

Release of Arsenic from Minerals to the Water Phase

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Abstract

Severe and widespread contamination by arsenic(As) in groundwater and drinking water has been recently revealed in rural and sub-urban areas of the Vietnamese capital of Hanoi with similar magnitude as 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 As concentrations in water supply. In the present study, laboratory-scale experiments were performed to assess the possible release of As from solid phase into water phase under both anaerobic and aerobic conditions. Various chemical equilibria governing the speciation of different ions in the water phase and in alluvial sediments are discussed. Under anaerobic conditions, the release of As seems to be closely related to the content of MnO₂ in sediments, the reduction of Fe(III) to Fe(II) and the formed sulfur content. Elevated MnO₂ content may inhibit the release of As to groundwater. The reduction of As concentrations in water phases could be due to the formation of Fe₂AsS or AsH₃. In aerobic conditions, the hydrothermal oxidation process was proposed as a plausible mechanism of release of As from As-rich mineral surfaces to water phases. In acidic conditions, As concentrations increased due to the more effective release from mineral surfaces. In neutral medium (pH ≈ 7), As release was less efficient, 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 As in surface waters of upstream sections of rivers in mountain areas in northern Vietnam and in underground water of River deltas and are critical for moving to the next stage in developing suitable techniques for lowering As 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 naturally occurring contamination by As in groundwater in Asian countries has received particular attention. The concern over serious health effects caused by As poisoning has been observed in Bangladesh and West Bengal, India (Chowdhury et al., 2000). In Vietnam, due to the similar composition of groundwater as in Bangladesh, elevated contamination by As has been anticipated. Public media have also voiced concern that As contamination in groundwater may become a key environmental problem in Asian developing countries in the 21st century (Christen, 2001).

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To address this issue a comprehensive monitoring survey of the status of As contamination in groundwater and drinking water in Hanoi, the capital of Vietnam and surrounding areas was undertaken (Berg et al., 2001). Our results clearly demonstrate widespread and elevated contamination by arsenic in groundwater and the water supply in sub-urban and rural areas of Hanoi (Berg et al., 2001). The magnitude of pollution was similar to that observed in Bangladesh, with a large number of well waters containing As concentrations exceeding the Vietnam standard of 0.05 mg l^{-1} . This severe situation led to further research towards the understanding of possible mechanisms of widespread As contamination in groundwater and the development of suitable techniques for lowering As concentrations. In 1992, D. V. Can (Can, 2001) observed extraordinary high As concentrations in water of some streams during field investigations in a highland area upstream of the Ma River in northern Vietnam. Subsequent surveys showed that various As-rich minerals, such as arsenopyrite occur widely in this area.

The possible mechanism of As contamination in water of streams in a mountain area may be due to the weathering of As-rich minerals (McArthur et. al., 2001). In Vietnam, there is a relatively large pyrite mine located about 60 km 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 As-rich minerals have been distributed to the land surfaces during gold mining. If the hypothesis is correct that weathering processes may be a cause of As in surface waters, the contamination by As in surface water would be a serious concern in the near future for a large area of northern Vietnam. In fact, surface water from the Red River has been evaluated and it has been found that As concentrations in some locations reached a level of 0.09 mg l^{-1} , exceeding the Vietnam Standard of 0.05 mg l^{-1}). This fact prompted the investigation of the mechanism of As release to surface water from mineral surfaces.

This study investigates the possible mechanisms of As contamination in groundwater, based on observations in well waters in the upper and lower aquifers of the Red River delta (Berg et al., 2001). The mechanisms of release of As from various solid phases were investigated under anaerobic and aerobic conditions. These experimental investigations may be useful for understanding the mechanism of As contamination in water sources and may be critical to developing suitable techniques for lowering As concentrations in water supply and drinking water in Vietnam.

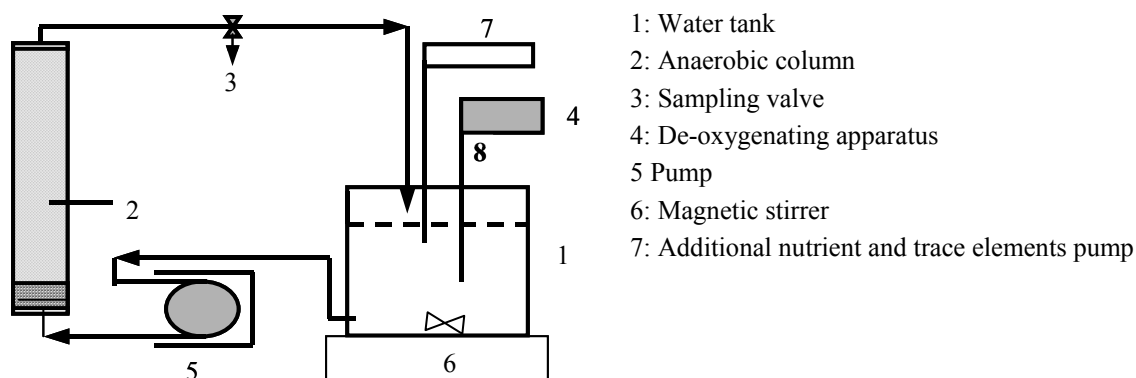
Methodology

Experimental setup for investigation of mechanism of As release to groundwater under anaerobic conditions

A batch experiment was performed to investigate the release of As in groundwater. The experimental setup is described in Figure 1. The main components consist of an anaerobic column, supply pump and the de-oxygenation apparatus. The anaerobic column has a height of 700 mm, a diameter of 45 mm and was constructed in 3 layers. The first layer consists of humus collected from the earth surface. The second layer is a coarse gravel (2 - 5 mm diameter) and the third layer contains clean sand spiked with 0.001 % As (relative to mass of the dry sand layers) in the form of AsO_4^{3-} and 0.005 % MnO_2 co-precipitated with 0.1% Fe(III) in the form of $\text{Fe}(\text{OH})_3$. The water phase is prepared as similar to natural water with the composition as shown in Table 1. To maintain anaerobic conditions 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 As 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 total As, Fe, Mn, nitrate, phosphate, ammonium, sulfate, sulfur and dissolved oxygen. Chemical analysis of these ions in water samples followed the methods described in Standard Methods for Examination of Water and Waste Water (Franson, 1995), (Table 2).

Experimental setup for the investigation of mechanisms of arsenic release to groundwater under aerobic conditions

The experimental apparatus is illustrated in Figure 2. The main component is an aerobic column. The column has a diameter of 45 mm, a length of 700 mm and is packed with 2 layers.

Table 1. Composition of the water phase in the anaerobic experiment.

Composition	Conc. (M)
Ca ²⁺	1.0 x 10 ⁻³
HCO ₃ ⁻	2.4 x 10 ⁻³
NO ₃ ⁻	3.0 x 10 ⁻⁴
SO ₄ ²⁻	5.2 x 10 ⁻³
Na-glutamate	1.2 x 10 ⁻³
PO ₄ ³⁻	6.0 x 10 ⁻⁷
Mg ²⁺	6.0 x 10 ⁻⁵

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

Composition	Analytical method
As	HVG - AAS
Fe, Mn	AAS
NO ₃ ⁻ , PO ₄ ³⁻ , NH ₄ ⁺	Colorimetry
SO ₄ ²⁻	Conductimetry
S ²⁻	Colorimetry (Methylene blue)
Oxygen	Iodometry

The lower layer consisted of minerals derived from weathering processes. This mineral was taken from Soc Son district, about 40 km north of Hanoi. The upper layer was sand spiked with 0.2 % arsenopyrite. Rainwater was used as the water phase. The water was continuously saturated in oxygen throughout the experiment. The temperature was kept constantly at 25 or 38°C. The 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 Table 3.

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

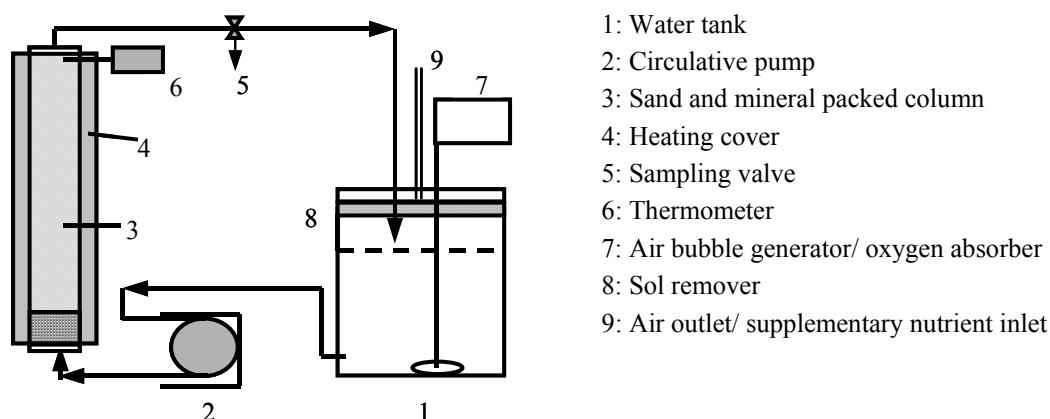


Table 3. Composition of the water phase (rain water) in aerobic experiment.

Parameters	As ($\mu\text{g l}^{-1}$)	SO ₄ (mg l^{-1})	NO ₃ (mg l^{-1})	Fe (mg l^{-1})	NH ₄ (mg l^{-1})	HCO ₃ ⁻ (mg l^{-1})
Concentration	0.8	11.6	8.2	0.087	2.4	13.6

Results and Discussions

Release of As from mineral surfaces to groundwater under anaerobic conditions

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

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

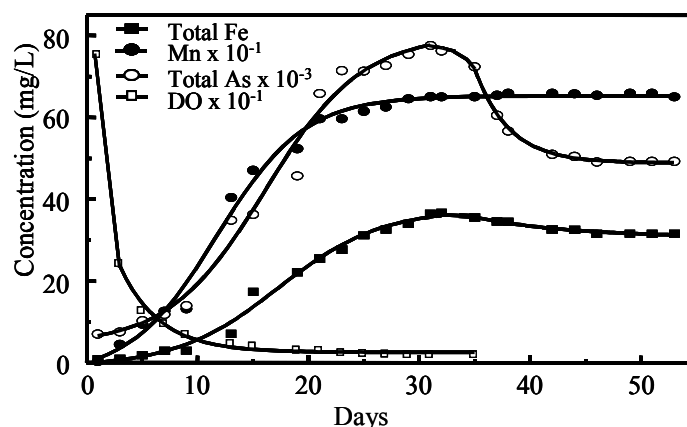
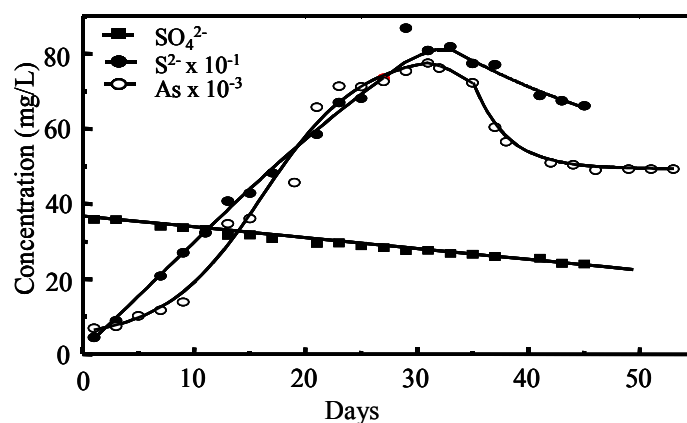
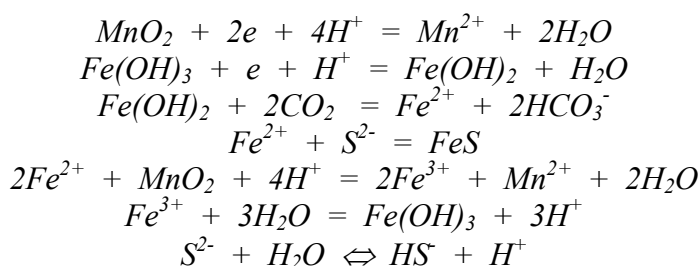
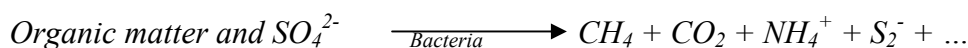


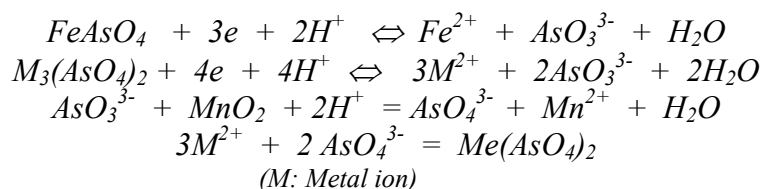
Figure 4. Chronological evolution of sulfate, sulfur and As concentrations in the water phase of the anaerobic experiment.



Chronological variations of various ions in the water phase indicate that the reduction of MnO_2 to Mn(II) started under oxygen - depleted conditions (dissolved oxygen $< 2.4 \text{ mg l}^{-1}$). The Mn(II) concentrations increased and remained relatively constant after 30 days. Fe concentrations increased slowly during the first days and the reduction of Fe(III) significantly increased after 15 days. At that time, more than 80 % of MnO_2 was reduced to Mn^{2+} . This result indicates that under anoxic conditions, the reduction of MnO_2 to 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 ($\text{pH} \approx 7$) (Nickson et. al., 1998). From day 15 to 30, concentrations of Fe(II) increased rapidly and then declined and remained relatively constant until the end of the experiment. The suspended precipitation of FeS was formed in the system when 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 takes place at the same time (Figure 3). It is therefore hypothesized here that As 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) takes place simultaneously (Nickson et. al., 2000). In addition, when the MnO₂ content in the solid phase was still high, the re-oxidation of AsO₃³⁻ to AsO₄³⁻ and the re-precipitation of arsenate are plausible. The process can be presented as follows:



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, it is hypothesized that there might be a formation of FeAsS and/or AsH₃. 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 matter in aquifers is closely related to the MnO₂ contents in alluvial sediments, the reduction of Fe(III) to Fe(II) and the amount of FeS formed. When MnO₂ levels in sediments are high, the reduction of Fe(III) and the release of As is inhibited.

In addition, the groundwater quality at various locations in Hanoi was also tested and found to have elevated arsenic concentrations in iron-rich water. In contrast, in manganese-rich water, concentrations of Fe and As were low (Table 4). These field observations are consistent with the results observed during the anaerobic experiment as discussed earlier. However, a number of chemical equilibria as well as interactions among various phases may complicate the behavior of arsenic in aquifers. Further studies are required for this topic.

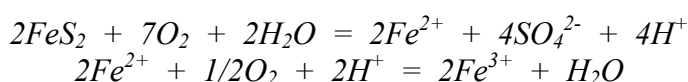
Table 4. Mean concentrations of Fe, Mn and total As in groundwaters collected from various locations in Hanoi city.

Metals level (mg l ⁻¹)	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 ²⁺	0.95	1.63	0.86	0.37	0.38	0.11	0.13	0.26
Total As	0.03	0.04	0.40	0.06	0.39	0.34	0.26	0.06

Note: 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.

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 atmosphere) with oxygen - rich water (dissolved oxygen >7 mg l⁻¹). The results are shown in Figure 5. Sulfate concentrations in the water phase increased at a rate of about 0.25 mg l⁻¹ per day. The oxidation of pyrite takes place according to the following reactions:



Arsenic concentrations also increased with time at a rate of 0.2 µg l⁻¹ per day, about 3 orders of magnitude lower as compared with sulfate concentrations. However, the oxidation processes that release sulfate to the water phase takes place in parallel with the release of arsenate from arsenopyrite:

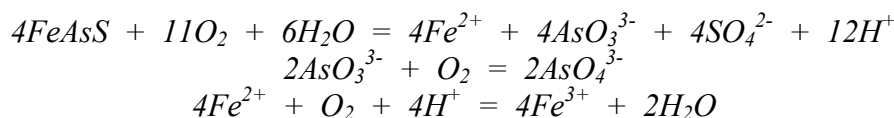
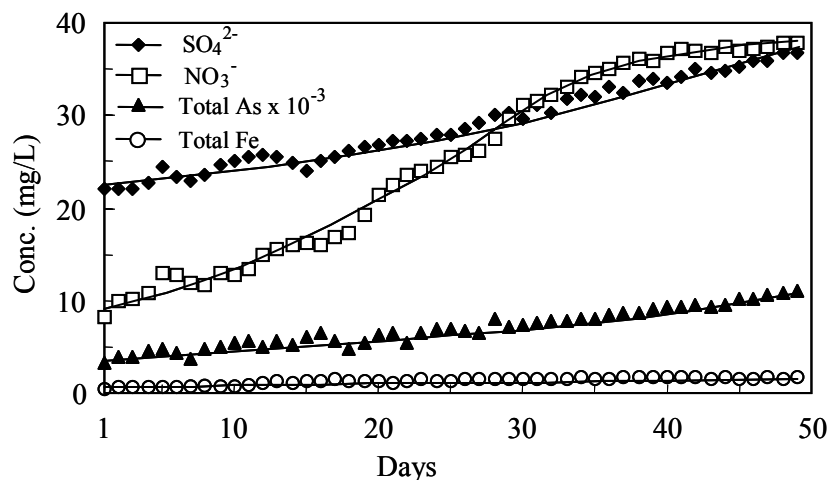


Figure 5. Chronological variation of Fe, sulfate, nitrate and As concentrations in water phase in aerobic experiment.



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 experimental conditions and a pH range of 6.3 - 6.8, most Fe³⁺ ions released from the mineral surfaces were hydrolyzed and re-precipitated in the form of Fe(OH)₃ and remained in the solid phase. Only small amounts of Fe were dissolved in the water phase in the form of Fe(OH)₂⁺ or bicarbonate (Barnes, 1997). This phenomenon led to the sorption of arsenate anions onto the solid phase and subsequently inhibited the release of As to the water phase. Sulfate ions were less strongly adsorbed and their concentrations were substantially greater than those of arsenate (Figure 5). During the experiment, the pH of the solutions slightly increased. When the pH was rapidly lowered through continuous CO₂ purging of the water solutions, the Fe and As concentrations apparently increased. For this, the re-dissolution of precipitate Fe(OH)₃ may be a plausible explanation.

The aerobic experiment was also performed at a higher temperature of 38°C. The oxidation process was faster as was evidenced by a 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 the 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, it is suggested here that hydrothermal oxidation is a main factor controlling the release of As from As-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 As is less efficient due to the co-precipitation to iron hydroxide phases. This phenomenon may be a possible explanation for the elevated As contamination in some streams observed in the headwaters of Ma River, Northern Vietnam. This river flows through an area with some gold mining sites with occurrences of arsenic-rich minerals.

Conclusions

Weathering processes are a potential cause for the release of As from As-rich minerals to water phases. Subsequently, As is trapped in alluvial soil layers and again released to water phases during anaerobic bio-disintegration. These are naturally occurring processes following a series of complicated mechanisms.

The preliminary experiments presented in the paper under both oxic and anoxic conditions provide insight into the mechanisms of widespread As contamination in water resources of Vietnam. Such work is critical in order for researchers to move to the next stage in developing suitable techniques for removing and/or lowering the As concentration in groundwater and drinking water in Vietnam.

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References

- Chowdhury, U.K, Biswas, B.K, Chowdhury, T.R, Samanta, G., Mandal, B., Basu, G.C, Chanda, C.R, Lodh, D., Saha, K.C, Mukherje, S.K, Roy, S., Kabir, S., Quamruzzaman, Q, Chakraborti, D. Groundwater arsenic contamination in Bangladesh and West Bengal, India. *Environ. Health Perspec.* 2000; 108: 393-397.
- Christen, K. The arsenic threat worsens. *Environ. Sci. Technol.* 2001; 35: 286A-290A.
- Berg, M., Tran, H.C, Nguyen, T.C, Pham, H.V, Schertenleib, R. and Giger, W. Arsenic contamination of groundwater and drinking water in Vietnam: A human health threat. *Environ. Sci. Technol.* 2001; 35: 2621-2626.
- Can, D.V. Preliminary assessment of the distribution, removal and accumulation of arsenic in hydrothermal depot bearing high arsenic content. *Scientific Technical Communication on Geology*. Department of Geology and Minerals of Vietnam, Hanoi 2001, 53-57.
- McArthur, J.M., Ravenscroft, P., Safinllah, S., Thirlwall, M.F. Arsenic in groundwater: Testing pollution mechanisms for sedimentary aquifers in Bangladesh, *Wat. Resources. Res.* 2001; 37: 109-117.
- Franson, M.A.H. *Standard Methods for the Examination of Water and Wastewater*. American Publication of Health Association, Washington DC, 1995.
- Nickson, R.T., McArthur, J.M., Burgess, W.G., Ravenscroft, P., Ahmed, K.Z., Rahman, M. Arsenic poisoning of Bangladesh groundwater. *Nature* 1998; 395: 338.
- Nickson, R.T., McArthur, J.M., Burgess, W.G., Ravenscroft, P., Ahmed, K.Z. Mechanism of arsenic poisoning of groundwater in Bangladesh and West Bengal. *App. Geochem.* 2000; 15: 403-413.
- Barnes, H.L. *Geochemistry of Hydrothermal ore deposits*. John Wiley & Sons, New York, 1997.