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SOURCES AND MECHANISMS OF GROUNDWATER CONTAMINATION DUE TO ARSENIC: A CASE STUDY IN HANOI CITY

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ABSTRACT

To identify the source and mechanism of arsenic contamination, groundwater and sediment samples were taken from the well fields for municipal water supply in Hanoi City. Groundwaters in the south zone were anaerobic and contained high levels of arsenic, ammonia, organic matter and iron. DOC, ammonia and phosphorus showed better correlations with arsenic in groundwaters than iron with arsenic. The iron contents in the sediment samples collected from four boreholes fell in a narrow range between 2.5 and 5.0 percent, whereas the arsenic contents varied significantly between <1µg/g and 22 µg/g. All but two soil samples with high arsenic contents (>10 µg-As/g-dry soil) were obtained from the peat layers. Sediments taken from the contaminated aquifer contained higher arsenic than the sediments obtained from the clean aquifer. Although solid-phase arsenic bound to ferric oxyhydroxide was more abundant than organic-bound arsenic, most of the arsenic in groundwaters was estimated to be leached from peat organic matter based on batch As-leaching experiments and the As/N ratios in the sediments and in groundwaters. Detection of pollens of arsenic-hyperaccumulating fern species and mangrove species suggested that arsenic was concentrated by the ancient fern species and mangrove ecosystems and subsequently buried in the sediment.

KEYWORDS

Groundwater, arsenic, ammonia, iron, peat organic matter, DOC

INTRODUCTION

Since the findings of widespread arsenic contamination in groundwaters in West Bengal, Bangladesh and Vietnam, arsenic is one of the major concerns in water supply in tropical Asian countries (BGS/MML, 1999; Berg et al., 2001). Numerous minerals containing arsenic have been reported, which could be sources of arsenic contamination in groundwaters (Huang, 1994). It is well known, however, that the major source of arsenic from old mines is arsenopyrite, which is oxidized when exposed to air and releases iron, sulphate and arsenic according to Eq. (1) (Bhumbla et al., 1994).

$$4FeAsS \text{ (arsenopyrite)} + 13O_2 + 6H_2O \rightarrow 4FeSO_4 + 4H_3AsO_4 \qquad (1)$$
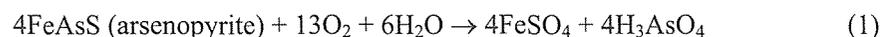
Williams (2001) contended that in the cases of mine tailings control of oxidation processes of arsenopyrite (FeAsS) is crucial to avoid groundwater contamination due to arsenic. They reported two pathways of arsenopyrite oxidation; (1) oxidation to scordite ($FeAsO_4 \cdot 2H_2O$) or ferric arsenate coatings, which are less soluble to water and thus minimizes arsenic contamination, and (2) oxidation to arsenolite (As_2O_3) that is highly soluble into water. In Bangladesh a similar mechanism of arsenic leaching was considered to be playing an important role until mid-1990s (BGS/MML, 1999).

Recently it has been well documented that the predominant reactions of arsenic leaching in Bangladesh is taking place under anaerobic condition. Nickson *et al.* (2000) considered that arsenic is bound to ferric oxyhydroxide (FOOH) and is leached into groundwaters when ferric oxyhydroxide is reduced by peat organic matter. They proposed the following equation.

$$4FOOH \text{ (limonite)} + CH_2O + 7H_2CO_3 \rightarrow 4Fe^{2+} + 8HCO_3^- + 6H_2O \qquad (2)$$
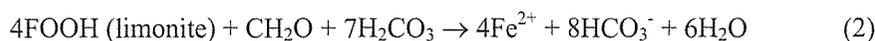
This equation was supported by the good correlation between diagenetically available iron and arsenic in soils, but the amount of bicarbonate found in groundwaters was significantly greater than what is predicted by Eq. (2). Nickson *et al.* (2000) estimated that this is due to dissolution of calcium bicarbonate. McAuthor et al. (2001) supported this mechanism, contending that arsenic is released by microbes from ferric oxyhydroxide, but not due to pyrite oxidation or exchange with fertilizer phosphate. Abul Fazal et al. (2001) examined these two arsenic leaching models expressed by Eqs. (1) and (2), and concluded that, though the evidences given by water quality reports support Eq. (2), the pyrite oxidation model should not be completely abandoned because data varied in time and space. Harvey et al (2002) presented the results of carbon isotope analysis for soil organic matter and inorganic carbon in pore waters, and suggested that the organic matter that caused arsenic leaching came from surface water infiltration.

In order to elucidate the sources and mechanism of arsenic contamination in Hanoi City, groundwater and soil-core samples were taken from the well fields of Hanoi Water Business Company. The contents of ammonia, organic carbon, iron and arsenic were analyzed along with other water quality parameters. Correlations between water quality parameters were examined in order to estimate the source and mechanisms of arsenic leaching. In addition the contents of these contaminants in sediment samples were analyzed, and based on the As/N and As/Fe ratios in groundwaters and in sediments the major source of arsenic in groundwaters was estimated. The solid forms of arsenic were classified into five groups by serial extraction, and pollen species was analyzed to estimate the origin of arsenic-rich peat layers.

MATERIALS AND METHODS

Sample collection and analysis. In the years 2000 and 2001 groundwater samples were taken three times from 35 wells out of a total of 98 wells that belong to HWBS. Temperature, pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), alkalinity, hydrogen sulfide, ferrous iron (Fe(II)) were analyzed at the sampling sites. Temperature, pH, and DO were measured by potable electrodes, and ORP was measured by a platinum electrode (Yokogawa K8229YL, Tokyo, Japan). Alkalinity was measured by acid titration method (Standard Method 19th Ed., 1995). Hydrogen sulfide was measured by gas phase H_2S monitor (Inspection Tube 4LT, Gastec Co., Japan) after bringing pH down to less than 2 by adding an aliquot of conc. HCl. Fe(II) was measured by calorimetric method using Hach DR-890.

Each of groundwater samples were stored in three 100-mL serum bottles and sealed with Teflon caps, and brought to the Environmental Engineering Laboratory, the University of Tokyo. Groundwater samples acidified by HNO_3 were used for the analyses of major cations and arsenic species. Samples acidified with HCl were used to determine ammonia, total nitrogen (TN) and dissolved organic carbon (DOC). Major anions were analyzed for the non-acidified samples. Major cations and metals were analyzed by ICP-AES (Perkin-Elmer Model Optima 3000), and trace metals and arsenic were measured by ICP-MS (Yokogawa Model 4500). Arsenic species were analyzed by a high-performance liquid chromatograph (HPLC, Shimadzu LC-10A) with a polymer-

based anion exchange column (Gelpack GL-LC-A15, L. 75mm, D. 4.6mm), coupled with ICP-MS. The mobile phase was 3mM phosphate buffer at pH 6.0.

Sediment samples were collected from four bore-holes dug in the water treatment plants(WTPs) I, V, VII and VIII. Sediment sample I represents a clean aquifer, II represents the aquifer influenced by the Red River, and VII and VIII were taken from contaminated aquifers in the south zone. Sediment samples were air-dried before analyses of carbon, nitrogen, iron and arsenic contents. There are several procedures proposed for sequential arsenic extraction from sediments(Ahmann et al., 1997; Pongratz et al., 1998; Turpeinen et al., 1999; Keon et al., Welzel et al., 2001). Following Ahmann et al. (1997) and Welzel et al. (2001) solid-phase arsenic was sequentially extracted. Analysis of pollen found in the sediment was performed in Hanoi University of Science. No crystalline forms of arsenic were detected by X-ray diffraction technique.

RESULTS AND DISCUSSION

Sediment analyses. Figures 1 (a) to (d) show the results of soil core analyses. Figure 1(a) shows the correlation between soil iron and total arsenic contents in the sediments. The maximum content of arsenic in the sediment was 22 µg/g, and most of the iron contents fell between 2.5 to 5 wt. percent. The average arsenic content in the world soils is reported to be between 5 to 6 µg/g (Bhumbla and Keefer, 1994; Huang Y. C., 1994; Matera and Le Hecho, 2001). Sedimentary rock contains 20 to 30 µg/g of arsenic (Huang 1994), and coal contains arsenic between 1 to 90 µg/g (Bhumbla and Keefer, 1994). As it can be seen in Figure 6(a) there is no correlation between iron and arsenic contents. It can be said that most of the soils that have high arsenic contents are peat, but some of the peat sediments have lower arsenic contents. Berg et al. (2001) constructed a similar graph between iron and arsenic contents in sediments collected from five bore-holes in Hanoi Province, and reported that they observed an increasing trend of arsenic contents when the iron contents increased. They found many sediments with very low iron (< 20 µg/g) and arsenic (<3 µg/g) contents. This was the reason why it looked like that arsenic contents in sediments increased as iron contents became higher. However, the arsenic contents of sediments with higher iron contents were mostly less than 10 µg/g in their study, which is only slightly higher than the aforementioned average arsenic content in soils. They reported that the peat sediments that contain very high arsenic (>15 µg/g) are outliers. Because we obtained peat samples with high As contents only from the aquifers in the As-contaminated south zone, it can be said that those peat sediments are not outliers, but can be the source of arsenic contamination in groundwaters. Figure 1(b) shows the correlation between the soil iron contents and soil arsenic bound to Fe and Al. This graph shows a similar results as Figure 1(a), having a peak of arsenic contents for the soil samples with iron contents between 3 to 4 wt. percent. These high As-content samples are peat sediments and there is no correlation between iron and arsenic contents.

Figure 1(c) shows the correlation between soil carbon and total arsenic contents. Except for the peat sediments, most of the other sediments had total arsenic contents between 0.1 to 10 µg/g. As for the peat sediments, there are two types; namely the sediments obtained from WF-I and V, which contain total arsenic between 4 to 7 µg/g, and do not have any correlation between soil carbon contents and arsenic contents; and the other type of peat sediments obtained from WF-VII and VIII, which exibited an increasing trend between carbon contents and total arsenic contents. Figure 1(d) shows the correlation between carbon contents and arsenic bound to organic matter. Although the data is slightly scattered they show a positive correlation between the carbon contents and the arsenic contents. The lower boundary is given by the data obtained from WF-I and V, and the upper

boundary is given by the data obtained from WF- VII and VIII. The regression ranges corresponds to an arsenic/carbon ratio between 50 and 100 μg-As/g-C.
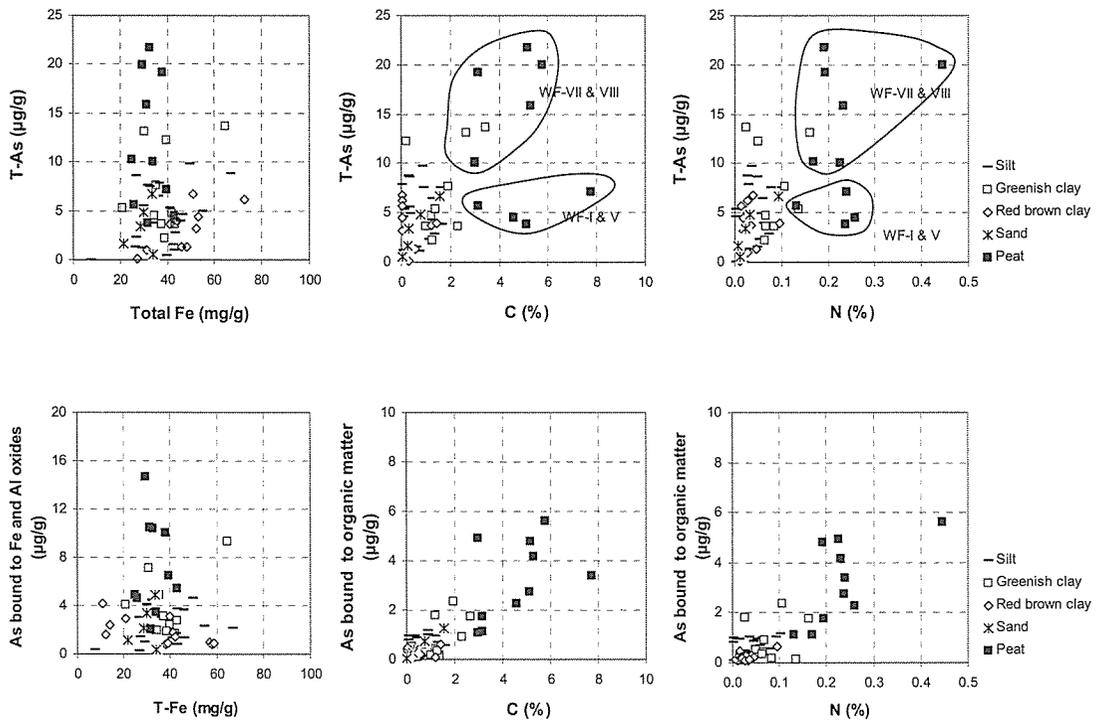
FIGURE 1. Correlation between elements in soils: a) total arsenic and total iron, b) arsenic bound to Fe and Al oxides and total iron, c) total arsenic and carbon content, d) arsenic bound to organic matter and carbon content, e) total arsenic and nitrogen content, and f) arsenic bound to organic matter and nitrogen content.

Figure 1(e) shows the correlation between nitrogen content and total arsenic in sediments. As discussed about the carbon contents, arsenic contents in the peat layers obtained in contaminated south zone(WF-VII and VIII) were high, whereas arsenic contents in the peat obtained in the northwest (WF-I) and the riverain(V) were low. Sediment nitrogen contents and organic-bound As contents can be correlated as shown in Figure 1 (f). Organic-bound-As/T-N ratio in peat sediments varied between 1.0×10^{-3} and 2.5×10^{-3} g-As/g-N. Since ammonia nitrogen is a conservative species, it can be used to estimate the amount of arsenic released from organic matter by assuming that the As/N ratio is constant. This assumption is based on the fact that arsenic in plants is often found to be combined with phytochelatines, which are systesized from gluthione (GSH, $C_{10}H_{17}N_3O_6S$). As shown in Figure 5(c) the maximum concentration of ammonia nitrogen in groundwaters was 28 mg/l, which gives an estimated maximum arsenic concentration of 70 μg/l in the groundwater. On the contrary, the maximum ratio of iron-bound As/T-Fe in sediments was 0.5×10^{-3} g-As/g-Fe. Since the maximum Fe concentration in groundwaters was 38mg/l, it gives a maximum arsenic concentration of arsenic in groundwater as 19 μg/l. As discussed in the preceding section, direct release of As(III) from iron-bound As(V) is thought to be a minor process(Langner et el., 2000). Hence, the amount of As released into groundwater from ferric oxyhydroxide is much less when we assume that arsenic can be released only after Fe(III) is reduced to Fe(II). The maximum concentration of Fe(II) in groundwaters was 13 mg/l, which correspond to an estimated arsenic

concentration of 6.5μg/l in groundwaters. Since iron is not a conservative species it is possible that dissolved ferrous iron was precipitated again. The most likely sink of Fe(II) is formation of pyrite (FeS$_2$) or marcasite (Hounslow, 1995). Sulfate concentration in the Red River was 5.4 mg/l to 7.8 mg/l during the sampling periods. Neither sulfate nor sulfide was detected in the groundwaters in the contaminated south groundwaters. Assuming that the groundwater in the south zone was recharged from the Red River, the maximum amount of Fe(II) that could be precipitated as pyrite is calculated to be 2.3 mg/l, which is only a minor portion of total Fe in contaminated groundwaters. These estimates suggest that decomposition of organic matter is a more important process of arsenic contamination in groundwaters than release of arsenic attached on or incorporated into ferric oxyhydroxide.

TABLE 1. Arsenic leaching in batch tests. Samples were anaerobically transferred to 100-mL serum bottles, filled with 60mL Mili-Q water, and autoclaved at 121 °C for 20 minutes. Serum bottles were then gently shaken for two weeks before water quality analyses. Duplicate tests were performed for each of sediment samples. N. D.: Not detected.

Sediment Sample No. (Well Field ID)	Sediment Sample weight (g)	Fe(II) (mg/L)	T-Fe (mg/L)	DOC (mg/L)	NH$_4$-N (mg/L)	PO$_4$-P (mg/L)	As(III) (μg/L)	As(V) (μg/L)	∑As (μg/L)	Est. Max. As leaching from T-Fe (μg/L)	Est. Max. As leaching from NH$_4$-N (μg/L)
7-1 (WF-VII)	5.3	N.D.	1.42	22.0	5.6	N.D.	7.0	4.6	11.6	0.7	14.0
7-2 (WF-VII)	5.3	N.D.	3.09	26.0	5.0	N.D.	10.7	6.0	16.7	1.5	12.5
30-1 (WF-VIII)	2.9	0.6	0.5	30.0	16.0	N.D.	16.1	11.5	27.6	0.3	40.0
30-2 (WF-VIII)	3.7	0.6	0.6	37.0	21.0	N.D.	22.1	4.6	26.7	0.3	52.5
37-1 (WF-VIII)	1.7	0.5	0.6	35	7.5	0.23	5.2	39.8	45.0	0.3	18.9
37-2 (WF-VIII)	1.5	0.5	0.4	26	6.3	0.20	18.3	50.8	69.1	0.2	15.8

In order to verify the hypothesis that arsenic can be directly released from sediment organic matter without release of iron, batch organic degradation tests were performed. Two peat samples with high arsenic contents were selected, and anaerobically transferred to 100-mL serum bottles. These bottles were filled with 60 mL of de-oxygenated Mili-Q water. Duplicate samples were prepared for each of the sediments. These serum bottles were then put into an autoclave, heated at 121 °C for 20 minutes in order to enhance organic degradation and to inactivate microbes so that microbial reduction of As(V) bound to the surface of ferric-oxyhydroxide and subsequent reaching of As(III) into water is inhibited. The concentrations of arsenic (arsenate and atsenite), ferrous and total iron, DOC and ammonia were analyzed after gently shaking at 20 °C for 2 weeks. As shown in Table 1, the amount of released iron into aquatic phasewas very small, whereas significant amount of DOC, ammonia, arsenate and arsenite were released. By comparing the results of batch leaching tests with the groundwater quality shown in Figure 2, we can conclude that, even without leaching from ferric oxyhydroxide, arsenic (arsenite and arsenate) can be leached into groundwater by degradation of peat organic matter. This result verifies our hypothesis that organic matter is one of the major sources of arsenic in groundwaters. DOC/N ratios in the batch test samples were higher(1.8〜4.1)

than those of groundwaters(ca.0.5), which indicates that dissolved organic matter was subsequently decomposed anaerobically in groundwaters. As(III)/ΣAs ratio was lower in batch samples than the groundwater samples, which indicates that anaerobic As(V) reduction was not a major mechanism of arsenic leaching in these batch tests. AS(V) released into groundwater was supposed to be slowly reduced in groundwaters.

Sources and mechanisms of arsenic leaching. The results of pollen analysis for the arsenic-rich peat layers suggested that these peat layers were derived from plio- to mid-Holocene estuarine sediments, represented by fern species, e.g., *Pteris sp.* and *Polypodium sp.*, and mangrove ecosystems, such as *Aegiceras sp. and Excoecaria sp.* Recent study by Meharg et al. (2002) revealed that a number of plants can hyperaccumulate arsenic. Fern species is well known to hyperaccumulate arsenic, *Pteris vittata* hyperaccumulated arsenic up to 22,630 µg/g (Ma et al., 2001) and the arsenic concentration in fronds of *Pteris vittata* increased up to 7600 µg/g as the concentration of arsenic in soil increased (Zhao et al. 2002). A native Thai fern species, *Pityrogramma calomelanos*, also hyperaccumulated arsenic up to 6380 µg/g (Visoottivisech et al., 2002). While the latter was not found in the Hanoi peat layers, pollens of *Pteris sp.* was found only in the peat layers with high arsenic contents. To date it is not known if there is any mangrove species that can accumulate arsenic (Micaela and Cox, 2002). Kirby et al. (2002) also reported that mangrove trees, main roots, leaves and bark have low arsenic concentration. However, they demonstrated that mangrove ecosystem can concentrate arsenic in their fine root zone by three ways; firstly by oxygenating the fine root zone facilitating dissolution of arsenic sulfides; secondly accumulating iron oxides in the root zone; and thirdly by attaching the epiphytic algae/fungi on fine roots. Arsenic is also concentrated by detritivores, which feed on mangrove detritus. The root zone of mangrove is maintained aerobic for respiration; hence ferrous iron is oxidized on root surfaces to ferric iron. In this process arsenic is being incorporated into iron oxide structure and/or adsorbed on the surface of iron oxides. Our experimental results, along with the above mentioned literature review, suggest that arsenic was hyperaccumulated by ancient fern species together with mangrove ecosystems, which were subsequently buried under Hanoi City. There are two processes of As leaching into groundwaters: As released by degradation of peat organic matter, and As released from ferric oxyhydroxide. The high concentration of ammonia in groundwaters, along with the As/N ratio in sediments, indicated that As released from peat organic matter was more significant than As released from ferric oxyhydroxide. Phosphorus released in the degradation of peat organic matter can facilitate organic leaching from iron oxyhydroxide. Although no in-depth analysis on the relationship between arsenic and phosphorus concentration in groundwaters were carried out in this study, on of the aquifers with high arsenic concentration showed a higher As/P ratio in groundwaters than other aquifers.

CONCLUSIONS

Although solid-phase arsenic bound to ferric oxyhydroxide was more abundant than organic-bound arsenic, most of the arsenic in groundwaters was estimated to be leached from peat organic matter based on batch As-leaching experiments and the As/N ratios in the sediments and in groundwaters. Detection of pollens of arsenic-hyperaccumulating fern species and mangrove species suggested that arsenic was concentrated by the ancient fern species and mangrove ecosystems and subsequently buried in the sediment.

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REFERENCES

Abul Fazal, M., Kawachi, T., and Ichion, E., Validity of the latest research findings on causes of groundwater arsenic contamination in Bangladesh, Water International, Vol. 26, No. 3, p.380-389, 2001

Ahman, D., Krumholz, L. R., Hemond, H. F., Loveley, D. R., and Morel, F. M. M., Microbial mobilization of arsenic from sediments of the aberjona watershed, Environmental Science and Technology, Vol. 31, pp. 2923-2930, 1997

American Public Health Association, American Water Works Association, and Water Environment Federation, Standard Methods for the Examination of Water and Wastewater, 19th ed., Washington D.C., U. S. A., 1995

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, *Environmental Science and Technology*, Vol. 35, No. 13, pp. 2621-2626, 2001

BGS/MML 1999 Groundwater studies for arsenic contamination in Bangladesh. Phase I: Rapid Investigation Phase. BGS/MML Technical Report to Department for International Development (UK), Six volumes.

Bhumbla, D. K. and Keefer, R. F., Arsenic Mobilization and Bioavailability in Soils, in *Arsenic in the Environment, Part I: Cycling and Characterization*, Nriagu, J. O., ed., ISBN 0-471-57929-7, Wiley, New York, 1994

Harvey, C. F., Swaets, C. H., Badruzzaman, A. B. M., Keon-Blute, N., Yu, W., Ali, M. A., Jay, J., Beckie, R., Niedan, V., Brabander, D., Oates, P. M., Ashfaque, K. N., Islam, S., Hemond, H., F., Ahmed, M., F., Arsenic Mobility and Groundwater Extraction in Bangladesh, Science, pp. 1602-1606, Vol. 298, 2002

Hounslow, A. W., Water Quality Data, CRC Lewis, 1995

Huang, Y-C., Arsenic Distribution in Soils, in *Arsenic in the Environment, Part I: Cycling and Characterization*, Nriagu, J. O., ed., ISBN 0-471-57929-7, Wiley, New York, 1994

Keon, N. E., Swartz, C. H., Brabander, D. J., Harvey, C., and Hemond, H. F., Validation of an Arsenic Sequential Extraction Method for Evaluating Mobility in Sediments, Environmental Science and Technology, Vol. 35, pp. 2778-2784, 2001

Kirby, J.; Maher, W., CChariton, A., Krikowa, F., *Spec. Anal.,* 16, 192-201, 2002

Langner, H. W. and Inskeep, W. P., Microbial reduction of arsenate in the presence of ferrihydrite, Environmental Science and Technology, Vol. 34, pp. 3131-3136, 2000

Matera, V. and Le Hecho, I, Arsenic behavior in contaminated soils: mobility and speciation, in *Heavy Metals Release in Soils*, Selim H. M. and Sparks, D. L. eds., Lewis, ISBN 1-56670-531-2, 2001

Ma. L. Q.; Komar, K. M.; Tu, C; Zhang, W. H.; Cai, Y.; Kennedy, E.D.; Nature, 409, 579-579, 2001.

McArthur, J. M., Ravenscroft, P., Safiulla, S., and Thirlwall, M. F., Arsenic in groundwater: Testing pollution mechanisms for sedimentary aquifers in Bangladesh, Water Resources Research, Vol. 37, No. 1, pp. 109-117, 2001

Meharg, A. M.; Hartley-Whitaker, J.; *New Phyto.*, 154, 29-43, 2002

Micaela, P; Cox, M. E.; *Environ. Internat'l*, 28, 433-449, 2002

Nickson, R. T., McArthur, J. M., Ravenscroft, P., Burgess, W. G., and Ahmed, K. M., Mechanism of arsenic release to groundwater, Bangladesh and Wast Bengal, Applied Geochemistry, Vol. 15, pp.403-413, 2000

Pongretz, R., Arsenic speciation in environmental samples of contaminated soils, Science of the Total Environment, Vol. 224, pp. 133-142, 1998

Turpeinen, R., Pantsar-Kallio, M., Hagblom, M., Kairesalo, T., Influence of microbes on the mobilization, toxicity and biomethylation ofarsenic in soil, The science of the Total Environment, Vol. 236, pp. 173-180, 1999

Visoottiviseth, P.; Francesconi, K.,; Sridokchan, W.; *Environmen. Poll.*, 118, 453-461, 2002

Welzel, W. W., Kirchbauer, N., and Prohaska, T., Arsenic fractionation in soil using an improved sequential exrtraction procedure, Analytica Chemica Acta., Vol. 436, pp. 309-323, 2001

Williams, M., Arsenic in mine waters: an international study, environmental Geology, Vol. 40. No. 3, pp. 267-278, 2001

Zhao, F. J., Dunham, S. J., and McGrath, S. P., Arsenic hyperaccumulation by different fern species, New Phytologist, Vol. 156, pp. 27-31, 2002