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Author(s)	Takizawa, Satoshi; Tran, Thi Viet Nga; Inoue, Masafumi et al.
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GROUNDWATER CONTAMINATION DUE TO ARSENIC, IRON, AMMONIA, AND ORGANIC MATTER IN HANOI CITY, VIETNAM

Takizawa Satoshi*, Tran Thi Viet Nga*, Inoue Masafumi*, Khatiwada Nawa Raj* Chu Van Ngoi and Mai Trong Nhuan

* Department of Urban Engineering, the University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, JAPAN

(E-mail: nga@env.t.u-tokyo.ac.jp; inoue@env.t.u-tokyo.ac.jp; nawaraj@env.t.u-tokyo.ac.jp; takizawa@env.t.u-tokyo.ac.jp)

Abstract

The investigations on groundwater contamination in Hanoi City, Vietnam were carried out in August and December 2000. Most of the water samples were taken from the deep wells that tap the lower aquifer. High concentration of arsenic (up to 110 $\mu\text{g/l}$), iron (up to 32 mg/l), ammonia (up to 29 mg/l) and DOC (up to 9 mg/l) were detected in the groundwater in the South of Hanoi, however, a lower concentration range of those species were found on the North part. The results showed very good correlation among different water quality parameters, such as DOC vs TN, $\text{NH}_4\text{-N}$ vs HCO_3^- , As vs Fe(II), $\text{NH}_4\text{-N}$ vs Fe(II), and As vs HCO_3^- . From these data combined with the hydro-geological profiles, a possible mechanism of simultaneous groundwater pollution by As, Fe(II), $\text{NH}_4\text{-N}$ and organic matter was discussed. Under anaerobic condition, there is a combination of the microbial oxidation of organic matter and reduction of Fe(III) to Fe(II). High As concentration in the deep groundwater may be derived from reductive dissolution of As-rich Fe oxyhydroxide minerals, and reduced by either microbial activities or chemical reaction, or both.

Keywords

Ammonia; arsenic; dissimilatory arsenic reducing bacteria; groundwater contamination; Hanoi City

INTRODUCTION

Because of its abundant potential in supplying water to Hanoi City, groundwater has been utilized since early 20th century. At present, the city relies on only groundwater abstracted from the 40-to-60m-depth aquifer of Pleistocene deposit. All eight Water Treatment Plants (WTPs) and a number of small water stations employ the same conventional water treatment process designed for iron removal and chlorination. The water system supplies 450,000 m^3/d of water to the population of 1.5 million in the urban districts (JICA, 1996). However since other contaminants such as organic matter, ammonia, and arsenic have been found in the South of the city (HWBC, 2000; Le Giao, 1995; Anderson and Norrman, 1998), the finished water is difficult to meet both the Vietnam drinking water standard and the WHO guideline. The problem is not easy to solve completely by only modification of treatment processes. Identifying the sources and understanding chemical/geological processes that involve in leaching of these contaminants would contribute to appropriate site selection for groundwater abstraction and long-term management of water resources.

With this background, a study was carried out for the following objectives: (1) to investigate the level and spatial distribution of groundwater contamination by arsenic, ammonia $\text{NH}_4\text{-N}$, organic matter, and iron in Hanoi City; (2) to find out correlation among the contaminants and other water quality parameters such as redox potential ORP, bicarbonate HCO_3^- , electrical conductivity EC, cations and anions; and (3) to estimate the possible factors and mechanisms involved in the groundwater contamination in Hanoi. In this paper, we present evidences for simultaneous natural

processes that give rise in concentration of ammonia, iron, arsenic and organic matter to the groundwater.

GEO-HYDROLOGICAL CONDITION

Hanoi area is a part of Red river delta belonging to Hanoi tectonic depression developed in neotectonic period. Precenozoic fundament has been separated into different blocks by deep faults such as Day river, Red river, Chay river, Vinh Ninh, Lo river and Thuy Anh - Do Son faults (Chu et al. 2000). Cenozoic cover of Hanoi area composes of following formations.

(i) Vinh Bao formation (N_2 *vb*). The rock of this formation is not exposed on the surface, only has been seen in the boreholes with depth of 77 to 97 meters, characterized by gravel, cobble, interbed with silt and sand. In the sediment of Vinh Bao formation there are many microfauna remains, spore and pollens. Thickness is not measured.

(ii) Le Chi formation (Q_I *lc*). It is not exposed on the surface. It has been seen in the borehole, distributed in Nhon and Cau Dien areas, extending to the south and south east of Hanoi. The formation divided into 3 members characterized by cobble, small gravel with a little sand (the lower); fine sand, silty sand of grey colour (the middle); silt, clay and sand of grey colour with plant remains (the upper). Total thickness is of 5.5 to 14m.

(iii) Hanoi formation (Q_{II-III} *hn*). Sediments of Hanoi formation belong to type of alluvial and proluvial facies. They are not exposed on the surface. Based on drilling material, the formation is divided into 3 member consisting of cobble, block, gravel with a little sand and clay (the lower); small gravel, sand and silty sand of grey colour (the middle); clayey silt, sandy silt of grey-yellow colour (the upper). Total thickness is 28m.

(iv) Vinh Phuc formation (Q_{III}^2 *vp*). It is exposed in Co Nhue, Xuan Dinh places. In other ones it has been seen in the boreholes, characterized by weathering surface with different colour. The formation with thickness of 35 to 53m consist of cobbles, gravel cobbles, sand with clay of yellow colour (the lower); silty sand with little clay, yellow sand (the middle); kaoline and clay, black clay (the upper). It is rich in plant remains. Lithofacies are alluvial and swamp.

(v) Hai Hung formation (Q_{IV}^{1-2} *hh*). Consist of sediment of swamp-lacustrine, marine and swamp lithofacies, characterized by sediment of swamp-lacustrine lithofacies formed before transgression, distributed nearly shoreline and consist of clayey silt bearing plant remains, peat and continental swamp, presented by black grey peat, clay of blue grey with gravel (the lower); marine sediment that consist of clay, silty clay of blue grey, distributed in Co Nhue, Xuan Dinh areas (the middle); sediment of swamp lithofacies formed after transgression consisting of clay, clayey silt of blue grey bearing peat (the upper). Total thickness is 9 to 17m.

(vi) Thai Binh formation (Q_{IV}^3 *tb*) covers a large square and consist of sediments of alluvial, lacustrine-alluvial and swamp lithofacies, characterized by cobbles, gravel, silty sand of light brown colour (the lower); cobble with clayey silt of grey and brown colour (the upper).

Among them, Hanoi aquifer that is often named Qp1 contains the most abundant water, and it is the main water supply source for the city (JICA, 1996). All the cenozoic covers have formed 3 aquifers such as Holocene, Pleistocene and Neogene aquifers. Characteristics of each aquifer are shown in the Table 1.

Table 1. Characteristics of aquifers in Hanoi

Indicator	Holocene aquifer	Pleistocene aquifer	Neogene aquifer
Stratigraphy	The lower part of Thai Binh formation (Q_{IV}^{3tb})	Q_{Ic} ; Q_{II-III}^{hm} and Q_{III}^{vp}	N_2^{vb}
Sedimentary composition	Cobble, gravel	Cobble, pebble with sand, gravel	Conglomerate, sandstone, weathering rock and fracture
Statics level under surface (m)	0.66 to 6.43	2 to 4	Undefined
Discharge in borehole (l/s)	0.48 to 29.01	1.7 to 54.41	Undefined
Discharge rate (l/sm)	0.18 to 20.87	0.17 to 23.7	0.005-0.87 to 1.42-3.75
Transmissivity m^2/day	20 to 1389	15.6 to 2565	840
Total mineralization (g/l)	0.202 to 0.580	0.15 to 40	Undefined
Content of Fe (mg/l)	1.24 to 29	2.5 to 40	Undefined
Type of water	Calcite bicarbonate	Calcite bicarbonate	Calcite bicarbonate
Quality	Potential pollution by NH^+ , NO_3^- , NO_2^- and As	Potential pollution by NH^+ , NO_3^- , NO_2^- and As	Good; no sign of pollution

Beside the above-mentioned aquifers there are two weakly permeable layers; Holocene (Q_{IV}^3) weak permeable layer is exposed on the surface with a thickness of 0.4 to 2.5m and has an average permeable coefficient of 0.049 m per day, the Pleistocene-Holocene (Q_{III-IV}) weakly permeable layer with a thickness of 6 to 12.4m lies between Holocene and Pleistocene aquifers. Somewhere it is thinned and creates "Hydrogeological Windows." Its average permeable coefficient is 0.023m per day. In addition Neogene aquifer is separated from Pleistocene aquifer by clay lens; this is why between all aquifers there is close hydraulic relationships.

MATERIALS AND METHODS

Two investigations on groundwater quality in Hanoi were carried out in August and December 2000. Groundwater samples were collected from 34 deep wells in eight well-fields of WTPs that exploit water from the Qp1 lower aquifer, and from 7 private wells that tap the Qh upper aquifer in the urban area (Map1). Other samples were also collected from the Red River and some fishponds in southern part.

Temperature, pH, dissolved oxygen DO, EC, ORP, alkalinity, sulfide and ferrous iron Fe(II) were measured immediately at the collection sites. Samples were analyzed for ammonia, nitrate, E. coli and total coliform group by HACH test kits in a laboratory at the Hanoi University of Civil Engineering. The HNO_3 acidified samples were transported to the laboratory of Department of Urban Engineering, the University of Tokyo where major cations were analyzed by Pekkin Elmer Optima 3000DV Inductively Coupled Plasma - Atomic Emission Spectrophotometer (ICP-AES) and heavy metals were analyzed by Hewlett Parkead 4500 Inductively Coupled Plasma - Mass Spectrometer (ICP-MS). Non-acidified samples were used for anion analysis by ion chromatography.

The total arsenic concentration was measured by ICP-MS. The determination of three arsenic species: arsenous acid As(III) (H_3AsO_3 , $H_2AsO_3^-$), arsenic acid As(V) ($H_2AsO_4^-$, $HasO_4^{2-}$) and dimethylarsenic acid DMAA ($((CH_3)_2AsO_2H$, $(CH_3)_2AsO_2^-$), was performed by HPLC-ICP-MS. The HPLC system consisted of a Shimadzu LC-10ADVP liquid chromatograph and a polymer-based anion exchange column (Gelpack GL-LC-A15, 75 mmx4.6mm), and the ICP-MS was used as chromatographic detector. A solution of 4mM phosphate buffer at pH 6 was used as the mobile phase. Signal for m/z 75 and 77 were monitored in the graphic mode. Peak integration was done manually by measuring the raw counts of the peak height. The details of the chromatograph and instrumental parameters are summarized in Table 1.

Table 2. Instrumental conditions for HPLC-ICP-MS

HPLC	
Column	Gelpack GL-LC-A15, 75 mmx4.6mm
Mobile phase	0.38 g/l (4mM) phosphate buffer (pH6)
Flow rate	1 ml min ⁻¹
Injection volume	100 µl
Detector	ICP-MS mass 75 & 77
ICP-MS	
Radio frequency power	1290W
Sample skimmer cones	Pt
Argon flow rate	
Plasma	16 l min ⁻¹
Auxiliary	1 l min ⁻¹

RESULTS AND DISCUSSION

Groundwater zones based on the water quality characteristics

The results show that groundwater quality varies by area. The groundwater samples were divided into three groups. The first group was the samples from the well-fields IV and V, contained Ca and HCO_3^- as main components and they showed low EC (<270 µS/cm); moderately low ORP (-85 to 115 mV) and SO_4^{2-} (0.5-6.2 mg/l). The samples originated from the well-fields I, II and III belonged to the second category. Compared to the first group, it contained higher content of Ca^{2+} , Mg^{2+} , Na^+ , Cl^- and HCO_3^- , resulting in high EC (328-758 µS/cm); high ORP (50 to -113 mV); high DO (1-3 mg/l); SO_4^{2-} (0.5-12 mg/l); almost no reduced species such as Fe(II); and low concentration of organic matter and arsenic (less than 2 µg/l). The last group was the samples taken from the southern part, including well-fields VI, VII and VIII. It presented a different trend of water quality, i.e., very low ORP (-65 to -117 mV) almost no DO, nitrate and sulfate, and high EC caused by high concentration of Ca, Mg, Na, Fe, NH_4^+ , Cl^- , NH_4 and HCO_3^- . Especially, iron, ammonium and arsenic had elevated concentrations as follows: total Fe 10-41mg/l, NH_4-N 5.3-29 mg/l and As 27-112 µg/l.

From the water quality data and spatial distribution of well-fields, we could divide the groundwater in Hanoi urban area into three zones, namely the belt along the Red River which includes the well-fields IV and V, the center- and west area covering the well fields I, II and III, and the southern area where well-fields VI, VII, and VIII are located.

Correlation between water quality parameters

DOC in groundwater had strong linear correlation with T-N, $\text{NH}_4\text{-N}$, PO_4^{3-} , and HCO_3^- . Consequently, $\text{NH}_4\text{-N}$, and HCO_3^- also had a linear correlation. In most of the samples about 80% of the T-N was $\text{NH}_4\text{-N}$, and the range of $\text{NO}_3\text{-N}$ in the groundwater was between undetected to 0.22 mg/L. Fe(II) was high in the south-well-fields. Fe(II) had a linear correlation with $\text{NH}_4\text{-N}$ except for the samples taken at the well-field of WTP N° VII, where the maximum $\text{NH}_4\text{-N}$ concentration of 29 mg/L was recorded but Fe(II) concentration varied between 4 and 8 mg/L.

In the center and west areas arsenic concentration was very low ($< 2\mu\text{g/L}$). In the area along with the Red River, arsenic concentration was moderately high ($< 30\mu\text{g/L}$), but the samples which are taken from the old wells located within the well-field VI-1 had high content of arsenic (85-112 $\mu\text{g/L}$). There was a correlation between arsenic and HCO_3^- , though the HCO_3^- data varied in a high range in different well-fields, indicating a possibility of multi factors responsible for the origin of HCO_3^- . It can be said that where arsenic concentration was high, Fe(II) concentration was also high, but it is difficult to find a linear correlation because there are sub-groups of data taken from each area. In well-fields VI and VII, the Fe(II) concentration was in the rather narrow range of between 4mg/L and 8 mg/L but the arsenic concentration varied between 27 and 95 $\mu\text{g/L}$.

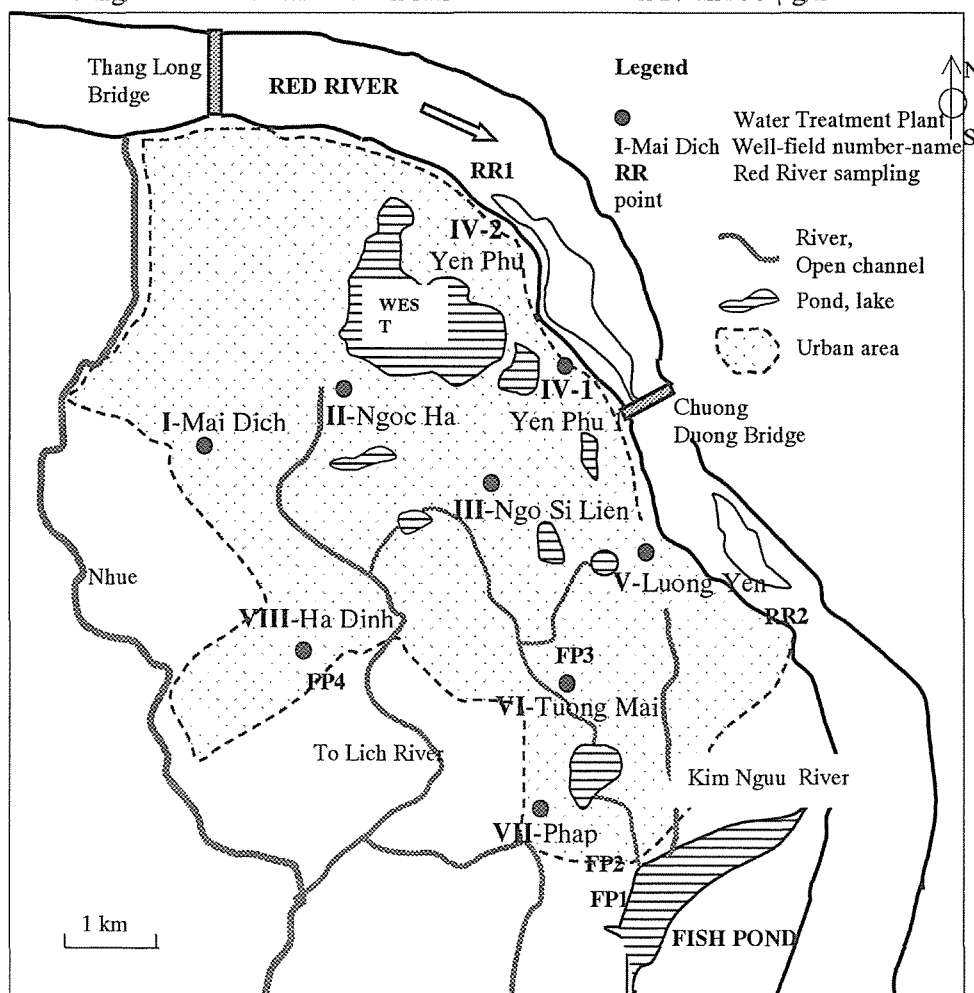


Figure 1: The water sampling locations at eight major well-fields, and some surface water sources (Red River and fishponds), in the urban area of the Hanoi City.

Mechanism of groundwater contamination in Hanoi City

All the major contaminants, i.e., arsenic, ammonia, iron, phosphorus and organic matter were detected in the anaerobic groundwater zones, which is indicated by little DO, low ORP, and depletion of sulfate. Ammonia and phosphorus may be degradation products of organic matter under anaerobic condition, and organic matter is mineralised into H_2O and HCO_3^- . High EC and alkalinity is thus detected in the contaminated areas. Concurrently ferric iron Fe(III) is reduced, using organic matter as the electron donor, to Fe(II) that is dissolved into groundwater. Correlation between Fe(II) and arsenic indicates that arsenic is dissolved into water while Fe(III) reduction is taking place. As(V) thus released into water may be reduced to As(III) under the anaerobic condition. These observations are in good agreement with the anaerobic arsenic release model proposed by Nickson et al. (1999) and Cumming et al. (1999).

However, it is important to note that in two of the south well-fields, i.e., VI and VII, ammonia, arsenic and bicarbonate released was not correlated with the dissolution of Fe(II), which indicate the existence of another primary anaerobic reaction to leach ammonia and bicarbonate. Anaerobic acidogenesis and sulfate reduction may be possible reactions which lead to ammonia and bicarbonate release in these places. The above-mentioned arsenic release theory alone may not be appropriate to explain the arsenic variation in well-fields VI and VII because the arsenic concentration varied in a wide range whereas the Fe(II) concentration was detected in a narrow range. In these well-fields the arsenic level was correlated with ammonia, bicarbonate and phosphorus, but not with Fe(II). This implies that there is a possibility of another mechanism of arsenic release into groundwater, which needs to be further investigated.

The As(III)/ T-As ratio in well-fields VI and VII was 0.86 on the average that was higher than 0.70 in well-field VIII. Especially 50% of the samples from well-fields VI and VII had a As(III)/T-As ratio of 1.00, indicating that all the arsenic detected was in the form of As(III). This implies that in these well-fields, in addition to the aforementioned arsenic contamination process, there may be another direct leaching of As(III) into the groundwater. Dissimilatory reduction of As(V) to As(III) has been recently reported with discovery of a number of anaerobic bacteria which can use As(V) for respiratory growth (Fig.1). For example, *Sulfurospirillum arsenophilum* (MIT-13) was first reported by Ahmann et al. (1997), was capable to reduce and mobilize arsenic. Zobrist et al. (2000) showed direct reduction and leaching of As(III) from As(V) mediated by *Sulfurospirillum barnesii* (SES-3) using lactate as an electron donor, and this reaction was independent of iron reduction. Langner et al. (2000) also demonstrated reduction of As(V) to As(III) by glucose-fermenting microorganism CN8, not as a results of coupling arsenic reduction with respiration. Other abiotic pathways under anaerobic environment have also been discussed, for example, As(III) can be released from As_2S_3 under a high bicarbonate concentration (Kim et al., 2000) or sulfate may reduce arsenic under acidic to neutral condition (Rochettee et al., 2000). These are possible mechanisms taking place in well-fields VI and VII.

Another important finding was a high level of arsenic in a number of wells located along the Red River, whereas most of the other wells in the same area showed low to medium arsenic contamination. These wells are located in the old well-fields inside the city area and a little away from the Red River. In these wells ORP was significantly lower than the new well-fields along with the river, and their water quality is also characterised by moderately high Fe(II), sodium, and chloride, and trace amount of hydrogen sulfide. But unlike the south well-fields, ammonia, T-N, DOC and bicarbonate concentrations were not high. These results suggest yet another pathway of anaerobic arsenic leaching that is decoupled with organic matter degradation.

5. CONCLUSIONS

Groundwater samples in Hanoi City were taken in August and December 2000, and analysed for arsenic, ammonia, iron, organic matter, and other major water quality parameters. The well-fields were classified into three distinctive areas based on the spatial distribution and water quality characteristics. The well-fields located to the south of the city were contaminated with high levels of arsenic, ammonia, phosphorus, iron, and organic matter. The correlation of these parameters, along with anaerobic conditions in these well-fields, indicated that arsenic release is taking place due to iron reduction coupled with organic matter oxidation. There are evidences that imply the existence of alternative pathway for the arsenic release that is not associated with iron reduction or organic matter degradation. Further investigation is necessary to elucidate the arsenic release mechanisms in each well-fields.

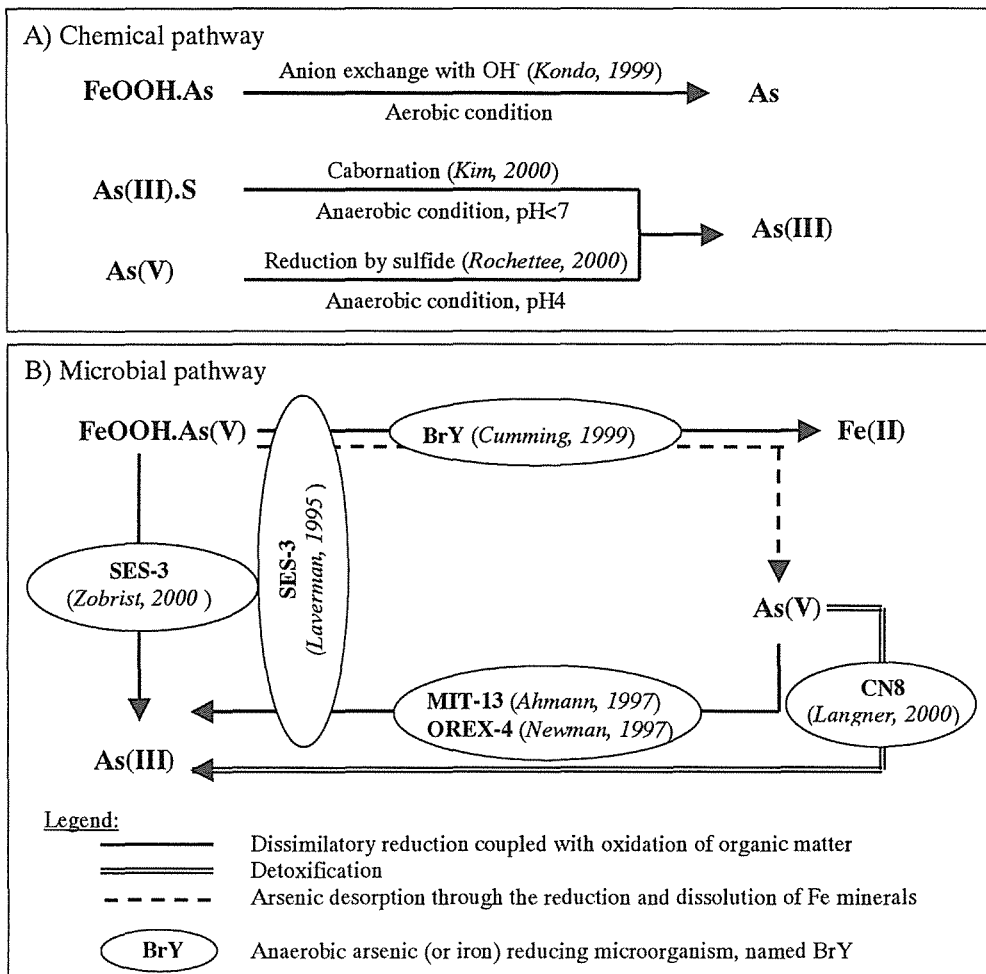


Figure 2. The arsenic reduction and dissolution processes through A) abiotic mechanism, and B) microbial activities, reported by different authors.

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