ARSENIC DISTRIBUTION IN NATURE AND THE ENVIRONMENTAL POLLUTION BY ARSENIC IN VIETNAM

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ABSTRACT

The rocks of hydrothermal deposits and surrounding rocks, sulfur, gold and polimetal ores as well as their weathering crust and soil are richer in As (5 - 216,824 ppm) than other formations (in magmatic rocks: < 13.1 ppm, in sedimentary rocks < 1.33 ppm; in coastal sediment: 0.11 - 200 ppm). Streamwater in areas of hydrothermal deposits (Ban Phung) and ground water in several places of Hanoi and VietTri cities have higher arsenic concentration than the other areas.

In Vietnam there are 3 zones of As pollution:

1. Mountain zone of ore deposits (Au-, Pb- and Zn- ores deposit, their weathering crust and soil in upper part of Ma river, Khau Au, Cho Don (Bac Can), Doi Bu (Hoa Binh) with very high As concentration. Only natural processes (hydrothermal and volcanic activities, weathering processes..) are the As pollution source.
2. In some places of delta plain with ground water polluted by As, the natural processes (oxidation of sulfur and arsenic minerals in the sediment, reduction of As bearing iron hydroxides..) and human activities are the main As pollution sources.
3. Coastal zone (sea sediment of Phu Yen, Quang Ngai coastal polluted by As...), As pollution is caused mainly by human activities, especially pesticide, fertilizers and chemical weapon utilization, chemical and glass industry, metal smelting, ore mining...

KEYWORDS: arsenic; geochemistry; pollution; rock; soil; groundwater

INTRODUCTION

Arsenic in low amount is a very necessary element and it is a strongly toxical substance when its amount is high enough to human body and the other biological organism. To minimum harmful effects and maximum useful characters of arsenic, there is a big need of studying environmental geochemistry of arsenic (source, distribution, behavior, pathways enter environment and human body, harmful effects and solutions for limiting these effects...). Environmental geochemistry of arsenic is the scientific basic to solve the whole environmental pollution caused by this element. There are a few such study and results of As environmental geochemistry and the As researches have only been concerning separate aspects of environmental pollution by arsenic. The paper is a small contribution to the solution of the problem.

Arsenic distribution in natural environmental components

Because of natural processes and human activities, As can migrate from one component of environment to the other leading to its complicated distribution in nature.

Arsenic in rocks and ores

The average arsenic content in Vietnam magma rock without hydrothermal change is lower than 13.1 ppm (N. K. Quoc, 1992), in sedimentary of North - Western, Vietnam: 0.28 - 1.33 ppm, in the shale of Co Noi formation (T1cn) - 0.93 ppm, in the sandstone, siltstone of Yen Chau formation (K2yc) - 0.47 ppm, carbonate rocks of Ban Pap formation (D2bp) - 1.33 ppm (Do Van Ai, 1994). That is the same of world carbonate (2 ppm) and sandstone (1.2 ppm).

Surrounding rocks of hydrothermal deposits normally contain high content of arsenic. As concentration in basaltic effusive rocks of Doi Bu deposit (Hoa Binh province) is about from 50 to 204 ppm according to Dr. Dang Mai (2000). Its concentration in the sandstone, siltstone, shalestone of Than Sa formation ($\in$ ts) of gold mineralization area (Bac Can province) is about 13.2 ppm; in the gold ore of Khao Au:1292 -1442 ppm; in the sericite schist, shalestone of Coc Xo formation (D_1 - D_2ecx) of Cho Don lead - zinc deposit (Bac Can province) – 97.8 ppm; in lead - zinc ore of Cho Don – 82,050 – 261,824 ppm (Do Van Ai, 2000). In general, the arsenic content in hydrothermal deposits is higher than that in the surrounding rocks and in the areas without mineralization. So the hydrothermal deposit areas are characterized by higher ecological toxicity than the other area.

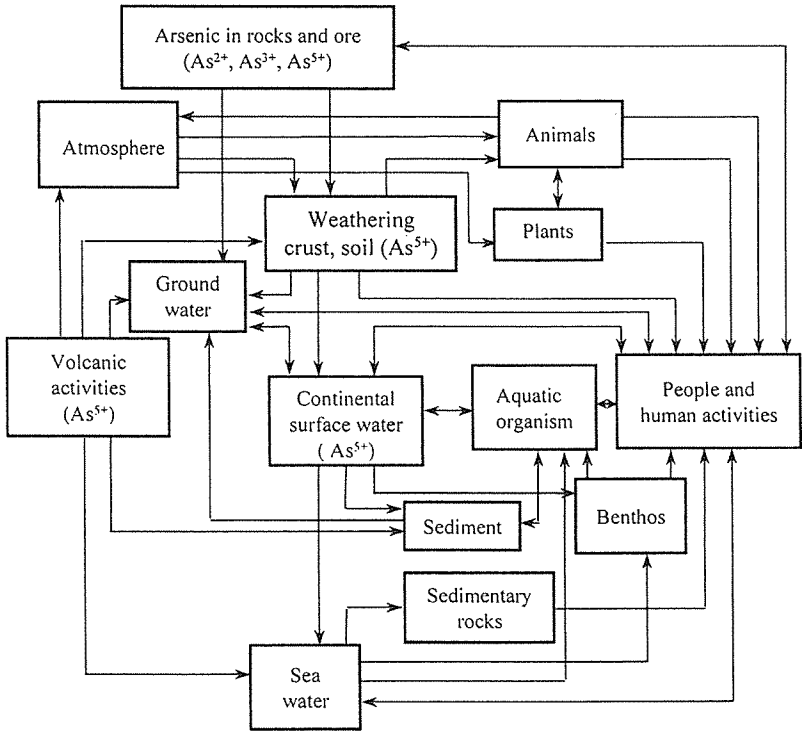

Fig 1. Scheme of the arsenic circle in the environment

Arsenic in soil and weathering crust

There is very little literature of geochemistry of arsenic in soil of Vietnam. Recent researches (Do Van Ai, 2000) on arsenic distribution in soil and weathering crust in Vietnam showed that:

The average arsenic content in the soil of North - Western is in a variable range of 2.6 – 11 ppm (Do Van Ai, 2000). Soil originated from metamorphic rocks (xerixit board, mica board, amphibolites of Nam Co formation PR_2-$\in_1$nc), soil on metamorphic rocks of Suoi Rieng formation (PR_1sc) have low arsenic content, about 2.6 ppm. The arsenic content in the sloping soil developed on carbonate rocks of Dong Giao formation (T_2dg) is 2.87 ppm, in the soil developed on the sandstone, siltstone, shalestone of Cam Thuy formation (P_2ct), in the sandstone, siltstone of Yen Chau formation (K_2yc) about 7.1 - 8.4 ppm, in the soil on shalestone of Ma river area (0 sm) – 9.35 ppm... (Do Van Ai, 1994). Weathering crust developed on the gold - ore in Doi Bu is richer by arsenic (5 - 2550 ppm, the average content is 372 ppm). Arsenic content in the soil and in feralit weathering crust developed on basalts of Vien Nam formation of the gold - ore in Doi Bu is 5 – 220 ppm, average of 161 ppm (Dang Mai, 2000).

Many kinds of soil in different landscapes is richer in arsenic than its parent rocks. For example, the arsenic contents in the soil and in their parent rocks for terigenerous rocks of Khau Au (Bac Can) gold ore are 16.9

ppm and 13.2 ppm respectively, of sedimentary and metamorphic rocks of ChoDon, lead-zinc deposit are 915 ppm (210-1,518 ppm) and 97.8 ppm

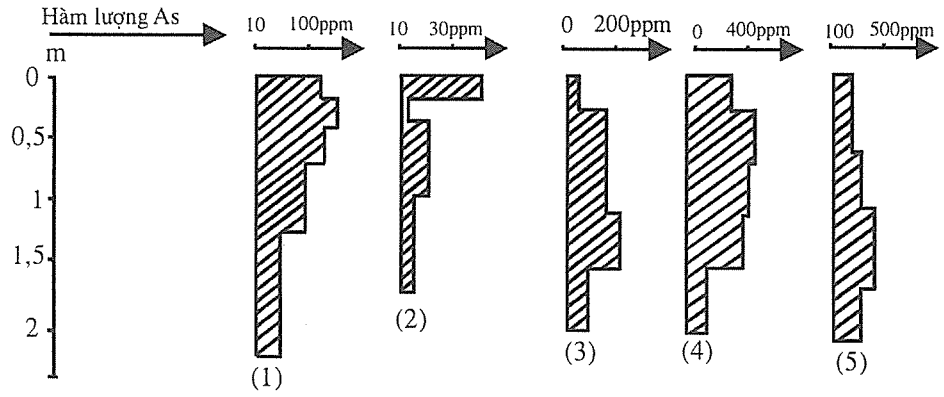

Fig 2. Arsenic distribution after the depth in the weathering crust

Note:
(1), (2) weathering crust on trachit alkali-acidic effusive rocks, trachit, trachit poocfia of Doi Bu zone, Luong Son, Hoa Binh province.
(3) Weathering crust on sandstone, siltstone of Khau Au, Cho Moi (Bac Can province)
(4), (5) weathering crust on xerixit shale of Cho Don (Bac Can province)

Arsenic normally concentrates in the upper parts of weathering crust and soil in the A-B and B horizons (Fig 1) because organic materials, colloids of iron-hydroxide and clays, absorb it. In the condition of dry weather, arsenic components normally exist in lightly mobile forms. On the contrary, in the condition of wet weather, arsenic-sulfur compounds are soluble and released. About 5-10% of the total As in soil could be released into the drainage solution.

Arsenic in the unconsolidated sediments

The total arsenic content in global ocean is 1 ppm (Vinogradov, 1967), in the quaternary fine sediment of Osaka, Kobe, Chiba, Fukuoka, Sendai (Japan) formations is of 1 - 30 ppm, in sea sediment of Plio - Pleistocene Osaka formation is 200 ppm (Mitamura, 1998; Masuda and Mitamura,1998). The arsenic content in the quaternary sediment of boreholes in Hanoi (6 - 63 ppm for brown clay sediment, 2 - 12 ppm for gray clay, 0.5 – 5 ppm for gray grown yellow sand) have linear relation with the content of $Fe(OH)_3$, FeOOH (R_{As-Fe}= 0.94), according to Nguyen Thi Chuyen, Pham Hung Viet (2000).Vietnamese shallow sea sediment contains As. The highest As content is characterized for seashore of BacLieu – Ca Mau and Phu Yen, Quang Ngai (Mai Trong Nhuan, Dao Manh Tien, 1997, 1998, 1999).

Arsenic in water

The arsenic content in ground water in some places of Northern Vietnam is about 0.0001 – 0.32 mg/l (Do Trong Su, 1997, see table 2). Arsenic concentration in ground water in some sites of Viettri, Hanoi and Haiphong cities (the average content of 0.014 – 0.34 mg/l) is higher than that of Bac Giang and Nam Dinh towns (the average content of 0.0038 – 0.0068). The reference of As concentration in groundwater of Norway and Japan are 0.00002 and 0.0003 - 0.0034 mg/l, respectively. The arsenic content in Pleistocene aquifer (0.0003 – 0,0937 mg/l) is lower than that in Holocene aquifer (0.0002 – 0.132 mg/l, Do Trong Su, 1997). The arsenic content in ground water in the Hanoi area with the quaternary organic material – bearing mud sediment is higher than the other areas (Nguyen Thi Chuyen et. al, 2000).

Table 1. The arsenic content in water (μg/l) of some areas in Vietnam (Do Trong Su and Dang Van Can)

Area		Rainy season		Dry season	
		Surface water	Ground water	Surface water	Ground water
South-Eastern of Ban Phung (upper part of Ma river)				430-1140	
Bac Giang town		5 – 43.7 / 24.2	0.1 – 12.2 / 6		1 – 19 / 6.8
Viet Tri – Lam Thao area		1 – 74.6 / 33	0.1 – 9.4 / 4.1		1 – 320 / 25.4
Hanoi	Holocene aquifer	3 – 107 / 26	0.2 – 118 / 5.9		0.2 – 132 / 33.9
	Pleistocene aquifer		0.1 – 28 / 12.7		0.3 – 93.7 / 14.4
Hai Phong city			0.3 – 15 / 4.1		1.7 – 96 / 13
Nam Dinh town			0.1 – 29 / 4.8		0.1 – 16.1 / 3.8

Arsenic in groundwater in Hanoi area

Raw waters (lower aquifer) and treated waters from the eight water treatment plants of Hanoi were analysed seven times between March 1999 and July 2000. The concentrations of September 1999, showed that more than 50% of number of water plants in Hanoi had As concentration equal to higher than Vietnam Standards of 0.050 mg/l (see Fig. 3., Michael Berg and Pham Hung Viet, 2000).

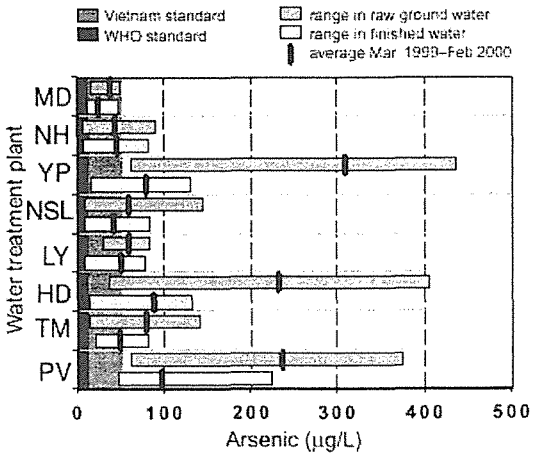

Figure 3. Arsenic concentration in some main well-fields of Hanoi Water Plants

The recently investigated results (Pham Hung Viet and Le Van Chieu, 2001) showed that the groundwater in qh and qp aquifer has signal of arsenic contamination with heavy metal such as arsenic, manganese and ammonia. The arsenic contamination area in two aquifers is mainly in the south and south-east area of the Hanoi. As concentrations in groundwater were evaluated in the comparison with Vietnam Standards (<0.05mg/L) and contamination percentage was counted based on samples which have As concentration beyoned Vietnam Standards in total 500 samples. The distribution of As contamination in qh and qp aquifers with 31.2% and 26.7% of contamination scale, respectively. Especially, this contamination areas were coinciding with distribution areas of the peat, mud layers as well as high pollution area of ammonia. The total iron contents and total arsenic contents in sediments showed almost linear correlation and the As contamination areas were coinciding with distribution areas of the peat, mud layers as well as high pollution area of ammonia in Hanoi. This may explain partly the source of As releasing from the sediment in to groundwater followed the reduction of iron oxyhydroxide mechanism as bellows:

$$4FeOOH + \underbrace{CH_2O}_{\text{Representative for organic matter}} + H_2CO_3 \xrightarrow{\text{Microbial metabolism}} 4Fe^{2+} + 8HCO_3^- + 6H_2O$$

Arsenic in the biological organism

Our recent researches on chemical composition of some kinds of foods of Son La showed that the average arsenic contents in dry paddy, corn seeds and cassava bulb are 0.97; 0.78 and 0.22 ppm, respectively, but lower than that of the world vegetables (110 - 200, 30 - 40 ppm, respectively). The As content in paddy is normally higher than in corn and cassava (Do Van Ai, 1995). Then, the arsenic content in the plants grown on fields in the mountains currently is quite low and equal to its content in plants of the other countries in the world before 1940 (0.3 - 0.5 ppm).

Epidemiological research of citizen living in the polluted area by arsenic in Song Ma district showed that, average arsenic content in urine (89.2 – 120.2 ppm), finger nail (1.72 - 1.85 ppm), hair (1.61 – 1.73 ppm) are higher than that in the normal areas (37.09± 24.54 ÷ 42.17 ± 39.08 (mg/l) and 1.64 ± 0.37 mg/kg. Rt-n^{SO4} = - 0,604, Rt-n^{NO3} = 0.591, respectively, Dao Ngoc Phong, 1993). There is rather closed relationship between As content in human body and in living environment, for example, the average arsenic content in hair of rural area's people is 0.4 – 1.7 ppm, of industrial area: 0.4 – 2.1 ppm, of strongly polluted area: 0.6 – 4.9 ppm.

The environment pollution by arsenic

Arsenic pollution sources are natural processes (volcanic effusion, magma activities, hydrothermal, weathering proceeses...) and especially human activities (fossil fuel burning, waste burning, smelting ore, metallurgy, exploitation and processing of ore, in particular sulfur ore and arsenal ore, production and use of pesticide, chemical fertilize, chemical weapons, water exploitation...) (fig1).

There are many electric thermal factories in our country (Pha Lai, Uong Bi, Ninh Binh, etc.); cement factories using coal as fuel (Chinfon – Hai Phong, Hoang Thach, Nghi Son, Ha Tien...); many metallurgical factories (Thai Nguyen, ...) and they are also arsenic pollution sources. The arsenic content presented in: phosphorus fertilizer of 2 – 12000 ppm, nitrogen fertilizer of 2 – 120 ppm, organic fertilize of 3- 25 and pesticide of 22 – 60 ppm. As an agricultural country, Vietnam has been using a great amount of fertilizer and pesticides contained As, consequently arsenic contents in the aquatic environment and sediment are increasing on time. In the wars, the enemies used many toxic substances containing As in Vietnam, causing pollution of water, soil and sediment by this element.

Environment pollution by As is recognized in many countries of the world: ground water pollution in Bangladesh and India (2000 mgAs/l), in Chile (800 mg/l), Taiwan (600 mgAs/l), Gana (175 mgAs/l), USA (8 mgAs/l); soil pollution in UK (2% As).

In Vietnam there are 3 main zones of As pollution: mountain, plain, coastal zones which differ each from another in the pollution sources, migration and concentration of As in the environment. The average arsenic content in variable listvenite rocks of many magnetite - ore zones in upper part of Ma river is 34 – 176 ppm, in soil: 51 – 76 ppm, in streamwater; 0.43 – 1.14 mg/l (Dang Van Can, 1992). Arsenic anomalies in soil and weathering crust of gold – ore in Doi Bu (Hoa Binh), Khau Au (Bac Can), lead – zinc ore of Cho Don have a high potential of As pollution. These arsenic anomalies are the origin of geochemical provinces in Vietnam: such as Lo Gam zone (100 –200 ppm), Song Da zone and Nghe tinh zone (100 –300 ppm), Kham Duc zone (200 – 300 ppm), specially in Ma river zone (100 – 500 ppm) (Nguyen Van Khuong, 1985, Nguyen Tien Dung, 1996).

The As content in water of Holocene aquifer in Hanoi is about 0.044 mg/l (0.0001 – 0.132 mg/l). Pleistocene aquifer has the content of 0.0001 – 0.0937 mg/l (Do Trong Su, 1992). Arsenic content in some of ground water samples from well-field in Hanoi exceeds Vietnam standard of 0.05 mg/l (Pham Hung Viet 2000). The south of Hanoi is characterized by a trend of As concentration in Holocene aquifer with As content of 0.05 – 0.08 g/l, meanwhile in the north of Hanoi anomalies are discovered in Pleistocene aquifer located in the boundary of Hong river and Duong river.

The average arsenic content in ground water at some sites of Viettri industrial zone (mainly chemical industry) exceeded the WHO guideline (0.010 mg/l). The weathering crust, aquifer and alluvium have rather high As contents. Weathering crust and soil horizons in the hill areas are favorable for water drainage and geochemical processes, especially oxidation releasing As into water.

Ground water at some sites in Hai Phong, Bac Giang, Thanh Hoa, Nam Dinh provinces also have arsenic content exceeding the WHO standard (Do Trong Su, 1996, Tran Huu Hoan, 1999).

There is a little of detail study on the problem of arsenic pollution in the South's delta plain that with intensive industrial and agricultural activities. The basic arsenic content in ground water of the South plains is not high, normally lower than Vietnam standard, but some sites such as Tra Vinh, Can Tho, Ben Tre towns and Ho Chi Minh city could have potential of as pollution in ground water.

The result of investigation of Center for Marine Geology and Mineral Resources, University of Science, Hanoi (Mai Trong Nhuan, Dao Manh Tien, 1995 - 2000) showed that Vietnam's coastal water had potential of As pollution in South-Eastern of Genh Hao estuary (Ca Mau), As = 0.36 – 0.4 mg/l. Coastal sediment in many parts of Vietnam has not been polluted by As, except the eastern of Hon Trau (Phu Yen province), the eastern of An Hoa (Quang Ngai province. 190 – 200 ppm, see table 2).

Table 2. The arsenic content in coastal water (μg/l) and sediment (ppm) of some areas in Vietnam (After Mai Trong Nhuan, Dao Manh Tien)

Area	Sea water at depth of (< 10m)	Sea water at depth of (10-30m)	Sea sediment
Mong Cai-Hai Phong	0.1 – 4.7 / 2.1	2.1 – 4.1 / 3.0	0.2 – 6.1 / 1.5
Hai Phong – Nga Son	0.1 – 3.6 / 1.8	0.1 – 8.6 / 2.5	0.1 – 0.89 / 0.31
Nga Son – Deo Ngang Deo Ngang – Hai Van	01 – 7.5 / 2.7	0.1 – 8.6 / 2.5	0.1 – 0.89 / 0.31
Dong Hon Trau (Phu Yen), An Hoa (Quang Ngai province)			190-200
Vung Tau – Tr Vinh – Bac Lieu	2 – 5.6 / 3.3	2 – 39 / 5.2	1.2-3.6
Bac Lieu – Ca Mau	1.6 – 4.0 / 3.7	2 – 39 / 5.2	0.8 – 3.6 / 2.1
Ca Mau – Ha Tien	0.4 – 4.2 / 1.9	0.2 – 4.0 / 2.21	0.11 – 0.9 / 0.43
The Vietnam standard for coatal water	0.05 mg/l		
Canada's standard method of sediment			7.24 (TEL)

CONCLUSION

1. The arsenic distribution in natural environment of Vietnam is as follows:

- The rocks of hydrothermal deposits and surrounding rocks, sulfur, gold and polimetal ore as well as their weathering crust and soil are richer in As (5 - 216,824 ppm) than other formations (in magmatic rocks: < 13.1 ppm, in sedimentary rocks < 1.33 ppm; in coastal sediment: 0.11 - 200 ppm).

- Streamwater in areas of hydrothermal deposits (Ban Phung) and ground water in several places of Hanoi, Viettri cities have higher arsenic concentration than the other areas.

2. There are three zones of As pollution in Vietnam
Mountain zone with rocks of hydrothermal deposits, gold, multi-metal, sulfur ore as well as their weathering products and soil (Ban Phung, Doi Bu, Khau Au, Cho Don, Tung Ba, Bac Me, Binh Gia, Nam XeTam Tuong, Quy Hop ore deposits...), As pollution is caused by natural processes.

Some places in plains with ground water are polluted by As. The source of As pollution is natural processes (oxidation of sulfur arsenic bearing mineral in sediment, reduction of Fe hydroxide containing arsenic...) and human activities.

Coastal zone with sea sediment of some areas of Quang Ngai, Phu Yen coast polluted by As. The main source of the As pollution is human activities, especially use of pesticides, herbicides and chemical weapon...

3. It is necessary to carry out a scientific program on environmental geochemistry of arsenic to study As history, source, behavior and fate in environment, impact of As on human body, animal as well as to propose the optimal methods for environment protection from As pollution in each area and the whole Vietnam territory.

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