Arsenic pollution in groundwater in the Red River Delta

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Abstract

The Red River Delta is located in northern Vietnam and has an area of 17,000 km². The delta is underlain by un-consolidated formations and Neocene sediments. It is one of the most developed economic areas of Vietnam. The economic development is closely linked to the use of the groundwater resources. Today the extraction of groundwater has become significant but is not always strictly controlled. This causes the lowering of the groundwater table, saline intrusion and pollution including arsenic pollution. Efforts to establish some knowledge of the arsenic levels in the Red River delta plain have started. However, to solve this problem from a regional perspective, the collaboration and support as well as exchange of experience of experts and international organizations is needed.

Introduction

Groundwater pollution, especially arsenic (As) pollution is harmful for human health if water is used for domestic purposes. In May 2001 the conference “Geology and Health” was held in Bangkok-Thailand. Reports at this conference show that in Bangladesh, China and India as well as in Cambodia, Myanmar, Pakistan, Thailand and Laos there are regions where groundwater is polluted by As.

In Vietnam during mineral exploration, areas with high As concentrations have also been discovered. In the Red River delta, in the Mekong River Delta and on the Thai Nguyen Plateau, levels of As have been investigated by the National Groundwater Monitoring Network. With sponsorship from UNICEF and in collaboration with the National University, the Northern Hydro-geological Engineering Geological Division (NHEGD) investigated As levels in groundwater in the Red River Delta. High As concentrations have been detected in some regions. The Red River delta plain is underlain by quaternary sediments. The development of the delta plain is related to a series of marine transgressions and regressions, as well as to tectonic activities. The sediments are mainly riverbed facies of widely varying thickness. Two main aquifers are recognized.

The Holocene inter-granular aquifer (qh)

This is the shallowest aquifer, distributed rather widely from the center of the plain to the sea, but there is only a narrow strip along the Red River. The thickness of this aquifer varies. It is 10-20m to 30-40m in the center of the plain from Nam Dinh-Thai Binh to the sea. In the plain margins, the aquifer is only 1.5-3m. The average thickness is 13.6m. This aquifer has high water potential with a hydraulic conductivity ranging from 95 to 1788 m³ d⁻¹. The average hydraulic conductivity is from 300-500 m³ day⁻¹.

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From the peak of the plain to Hanoi the water is ‘fresh’ with a TDS ranging from 0.189 to 0.445 g l\(^{-1}\) and predominance of calcium-magnesium bicarbonate. From Hanoi to Cam Giang, An Thi and Khoai Chau the water is still fresh but due to a decreasing permeability, the hydraulic gradient and the shallow water table the TDS is increasing. The water type is dominated by HCO\(_3\)-Ca → HCO\(_3\)-Ca-Na → HCO\(_3\)-Cl-Ca-Na → Cl-HCO\(_3\)-Ca-Na. From Hung Yen and Hai Duong to the sea the water changes from fresh to saline although not completely and areas of fresh water still exist. The water type in the fresh areas is now dominated by HCO\(_3\)-Ca → HCO\(_3\)-Cl-Na and Cl-HCO\(_3\)-Na. There is a transition zone with a TDS of 1-6 g l\(^{-1}\), where the water type is HCO\(_3\)-Cl-Na → Cl-HCO\(_3\)-Na. In the saline area the TDS is high, up to 3 g l\(^{-1}\) or more. This aquifer is sufficient for small-scale water supply.

*The Pleistocene inter-granular aquifer (qp)*

This is the main aquifer it is distributed widely under the Red River Delta but it is exposed only in the margins of the plain (Figure 1). The qp aquifer is composed of two layers the upper layer consisting of medium to coarse sand mixed with gravel and lower layer composed of cobbles and pebbles mixed with sand. A clay layer separates the two, but this clay separation is not always there, and as a consequence the two sub-aquifers have the same water level.
The thickness of the qp aquifer varies widely from several meters in the northwest margin to approximately 100m in the centre and the southeast (Figure 1.). The upper level has good water potential with hydraulic conductivity ranging from 48 to 756m$^3$ d$^{-1}$. In comparison, the lower section of the qp aquifer has a better potential for water, with hydraulic conductivity ranging from 700 to 2000m$^3$ d$^{-1}$. Most of the production wells draw from the lower section of the qp aquifer.

The Pleistocene aquifer has sufficient potential for large-scale water supply. In recent times, the groundwater abstraction in Hanoi, Hai Duong, Hung Yen, Vinh Yen, Phuc Yen towns and Kien An-Hai Phong, Hai Hau, Nghia Hung-Nam Dinh provinces totals over 1,000,000 m$^3$ d$^{-1}$.

*The negative effects of groundwater pumping*

Currently groundwater is abstracted in Vietnam in general and in the Red River Delta in particular in the following manner.

1. *Public exploitation wells:* These wells are managed by special public organizations (Clean Water Business Companies). The construction of these wells is based on the results of water exploration programs carried out by competent organizations. These wells operate within urban areas and industrial zones. Total water abstraction volume is approximately 500, 00 m$^3$ d$^{-1}$ and in the Hanoi area is approximately 400,000 m$^3$ d$^{-1}$.

2. *Private Wells:* These wells are exploited by other organizations such as hospitals, schools, enterprises and factories. These wells are built without investigation, and without permits from a competent organization. Total abstraction from private wells is currently estimated as 250,000 m$^3$ d$^{-1}$.

3. *UNICEF wells:* In rural areas people use groundwater from dug wells or from UNICEF sponsored small, shallow wells. In the beginning each house had its own well. Now this water supply system has improved and in some communities there is a public water supply system served by one or more big wells. Total production from these wells is of the order of 400,000 – 500,000 m$^3$ d$^{-1}$.

Groundwater pumping has negative impacts on the environment in general and on the groundwater environment in particular. The impacts are degradation of water resources, salt intrusion and pollution. The degradation of water sources includes the lowering of the water table and the enlarging of the cone of depression. Research indicates that cones of depression have formed in Hanoi, in Vinh Yen, in Hai Phong, in Nam Dinh and in Thai Binh.

The cone of depression in the Hanoi area has been investigated from 1992 to present. The results indicate that the size of the area that has been affected by heavy abstraction and where the water level is below 0m is 269.34km$^2$ (2001 Data). Within this area there is a core that has been strongly affected and where the water level is below -8m. This central core of depression now covers an area of 97.84km$^2$, and expands at the rate of 4.2km$^2$ yr$^{-1}$. In addition a very strongly affected area with water levels below -14m occupies 28.61km$^2$. This deepest part of the cone is expanding at the rate of 2.3km$^2$ yr$^{-1}$.
Figure 2. Map showing the cone of depression south of Hanoi (August 2001 Data)

Legend

Observation well
Water level of qp aquifer

<0m: 263.57 km²
<-8m: 96.90 km²
<-14m: 26.69 km²
In addition to the constant expansion of the area affected by heavy abstraction and an enlargement of the cone of depression (Figure 3.), the general water level is also lowered. In Hanoi, the water level measured in observation well P41a on the Ha Dinh well field in 2002 was 32.43m (Figure 4), this was 1.22m deeper than in the same period in 2001.

Figure 4. Lowering of water level in observation well P41a – Hanoi area (1991-2002)
Moreover, in Hai Hau, in observation well Q109a (Figure 5), the deepest water level in 2002 was 6.60m. This is 0.44m deeper than in the same period in 2001. In addition, in Kien An-Hai Phong, in observation well Q164a (Figure 6), the deepest water level is 11.73m, 0.94m deeper than in the same period in 2001.

Figure 5. Lowering of water level in the observation well Q.109a in Hai Hau, Nam Dinh and observation well Q164a in Kien, An-Hai Phong (1993-2002)

On the whole the water level in the Pleistocene aquifer has been declining. This, mainly recent, lowering of the water level has led to several forms of pollution and to saline intrusion into the aquifer.

*Arsenic levels in the Red River Delta plain*

The presence of an As problem was recognized during geology-hydrogeology surveys and in mapping and surveying for minerals in Vietnam in general and in the Red River Delta plain in particular. Arsenic is detected in mining areas, ore outcrops and in areas where industrial wastes contains As. Arsenic occurs naturally in areas mineralized with sulfide minerals and gold and in areas of volcanic activities. The main As liberating mechanism is weathering. The main areas in Vietnam of As concentration are in Pia Oac, Ngan Son, Pac Lang, Chay River, North Tam Dao, Cho Don-Cho Dien, Dao Vien-Chiem Hoa-Na Hang-Tung and Bac Me.

Arsenic also occurs in metamorphic intrusive volcanic formations containing arsenopyrite, pyrite and gold such as in the Hien River, Binh Gia, east of the Chay River, in Nam Xe-Tam Duong, in the downstream part of the Da River. Arsenic concentration in gold ore in the basalts of the Vien-nam formation in Doi Bu (Hoa Binh) is 50-204 mg kg\(^{-1}\). In sandstone, siltstone and in the siliceous shale of the Than Sa formation in a mineralized zone of sulfur-gold-quartz in Khau Au-La Hien (Bac Can, Thai Nguyen) AS concentration is 13.2 mg kg\(^{-1}\) and in the ore is 1292-1442 mg kg\(^{-1}\).
Further, in the sericite shale and clay shale of the Coc Xo formation in the zinc-lead ore area of Cho Don (Bac Can) As content is 97.8 mg kg\(^{-1}\) with As concentration in the ore ranging from 8.205-261.824 mg kg\(^{-1}\). According to Dang Van Can, 2000 As in water of the ore zone in Lang Vai (Dam Hong) is 0.73mg l\(^{-1}\). In Bo Sinh-Moc Chau District, Son La Province the As level in springs of the right side of the Ma river is 0.43-1.13 mg l\(^{-1}\). Do Tuyet, 1998 reports As concentrations in karst water at Tay Bac of 2.8mg l\(^{-1}\) in Tra commune, 2.67mg l\(^{-1}\) in Chien hamlet, 2.29mg l\(^{-1}\) in Ngan commune and 3.14mg l\(^{-1}\) in Chien Bui.

In the Red River Delta plain, the industrial zones discharge waste containing As. In the Viet Tri industrial zone the As concentration in groundwater is higher than the Internationally accepted standard limitation with a maximum value of 0.32 mg l\(^{-1}\). In Thuong Dinh industrial zone, Hanoi area, As in wastewater is 0.145-0.346mg l\(^{-1}\), higher than the standard limitation (Nguyen Van Duc, 2001). This wastewater is not treated.

In 1999 with sponsorship from UNICEF, the As level has been studied in 7 provinces of the Red River Delta plain. A total of 1228 samples were taken and analyzed. The results showed that 740 out of 1228 have an As concentration <0.01 mg l\(^{-1}\), 1075 samples have an As concentration <0.05 mg l\(^{-1}\) and 153 samples have an As concentration >0.05 mg l\(^{-1}\) with a maximum value of 0.6 mg l\(^{-1}\).

Since 2001, the Northern Hydro-geological Engineering Geological Division has been studying As levels in groundwater in the Red River delta plain. Samples are taken twice per year, stored and preserved in accordance with ISO 11969 and Vietnamese standard-TCVN 6626. The results show that out of a total of 34 samples, 17 samples have >0.001mg l\(^{-1}\) of As, 5 samples have >0.05mg l\(^{-1}\). The maximum value is 0.428 mg As l\(^{-1}\) (Q58a-Dan Phuong-Ha Tay). In 2002, 18 samples out of 85 samples (21%) having a higher concentration than the standard limitation. Fourteen of these samples are from the qp aquifer with As concentrations of 0.067 mg l\(^{-1}\) (Q88b-Ha Nam) and 0.406 mg l\(^{-1}\) (Q58a-Ha Tay). The remaining samples are from the qh aquifer with values of 0.088 mg l\(^{-1}\) (Q85a-Ha Nam) and 0.440mg l\(^{-1}\) (Q56-Ha Tay).

Table 1. Arsenic and other heavy metals in the Red River Delta plain in 2002

<table>
<thead>
<tr>
<th>No</th>
<th>Element</th>
<th>Vietnamese Standard (mg l(^{-1}))</th>
<th>Season</th>
<th>No. of samples</th>
<th>Number of samples having higher concentration than Vietnamese Std. mg l(^{-1})</th>
<th>%</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>As</td>
<td>0.05 (TCVN 5944 -1995)</td>
<td>Dry</td>
<td>43</td>
<td>9 20.9 0.067 0.440</td>
<td>20.9</td>
<td>0.067</td>
<td>0.440</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rainy</td>
<td>42</td>
<td>9 21.0 0.080 0.364</td>
<td>21.0</td>
<td>0.080</td>
<td>0.364</td>
</tr>
<tr>
<td>2</td>
<td>Mn</td>
<td>0.1 (TCVN 5944-1995)</td>
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<td>43</td>
<td>36 83.7 0.11 2.99</td>
<td>83.7</td>
<td>0.11</td>
<td>2.99</td>
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<tr>
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<td></td>
<td></td>
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<td>42</td>
<td>36 85.7 0.12 1.59</td>
<td>85.7</td>
<td>0.12</td>
<td>1.59</td>
</tr>
<tr>
<td>3</td>
<td>Be</td>
<td>0.0002 (BKHCNMT-1993)</td>
<td>Dry</td>
<td>43</td>
<td>39 90.7 0.0002 0.0064</td>
<td>90.7</td>
<td>0.0002</td>
<td>0.0064</td>
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<tr>
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<td>9 21.4 0.0002 0.0090</td>
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<td>0.0002</td>
<td>0.0090</td>
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<tr>
<td>4</td>
<td>Ni</td>
<td>0.02 (WHO 1984)</td>
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<td>43</td>
<td>12 27.9 0.020 0.092</td>
<td>27.9</td>
<td>0.020</td>
<td>0.092</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Rainy</td>
<td>42</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Cr</td>
<td>0.05 (TCVN 5944-1995)</td>
<td>Dry</td>
<td>43</td>
<td>0 - - - -</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Rainy</td>
<td>42</td>
<td>2 4.8 0.055 0.066</td>
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<td>0.055</td>
<td>0.066</td>
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<tr>
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<td>Cd</td>
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<td>-</td>
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<td>-</td>
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<tr>
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<td>2 4.8 0.0110 0.0173</td>
<td>4.8</td>
<td>0.0110</td>
<td>0.0173</td>
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</table>
In 2001-2002, UNICEF Hanoi collaborated with the Northern Hydro-Geological Engineering Geological Division and the University for Natural Science/National University to sample and analyze environmental parameters, including some heavy metals. The study areas are Hanoi city and some provinces including Thai Binh, Nam Dinh and Ninh Binh. The results are presented in Table 2 and Figures 6 and 7.

**Hanoi City:**
- North of the Red River and Duong River, 8 out of 112 samples in Dong Anh district had an As concentration higher than the Vietnamese Standard of 0.05 mg l\(^{-1}\).

**Gia Lam area:**
- *qh aquifer:* In the dry season 8 samples (40%) had a higher As concentration than the Vietnamese Standard. In contrast, in the rainy season only 2 samples exceeded the Vietnamese As Standard.
- *qp aquifer:* In dry season 13 samples had a higher As concentration than the Vietnamese Standard and in the rainy season just 2 samples.

**Tu Liem area:**
- *qh aquifer:* In the dry season 8 samples (14.5%) had a higher As concentration than the Vietnamese Standard and in the rainy season just 1 sample.
- *qp aquifer:* In comparison with the qh aquifer, in the dry season 9 samples taken from the qp aquifer contained As at concentrations exceeding the Vietnamese Standard. In the rainy season this decreases to just 3 samples.

**Thanh Tri area:**
- *qh aquifer:* In the dry season 43 samples (59.7%) exceeded the Vietnamese Standard for As in drinking water. In the wet season, this decreases to 29 samples (40.3%).
- *qp aquifer:* In the dry season 13 samples (54.2%) exceeded the Vietnamese As Standard. This declined to 9 samples (39.1%) in the rainy season.

**Urbanized area of Hanoi:**
- *qh aquifer:* In the dry season and rainy season 18 samples (38.3%) and 12 samples (26.1%) had As concentrations exceeding the Vietnamese standard.
- *qp aquifer:* In the dry season 17 samples (39.5%) contained As at concentrations exceeding 0.05 mg l\(^{-1}\). In the rainy season this decreased to 8 samples (19.0%).

**Nam Dinh province:**
- The total number of samples collected was 125 of which 11 samples had an As concentration higher than the Vietnamese standard. These samples were located mainly north of My Loc, Xuan Truong and Nam Dinh city.

**Ninh Binh province:**
- Eight out of a total number of samples of 75 had an As concentration exceeding 0.05 mg l\(^{-1}\). These samples were concentrated southeast of Ninh Binh town and the centre of Kim Son.
Thai Binh province:
- Out of 125 samples collected only 1 sample contained As at a concentration >0.05 mg l⁻¹ (Vietnamese Standard).

Some possible mechanisms causing arsenic pollution in groundwater

The Red River delta plain is composed of fine unconsolidated sediments such as clay, peat and organic matter, and it is in these materials that heavy metals and As concentrate and are retained. The results for As in soils in 4 wells in Hanoi as reported by the University for Natural Science/National University and the Northern Hydro Geological Engineering Geological Division showed that the maximum value ranges from 6-33.0 mg kg⁻¹ and that soil As correlates well with iron concentration. Arsenic may be absorbed by iron Oxy-hydroxide in areas of heavy groundwater pumping. During the disintegration of organic matter in peat, a large amount of methane is formed. Methane combines with As forming a methyl-As compound that dissolves in groundwater. In the Hanoi area, As sources can be clay and peat layers at depths of 0-40m. In addition, human activities including urban areas, factories and residential areas in the Red River Delta plain contribute untreated waste and wastewater which discharges into the drainage system. Also agricultural activities introduce fertilizers and pesticides containing As. The above-mentioned are the main reasons for groundwater pollution. However, the strong groundwater abstraction is the main factor causing pollution, especially in the centre of the well fields. The lowering of the water level causes an increase in the velocity of groundwater flow, and increasing percolation of water.

Some methods to mitigate arsenic in groundwater

- Continued investigation into the degree of As pollution and the scale of distribution of As in vulnerable areas of the Red River Delta plain and vicinity.
- Assessment of water sources free of As for water supply as part of integrated groundwater management.
- Treatment of waste from industrial, domestic and agricultural activities.
- Investigate and implement appropriate technologies and treatment models for protect community health from elevated levels of As in groundwater.
- Intensive collaboration between national and international organizations to exchange information and experiences.
<table>
<thead>
<tr>
<th>Criteria</th>
<th>Number of samples</th>
<th>Arsenic (mg l⁻¹)</th>
<th>Manganese (mg l⁻¹)</th>
<th>Iron (mg l⁻¹)</th>
<th>Ammonia (mg l⁻¹)</th>
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<td></td>
<td></td>
<td>&gt;0.05 %</td>
<td>&gt;0.1 %</td>
<td>&gt;0.3 %</td>
<td>&gt; 3 %</td>
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<td>6.1</td>
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<td>8</td>
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Figure 6. Map of As pollution in the qp aquifer within the Hanoi area
Figure 7. Arsenic concentration in groundwater in Thai Binh, Nam Dinh and Ninh Binh provinces.
References


