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# GROUNDWATER CONTAMINATION IN HANOI CITY DUE TO AMMONIA, ARSENIC, IRON AND ORGANIC MATTER.

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**Abstract:** Analyses of groundwater quality in Hanoi City were carried out to investigate the extent and mechanisms of contamination. 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  $\text{mg/l}$ ) and ammonia (up to 35  $\text{mg/l}$ ) 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 groundwater in the South was also associated with very low ORP of less than -100mV, and contained very high COD of up to 25  $\text{mg/l}$  and high  $\text{HCO}_3^-$  concentration. These results showed very good correlation among different water quality parameters, such as As vs Fe(II),  $\text{NH}_4\text{-N}$  vs Fe(II), COD vs  $\text{NH}_4\text{-N}$  and As vs  $\text{HCO}_3^-$ . From these data combined with the hydrogeological profiles, a possible mechanism of simultaneous groundwater pollution by As, Fe(II),  $\text{NH}_4\text{-N}$  and organic matter was proposed . Under anoxic condition, there is a combination of the microbial oxidation of organic matter and reduction of Fe(III) to Fe(II). As a result, high As concentration in the deep groundwater may be derived from reductive dissolution of As-rich Fe oxyhydroxide of the aquifer material

## KEYWORDS

Groundwater contamination, arsenic, ammonia, iron, organic matter, water supply

## INTRODUCTION

### *Water supply in Hanoi*

The water supply system in Hanoi, Vietnam dates back to 1894, when the French colonists developed the first water supply system by using the surface water of the Red River. Because of its abundant potential in supplying water to the city, ground water has been utilized since early 20<sup>th</sup> century. Presently, Hanoi Water Business Company (HWBC) uses groundwater through eight major water treatment plants (WTPs) and a number of small water supply stations to provide 450,000  $\text{m}^3/\text{d}$  to a population of 1.4 million in urban district (JICA, 1996).

The monitoring results from Hanoi Water Business Company (HWBC) since 1989 and a number of other studies on groundwater quality showed that main water quality problems were due to high concentration of organic matter, iron, manganese, ammonia and microorganisms, making it difficult to meet the drinking water standards. Recently, high concentration of arsenic was also reported in some areas of the city.

In this paper, we will show the present extent of groundwater contamination due to arsenic (As), iron (Fe), ammonia ( $\text{NH}_4\text{-N}$ ) and organic matter, which cause problems in the water supply system in Hanoi . The correlation among different water quality parameters, as well as the possible mechanisms of groundwater pollution associated with these pollutants will also be discussed.

### *Groundwater and geological profile*

Hanoi is located on the Bac Bo Plain delta, which covers an area of about 11000 $\text{km}^2$ . The Bac Bo Plain is composed of Quaternary sediments, with a thickness between 50-90m, resting on the Tertiary deposit of Neogene age. They are unconsolidated to sandstone. The unconsolidated Quaternary sediment consists of sand and gravel interbedded with fine material such as clay and silt, often contain organic matter (Tran Minh, 1993).

The groundwater system beneath Hanoi can be described as two-layer aquifer systems of sand and gravel, i.e. Thai Binh-Vinh Phuc upper aquifer (Qh) and Hanoi-Vinh Phuc lower aquifer (Qp). Both are covered and separated by impermeable clay layers. 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.

## MATERIALS AND METHODS

During August and September 2000, groundwater samples were collected from 34 deep wells in 8 major WTPs that exploit water from the Qp1 lower aquifer and from 7 wells that tap the Qh upper aquifer within the urban area. Other 5 samples were collected from the Red River and some fishponds in the South.

Temperature, pH, Dissolved oxygen (DO), Electrical conductivity (EC), Oxidation-reduction potential (ORP) and ferrous iron Fe(II) were measured immediately at the collection sites. Samples were analyzed for total iron, manganese, ammonia, nitrate, E. coli and total coliform group by HACH test kits, at Hanoi University of Civil Engineering laboratory.  $\text{HNO}_3$  acidified samples were transported to the laboratory of Department of Urban Engineering, the University of Tokyo where major cations were analyzed by Inductively Coupled Plasma - Emission Atomic Adsorption (ICP-EAS) and heavy metals were analyzed by Inductively Coupled Plasma - Mass Spectrometer (ICP-MS). Non-acidified samples for anion analysis were done by Ion Chromatography.

For arsenic, its total concentration was measured by ICP-MS. The determination of three As species: arsenous acid As (III), arsenic acid As (V) and dimethylarsenic acid (DMAA) was performed by HPLC-ICP-MS. The HPLC system consisted of a Shimadzu LC-10ADVP liquid chromatograph, and a polymer-bases anion exchange column (Gelpack GL-LC-A15, 75 mmx4.6mm). An 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.

## RESULTS AND DISCUSSION

### Physicochemical characteristics of groundwater

#### *Ionic component of the deepwell water.*

From the results of major ionic components analysis of groundwater from lower aquifer Qp1 (Na, K, Mg, Ca, Cl,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$ ), three distinct geographic areas were identified and described below and shown in Fig. 1.

(i) Zone 1 - Yen Phu and Luong Yen WTP areas. Groundwater contains  $\text{Ca}(\text{HCO}_3)_2$  as major component and low EC values.

(ii) Zone 2 - Mai Dich, Ngoc Ha, and Ngo Si Lien WTP areas. Groundwater contains  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$  as the major components and high concentration of NaCl and KCl.

(iii) Zone 3 - Phap Van, Tuong Mai (3a), and Ha Dinh WTP (3b) areas. Groundwater contains high concentration of  $\text{HCO}_3^-$ . The concentration of cations such as Na, K, Ca, Mg increases with the concentration of  $\text{HCO}_3^-$ . No  $\text{SO}_4^{2-}$  was detected in the groundwater from this zone.

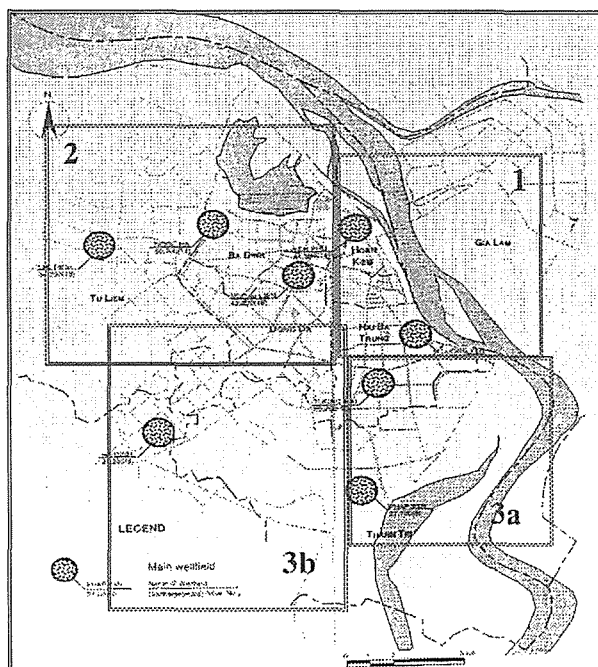


Fig 1. Three distinct geographic area due to the groundwater characteristics in Hanoi.

#### *Arsenic concentration in the groundwater.*

The arsenic concentration in the 41 wells (which tap Qp1 and Qh) ranged from 0.7 to

112  $\mu\text{g/l}$ . Among them, 13 samples were found to have As concentration less than 10 $\mu\text{g/l}$ , 12 samples from

10-50  $\mu\text{g/l}$  and 16 samples above 50  $\mu\text{g/l}$ . The samples which had As concentration above 50  $\mu\text{g/l}$  were mainly originated from Zone III. At present, finished water has not been analyzed yet. However, with consideration of the Vietnamese drinking water standard for arsenic (Max. 50  $\mu\text{g/l}$ ), the acceptable water quality can be achieved with the current water treatment process.

**Arsenic species** For the samples having As concentration greater than 50  $\mu\text{g/l}$ , three arsenic species As (III), As (V) and DMAA were determined. All most all the detected arsenic was inorganic. This suggested a possible source of arsenic pollution originating from inorganic matter.

The ratio of As(III)/As(V) range from 0.023 to 1.192. In the study on Arsenic pollution in groundwater in Fukuoka (Japan), Kondo (2000) suggested that the distribution among the As(III) and As(V) is influenced by ORP of the water. However, in this study the As(III)/As(V) ratio was the poorly correlated with ORP figure.

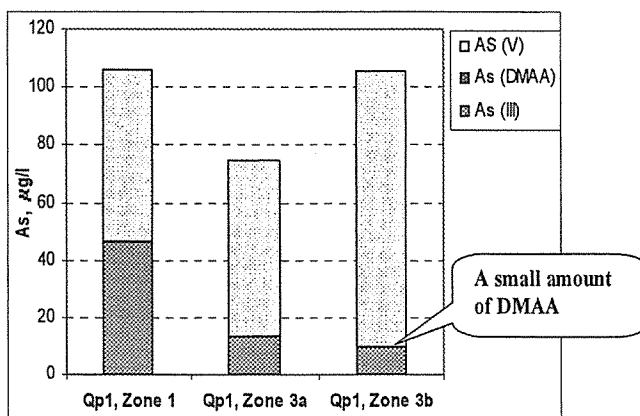


Fig. 1: The ratio of As(III) and As(V) in different zones in the aquifer

**Iron and Ammonia:** High iron concentration of up to 32  $\text{mg/l}$  was detected in the samples from the South that were much higher than those from the North. The similar trend was also observed with ammonia figures. The increase of total iron concentration associated with the amount of ferrous iron.

Fig. 3 shows the relationship between As and Fe(II) concentration. In the lower aquifer Qp1, the increase of As concentration associated very well with the amount of  $\text{Fe}^{2+}$ . However, all samples from upper aquifer Qh had high iron concentration of above 8 $\text{mg/l}$ , whereas As concentration range of 0.6-90 $\mu\text{g/l}$ , showing a different trend from the deep aquifer. It suggests in the release of As into groundwater might result from different mechanisms in the lower and upper aquifer systems.

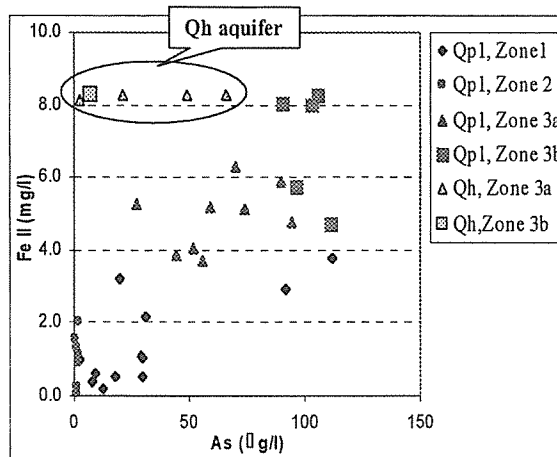


Fig. 2: Relationship between Arsenic and Fe(II) concentration in groundwater

**ORP of the groundwater:** High concentration of  $\text{NH}_4\text{-N}$ , Fe and As were detected only at low ORP of less than  $-100\text{mV}$ . It indicated a very strong anoxic condition. In addition, these waters were also almost free of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , indicating sulfate reduction was taking place. However, there has been no  $\text{H}_2\text{S}$  data supporting this hypothesis yet.

**COD of the groundwater** at the WTP located in the South (Phap Van, Tuong Mai, Ha Dinh) ranges from 8 to 25  $\text{mg/l}$ , which is much higher than those from the North. It shows good correlation with the trend of ammonia, iron and arsenic. High COD may result from abundant organic compounds in the groundwater.

## Mechanism of groundwater pollution

Based on the discussion made above, a model showing the possible mechanisms describing the quality of groundwater in Hanoi City has been proposed as shown in Fig 4.

As shown in Fig 4, the oxidation of organic matter is coupled either with the reduction of Fe(III) to Fe(II) or  $\text{SO}_4^{2-}$  to  $\text{S}^{2-}$ . As a result, arsenic may be derived from reductive dissolution of As-rich iron oxyhydroxide under anoxic condition. Development of very low redox potential could be the result of the microbial oxidation of organic compounds. No detection of  $\text{SO}_4^{2-}$  also indicates sulfate reduction is taking place under strongly anaerobic conditions. Sulfide and a part of ferrous iron Fe(II) produced in the above mentioned processes may combine to form insoluble FeS, which might be the cause of no sulfide in groundwater rich in arsenic and ammonia.

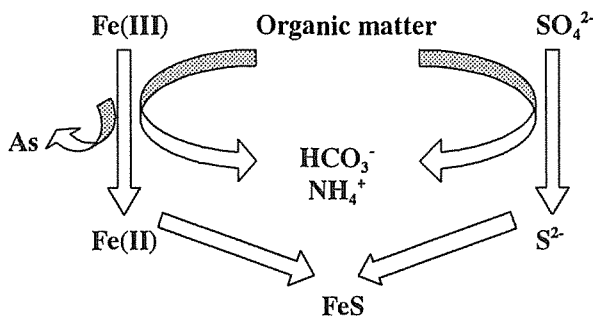
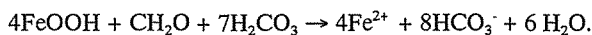


Fig 4: Model of the mechanism of groundwater pollution in groundwater in Hanoi

According to Hiroyuki (1999), Nickson (2000), the process dissolves Fe-oxyhydroxides and releases to groundwater both  $\text{Fe}^{2+}$  and As as the following stoichiometry equation:



The results coincided very well with the above equation. Fe(II) and As concentration show a good correlation with the  $\text{HCO}_3^-$ . It suggests that in the Qp1 aquifer As is released to groundwater through reduction of arsenious iron oxyhydroxides when anoxic conditions develop.

## CONCLUSION

High concentration of As (up to 110  $\mu\text{g/l}$ ), Fe (up to 39  $\text{mg/l}$ ) and  $\text{NH}_4\text{-N}$  (up to 35  $\text{mg/l}$ ) were detected in the groundwater in the South of Hanoi, that were much higher than those in the North. The contaminated water associated with very low ORP of less than -100mV, and contained very high COD of up to 25  $\text{mg/l}$  and high  $\text{HCO}_3^-$  concentration. These results show very good correlation among different water quality parameters, such as As vs Fe(II),  $\text{NH}_4\text{-N}$  vs Fe(II), COD vs  $\text{NH}_4\text{-N}$  and As vs  $\text{HCO}_3^-$ .

From these data combined with the geological-hydrogeological profiles, a possible mechanism of simultaneous groundwater pollution by As, Fe(II),  $\text{NH}_4\text{-N}$  and organic matter can be proposed. Under anoxic condition, there is a combination of the microbial oxidation of organic matter and reduction of Fe(III) to Fe(II). As the results, high As concentration in the deep groundwater may be derived from reductive dissolution of As-rich Feoxyhydroxide of the aquifer material.

General speaking, high concentration of arsenic is detected in the samples from deep groundwater in the South, however, the problem is not so serious when compared to Bangladesh, Taiwan, and Fukuoka (Japan) cases. At present, finished water has not been analyzed yet. However, with consideration of the Vietnamese drinking water standard for arsenic (Max. 50  $\mu\text{g/l}$ ), the acceptable water quality can be achieved with the current water treatment process.

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