groundwater under anaerobic conditions

The anaerobic experiment was run for 56 days. The various parameters of water phase in the outlet of the system were measured and results are expressed in Fig. 3 and Fig. 4.

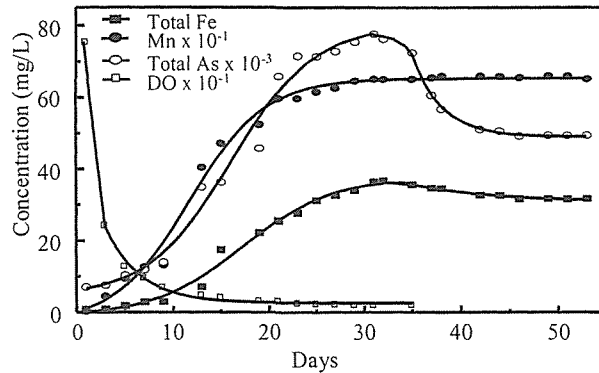


Figure 3. Chronological evolution of Fe, Mn and As concentrations in the water phase of the anaerobic experiment.

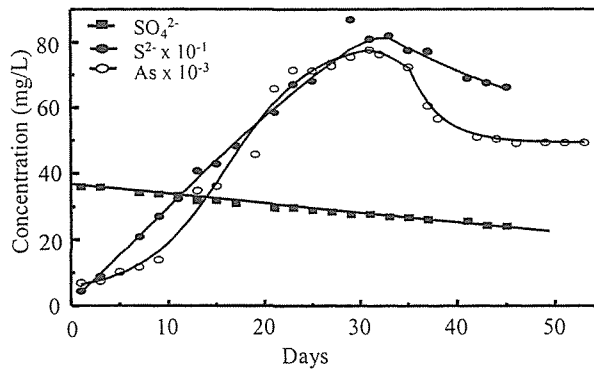
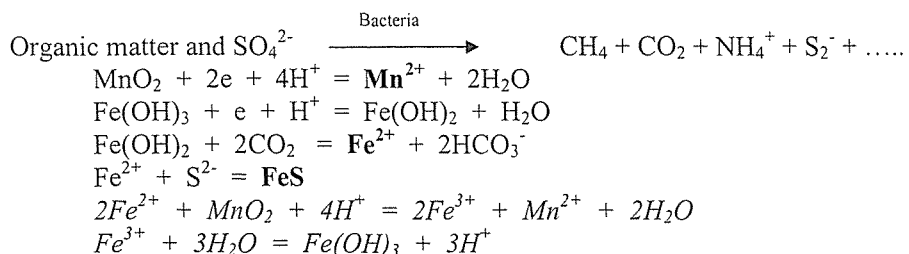
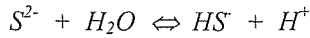


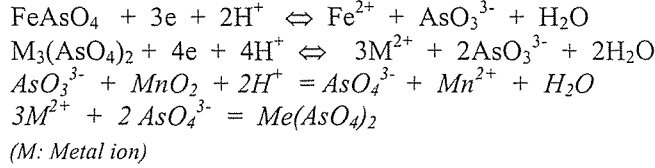
Figure 4. Chronological evolution of sulfate, sulfur and arsenic concentrations in the water phase of the anaerobic experiment.

Chronological variations of various ions in water phase indicate that the reduction of  $\text{MnO}_2$  to  $\text{Mn(II)}$  started under oxygen - depleted conditions (dissolved oxygen < 2.4 mg/L). The  $\text{Mn(II)}$  concentrations increased and remained relatively constant after 30 days. Fe concentrations increased slowly during the first days and the reduction of  $\text{Fe(III)}$  significantly increased after 15 days. At that time, more than 80 % of  $\text{MnO}_2$  was reduced to  $\text{Mn}^{2+}$ . This result indicates that under anoxic conditions, the reduction of  $\text{MnO}_2$  to  $\text{Mn(II)}$  was faster than the reduction of Fe. This phenomenon can be explained by the higher redox potential of  $\text{MnO}_2/\text{Mn}^{2+}$  as compared to that of  $\text{Fe(OH)}_3/\text{Fe}^{2+}$  in the relatively neutral medium ( $\text{pH} \approx 7$ ) [7]. From day 15 to 30, concentrations of  $\text{Fe(II)}$  increased rapidly and then declined and remained relatively constant until the end of the experiment. The suspended precipitation of  $\text{FeS}$  was formed in the system when  $\text{Fe(II)}$  concentrations decreased. Overall, the mechanisms of various processes involved in the anoxic system can be expressed by the following reactions:





The dynamics of As in the anoxic water phase indicate that the release of As and Fe(II) to the water took place at the same time (Fig. 3). We hypothesize that arsenic in alluvial sediments is mainly present in the form of arsenate [As(V)] and predominantly adsorbed onto Fe(III) hydroxide. In the anaerobic experiment, when Fe(III) is reduced to Fe(II) in the presence of dissolved bicarbonate, the reduction of As(V) to As(III) took place simultaneously [8]. In addition, when the MnO<sub>2</sub> content in the solid phase was still high, the re-oxidation of AsO<sub>3</sub><sup>3-</sup> to AsO<sub>4</sub><sup>3-</sup> and the re-precipitation of arsenate are plausible. The process can be depicted as following:



After 30 days, As and Fe(II) concentrations decreased, but not as a result of the lower reduction of Fe(III) to Fe(II). The decreased Fe(II) concentration is related to the formation of precipitated FeS. For the reduction of As concentration after 30 days, we hypothesize that there might be a formation of FeAsS and/or AsH<sub>3</sub>. The reasons for the concomitant decrease of both As and Fe concentrations need further investigations.

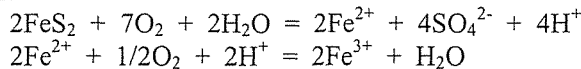
The chemical processes described above suggest that the release of As under anaerobic reduction of organic matters in aquifers is closely related to the MnO<sub>2</sub> contents in alluvial sediments, the reduction of Fe(III) to Fe(II) and the amount of formed FeS. When MnO<sub>2</sub> levels in sediments are high, the reduction of Fe(III) and the release of As is inhibited. We also further tested the groundwater quality at various locations in Hanoi and revealed that elevated arsenic concentrations were found in iron-rich water. In contrast, in manganese-rich water, concentrations of Fe and As were low (for an example, see Tab. 4). These field observations are consistent to the results we found in our anaerobic experiment as discussed earlier. However, a number of chemical equilibrium as well as interactions among various phases may complicate the fate and behavior of arsenic in aquifers. Further studies are required for this topic.

Table 4. Mean concentrations of Fe, Mn and total As in groundwaters collected from various locations in Hanoi city. MD, NH, NSL, LY, YP, PV, HD and TM refer to the following locations: Mai Dich, Ngoc Ha, Ngo Sy Lien, Luong Yen, Yen Phu, Phap Van, Ha Dinh and Tuong Mai, respectively.

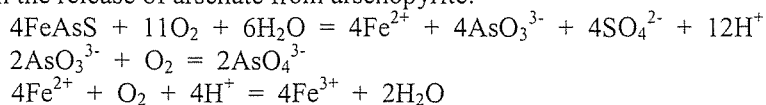
Metals level (mg/L)	Location							
	MD	NH	NSL	LY	YP	PV	HD	TM
Total Fe	0.31	0.62	1.20	2.15	4.78	4.50	8.33	5.64
Mn <sup>2+</sup>	0.95	1.63	0.86	0.37	0.38	0.11	0.13	0.26
Total arsenic	0.03	0.04	0.40	0.06	0.39	0.34	0.26	0.06

#### **Release of arsenic from mineral surfaces to groundwater under aerobic conditions**

The aerobic experiment was run for 50 days at atmospheric conditions (25°C and 1 atm.) with oxygen - rich water (dissolved oxygen >7 mg/L). The results are shown in Figure 5. Sulfate concentrations in the water phase increased after with a rate of about 0.25 mg/L per day. The oxidation of pyrite took place according to the following reactions:



Arsenic concentrations also increased with time at a rate of 0.2 µg/L per day, about 3 orders of magnitude lower than did sulfate concentrations. However, the oxidation process that release sulfate to the water phase took place in parallel with the release of arsenate from arsenopyrite:



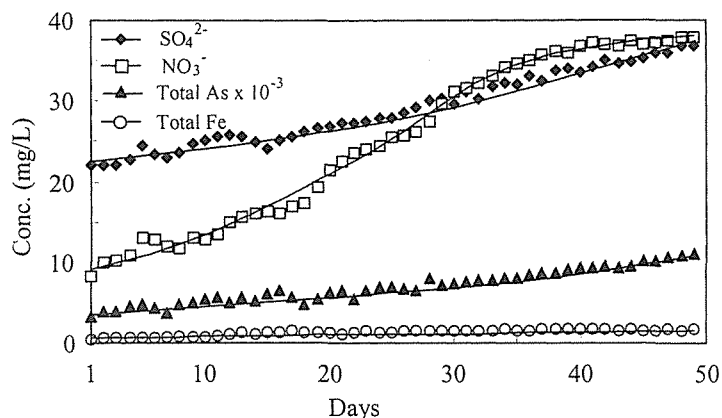


Figure 5. Chronological variation of Fe, sulfate, nitrate and As concentrations in water phase in aerobic experiment.

In addition, a certain amount of Fe was also released to the water. Nevertheless, Fe concentrations were actually found to be low and their chronological increase was negligible. Under oxic conditions of our experiment and pH range of 6.3 - 6.8, most Fe<sup>3+</sup> ions released from the mineral surfaces were hydrolyzed and re-precipitated in form of Fe(OH)<sub>3</sub> and remained in the solid phase. Only small amount of Fe were dissolved in the water phase in the form of Fe(OH)<sub>2</sub><sup>+</sup> or bicarbonate [9]. This phenomenon led to the sorption of arsenate anions onto the solid phase and subsequently inhibited the release of arsenic to water phase. Sulfate ions were less adsorbed and their concentrations were substantially greater than those of arsenate, as observed in Fig. 5. During the experiment, the pH of the solutions slightly increased. When the pH was rapidly lowered through continuous CO<sub>2</sub> purging of the water solutions, the Fe and As concentrations apparently increased. In this case, the re-dissolution of precipitate Fe(OH)<sub>3</sub> may be a plausible explanation.

We also performed the same aerobic experiment at a higher temperature of 38°C. The oxidation process was faster as was evidenced by more rapid elevation of sulfate concentrations. However, the chronological dissolution of Fe and As in the water phase remained relatively similar to that observed in experiment at 25°C. Nitrate concentrations increased at both temperatures due to nitrification of ammonium that was present in the inlet solutions and the release of nitrate from the sediment material packed in the lower part of the aerobic column.

Considering these observations, we suggest that hydrothermal oxidation is a main factor for releasing arsenic from arsenic-rich mineral surfaces to surface water. The mechanism of this process was similar to the oxidation of sulfide to sulfate. At acidic pH values As concentrations increased substantially. Under neutral pH conditions, the release of arsenic is less efficient due to the co-precipitation to iron hydroxide phases. This phenomenon may be a possible explanation for the elevated arsenic contamination in some streams observed in upstream of Ma River area, Northern Vietnam. This river flows through the mountain-rock area and some gold mining sites with arsenic-rich minerals.

## Conclusions

The weathering processes are a potential source for the release of arsenic from arsenic-rich minerals to water phases. Subsequently, arsenic is trapped in alluvial soil layers and again released to water phases during anaerobic bio-disintegration. These are naturally occurring processes that undergo a series of complicated mechanisms. Our preliminary experiments under both oxic and anoxic conditions provide insight into the mechanisms of widespread arsenic contamination in water resources of Vietnam. Such work is critical for us to move to the next stage in developing suitable techniques for removing and lowering arsenic concentration in groundwater and drinking water in Vietnam.

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