Abstract

Groundwater quality data taken in August and December 2000 revealed that the groundwaters in Hanoi are contaminated by arsenic (up to 110 µg/l), iron (up to 32 mg Fe/l), organic matter (DOC up to 12 mg/l), and ammonia (up to 29 mg-N/l). Data on trace metals, as well as conventional water quality parameters such as pH, ORP, major cations and anions, were used to analyse groundwater flow and the mechanisms of groundwater contamination using multivariate data analysis methods. The results of Cluster Analysis (CA) demonstrated that the groundwater flow and characteristics were separated into three different zones, namely the Riverain zone, the Northwest zone, and the South zone where the highest levels of arsenic, iron, organic matter and ammonia were detected. Principal Component Analysis (PCA) showed strong correlation among two groups of trace metals: the first group includes Cd, Co, Mg, Mn, and Sr and these metals are considered to be leached out from rock minerals under moderately oxidizing conditions. The second group contains As, B, Ba, Cr, Cs, Fe(II), Mo, P, Pb, Rb, Ti, DOC and bicarbonate, and these are negatively correlated with SO₄²⁻ and ORP, which indicates that these elements are eluted from organic matter and/or iron oxyhydroxide under anaerobic conditions. Further analyses of data obtained in the contaminated groundwaters by PCA and correlation between As and DOC suggest that there may be two possible mechanisms of arsenic release: reduction of iron oxyhydroxide and anaerobic degradation of organic matter in the peat layers.

Keywords

Ammonia; arsenic; groundwater contamination; Hanoi; multivariate data analysis; tracers

Introduction

Hanoi is located on the Bac Bo Plain delta, which covers an area of about 11,000 km². The delta sediment is made of alluvial river and lake deposits from the Plio-Pleistocene to the Late Holocene. It consists of sand and gravel embedded with clay, silt, and organic matter.

The groundwater system beneath Hanoi has two aquifer systems, i.e., Thai Binh-Vinh Phuc upper aquifer (Qh) and Hanoi-Vinh Phuc lower aquifer (Qp). These aquifer systems are separated by an impermeable clay layer. The upper aquifer system can be further separated into two small aquifers (Thai Binh and Hai Hung) in the Holocene deposit. Thai Binh is interstitial aquifer of recent alluvial sediment characterized by sand, clayey sand and sandy clay. Hai Hung aquifer originated from lake-marshland, river-marine sediments of the late-middle Holocene; it consists of silt, clayey sand, and sand. The lower aquifer system includes Vinh Phuc and Hanoi aquifer in the Pleistocene, river-proluvial deposits characterized by sand and gravel. Among these aquifers, Hanoi aquifer contains the most abundant water, and it is the main water supply source for the city (JICA, 1996).

Groundwater has been abstracted as the only source of water supply in Hanoi City for more than a century. At present, eight Water Treatment Plants (WTPs) and several small water stations operated by the Hanoi Water Business Company provide 450MLD of water to the population of 1.5 million in urban districts (JICA, 1996). Recently groundwater pollution due to arsenic, iron, ammonia and organic matter has been reported. These reports raised people’s concern on the safety of their drinking water and groundwater contamination has become a priority issue in Hanoi city. Although numerous researches on groundwater quality have been carried out, the mechanisms controlling elution of these...
contaminants have not yet been elucidated. Multivariate data analysis has been successfully applied to analyse groundwater contamination from anthropogenic sources (Helena et al., 2000; Christopher and Brandes, 2001) In this study groundwater samples from all eight well-fields in Hanoi City were analysed for As, Fe, NH₄-N, organic matter, major cations and anions and trace metals. Cluster Analysis (CA) and Principal Component Analysis (PCA) were used to elucidate the groundwater flow regimes and the reaching processes of these contaminants.

Materials and methods
Groundwater sampling in Hanoi was done twice in August and December 2000. Groundwater samples were taken from 41 sites, including 36 deep wells from the well-fields of eight WTPs and 7 shallow wells in households. Other samples were collected along the Red River and fishponds in the South of Hanoi City. Temperature, pH, dissolved oxygen (DO), electrical conductivity (EC), oxidation–reduction potential (ORP, Eh), alkalinity, sulphide and ferrous iron Fe(II) were measured immediately at the sampling sites. Samples were analysed for ammonia, nitrate, E. coli and total coliform group by Hach test kits in a laboratory at the Hanoi University of Civil Engineering. Samples acidified by HNO₃ were transported to the laboratory of Department of Urban Engineering, the University of Tokyo where major cations were analysed by ICP-AES (Perkin Elmer Optima 3000DV) and heavy metals were analysed by ICP-MS (Hewlett Packard 4500). Non-acidified samples were also transported to Tokyo and used for anion analysis by ion chromatography (Yokogawa IC 7000 RS) and TOC analysis (Shimadzu TOC-5000).

Multivariate data analysis was performed using the data obtained and statistical software (SPSS-Window v. 10.0).

Results and discussions
Characteristics and trace metal contents of groundwater
Table 1 presents the summary of groundwater quality data in the study area. The groundwater quality varies extensively among the well-fields. High concentration of As (up to 110 µg/l), Fe (up to 32 mg/l), DOC (up to 12.6 mg/L), and NH₄-N (up to 29 mg/l) are detected in samples from groundwaters in the south region (Phap Van, Tuong Mai and Ha Dinh well-fields), whereas the levels of these contaminants are significantly lower in the rest of groundwaters (Mai Dich, Ngo Si Lien, Ngoc Ha, Yen Phu and Luong Yen well-fields). The contaminated groundwaters also contain high amounts of reduced species, such as Fe(II) (6–20 mg/l), As³⁺ (30–90 µg/l), and no SO₄²⁻, and have very low ORP (less than −100 mV), indicating a strong anaerobic condition within the aquifer. The concentration ranges of

<table>
<thead>
<tr>
<th>Well-field</th>
<th>W</th>
<th>N</th>
<th>EC</th>
<th>As</th>
<th>Fe</th>
<th>NH₄-N</th>
<th>DOC-C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aug</td>
<td>Dec</td>
<td>Aug</td>
<td>Dec</td>
<td>Aug</td>
<td>Dec</td>
<td>Aug</td>
</tr>
<tr>
<td>1 Luong Yen</td>
<td>233</td>
<td>204</td>
<td>23.7</td>
<td>21.8</td>
<td>3.12</td>
<td>1.58</td>
<td>0.45</td>
</tr>
<tr>
<td>2 Yen Phu</td>
<td>366</td>
<td>334</td>
<td>40.4</td>
<td>40.6</td>
<td>3.51</td>
<td>3.71</td>
<td>0.96</td>
</tr>
<tr>
<td>3 Mai Dich</td>
<td>338</td>
<td>276</td>
<td>1.2</td>
<td>0.9</td>
<td>1.38</td>
<td>0.70</td>
<td>0.04</td>
</tr>
<tr>
<td>4 Ngoc Ha</td>
<td>478</td>
<td>336</td>
<td>1.8</td>
<td>1.3</td>
<td>2.29</td>
<td>0.88</td>
<td>1.69</td>
</tr>
<tr>
<td>5 Ngo Si Lien</td>
<td>477</td>
<td>407</td>
<td>1.5</td>
<td>1.2</td>
<td>2.06</td>
<td>1.44</td>
<td>1.00</td>
</tr>
<tr>
<td>6 Phap Van</td>
<td>603</td>
<td>504</td>
<td>73.2</td>
<td>61.4</td>
<td>16.94</td>
<td>10.85</td>
<td>13.95</td>
</tr>
<tr>
<td>7 Tuong Mai</td>
<td>367</td>
<td>274</td>
<td>50.7</td>
<td>38.2</td>
<td>16.60</td>
<td>9.71</td>
<td>4.99</td>
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<tr>
<td>8 Ha Dinh</td>
<td>460</td>
<td>361</td>
<td>101.3</td>
<td>83.9</td>
<td>26.74</td>
<td>16.95</td>
<td>5.63</td>
</tr>
</tbody>
</table>

Note: a: µS/m; b: µg/l; c, d, e: mg/l
N: number of samples taken from each well-field
W: well name, the first letter denoted well-field name
arsenic detected in this study are about one-third of other reports (Berg et al., 2001), though the tendency of higher contaminant levels in the rainy (August) season than the dry (December) season was the same. Although we took from about a half of the groundwater wells in the 8 well-fields, we found significant difference of arsenic levels in the same well-fields, especially in those well-fields extending over wide areas. Therefore we think that one grab sample may not represent the groundwater quality in the well-fields, and it is important to access the variation of groundwater quality in any well-fields.

Hydrogeochemical characterization

Piper diagram. From the data on major cations and anions (Na, K, Mg, Ca, Cl\(^{-}\), HCO\(_3\)^{2-}\) and SO\(_4^{2-}\)), a piper diagram was constructed to visualize the relationship between major ions and to characterize each well-field tapping from the lower aquifer (Figure 1).

From this graph the groundwaters can be classified into three groups: two Riverain well-fields (Yen Phu and Luong Yen), the Northwest well-fields (Mai Dich, Ngoc Ha, and Ngo Si Lien), and the South well-fields (Phap Van, Tuong Mai, and Ha Dinh). The Riverain groundwaters contain high percentages of Ca\(^{2+}\), and it gradually decreases as the distance from the Red River increases. Although the Mg\(^{2+}\) percentages in the South groundwaters were almost constant at 20%, they varied in the Northwest well-fields. As for the anions, more than 95% was HCO\(_3\)^{−} in the Riverain groundwaters, whereas Cl\(^−\) concentration increased in other well-fields. SO\(_4^{2−}\) concentration was very low in all well-fields, and especially in the South well-fields no SO\(_4^{2−}\) was detected.

Cluster analysis. Forty-five physico-chemical water quality parameters of the samples taken from the lower and upper aquifers, the Red River, and fish ponds were analysed and the data were exported to a personal computer for CA. Figure 2 shows a dendrogram obtained from data analysed in December 2000. Three different families are distinguished, i.e. two groundwater families and one fishpond family. The Family-1 can be further separated into two sub-families, making up three groundwater types in total, which agree with the result of the Piper diagram. One of the advantages of CA over a Piper Diagram is that we can draw a groundwater map such as that shown in Figure 3. Similar maps can be drawn with data obtained in August and December 2000 except for three wells: Y41, Y42, and M17. These wells are located in the North and along the Red River, and hence they are
included in the Riverain-zone when the water level is higher in the rainy season (August), but they belong to the Northwest-zone in the dry season (December) when the groundwater recharge from the Red River is less.

These findings demonstrate the usefulness of multivariate data analysis using trace elements for the analysis of groundwater flow, as well as for groundwater quality characterization. The ground water flow chart (Geochemical Society of Vietnam, 1996) indicates that there are two cones of water table: one near the Mai Dich well-field and another near the Phap Van well-field. The groundwater map obtained in our study using multivariate data analysis matches this groundwater map very well.

The dendrogram in Figure 2 indicates that the deep groundwater in the Riverain and the Northwest zones have close hydrological relation with the Red River, and the groundwaters in the south have little hydrological correlation with the fishponds located above those wells, negating the possibility of “vertical” groundwater contamination by contaminated surface waters. One question left in this analysis is that there is one fishpond sample taken near the Tuong Mai well-field that is closely correlated with the deep groundwaters in the South-zone (Family-3). This fish pond water is characterized by high levels of DOC and NH₄-N, which is commonly found in the deep groundwaters in the South and uncommon in other fish pond samples. Further data should be obtained to confirm the correlation with this fish pond and deep groundwaters in the South.

**Principal component analysis (PCA).** PCA was used to analyse the processes affecting groundwater contamination. Forty-five physical–chemical parameters and trace metals were used for this analysis of groundwater samples collected in August 2000, and 45 parameters plus Hg, Mo, P and HCO₃ were used in December 2000. From the similarity matrix, the five principle components (PCs) were extracted that have an eigenvalue of more than 1 and which explained 76% of total variables.

C1 explains 31% of the total variables and is contributed to mainly by Fe, Fe(II), As, NH₄-N, TN, P, and DOC, which indicates that these contaminants occur in concurrent processes. PC2 explains about 19% of the residual variables, and is mainly derived from Temp, ORP, Si, Mg, Mn, Na, Cl, V, Co, Ni, Cd, Sr. The main exchangeable cations Na, Mg, Sr, and Si correlate positively, probably indicating processes of dissolution and/or precipi-
tation of common minerals such as dolomite or chloride. The PC3 (11%) is possibly due to calcite dissolution, which raises the concentration of HCO$_3^-$ and Ca in groundwater. PC4 (8%) is associated with mercury. PC5 (6%) may also be indicative of river water infiltration due to the presence of Ti, Zr, and Sb which are commonly found in the Red River and groundwater samples located along the river.

Correspondence analysis of water quality parameters using PC1 and PC2 shows different metals associated with these two geochemical processes (Figure 4). PC1 is considered to represent anaerobic degradation of organic matter and dissolution of Fe(II). In these processes, trace metals contained in organic matter are leached out, as well as iron-bound elements such as As and P. Fe(II), DOC, NH$_4$-N and HCO$_3^-$ concentrations are also very high. The correlation among these parameters support the anaerobic arsenic leaching model proposed by Nickson et al. (2000).

$$4\text{FeOOH (limonite)} + \text{CH}_2\text{O} + 7\text{H}_2\text{CO}_3 \rightarrow 4\text{Fe}^{2+} + 8\text{HCO}_3^- + 6\text{H}_2\text{O}$$ (1)

The trace and base metals and elements explained by PC1 are As, B, Ba, Cr, Cs, Fe, P, Mo, Rb, Ti. As and P are known to have similar characteristics to bind iron oxyhydroxide, and these elements can be leached out when FeOOH is reduced by the above equation. Rb is contained in organic matrix, and hence the Rb/Sr ratio is used as an index of organic pollution (Nirel et al., 1999). Cs and Rb are essential elements for plant uptake, therefore were

Figure 3 Distribution of three distinct groundwater zones in Hanoi urban area.
commonly enriched in plant remains. Siegel (2001) found in his cluster analysis of arsenic-contaminated ocean sediments Fe, P and As are closely associated, as well as Cr, Pb and Rb.

PC2 is considered to represent natural dissolution of minerals. Metals and non-metal elements included in this group are Cd, Co, Mg, Mn, Sr, Na, and Si. Sr, as well as Si, is commonly leached out in weathering processes (Nirel et al., 1999). Angstrom (2001) reported that Co, Mn, and Ni were eluted by exposing sulfide-bearing sediments to oxygen, but lower proportions of Fe, Al, Cr, and V were released. This report is consistent with our results if we assume that PC1 is undergoing anaerobic processes, whereas PC2 is for slightly aerobic processes.

**Heavy metal tracers for the analysis of groundwater contamination**

For more detailed analysis of groundwater contamination processes PCA was applied to the data obtained only in the contaminated South zone. As shown in Figure 6 there are two principal components representing iron reduction and arsenic leaching (PC1) and anaerobic organic degradation (PC2). It is interesting that there are no metals associated with PC1, whereas several trace metals were leached out into the groundwater in the organic degradation process (PC2). Correspondence analysis shown in Figures 6 and 7 indicates that groundwater contamination in Ha Dinh well-field (denoted by H) is probably caused by iron reduction and simultaneous arsenic reaching. In Ha Dinh ammonia and organic contents in groundwater are not very high. On the contrary, groundwaters in Phap Van well-field (denoted by P) seem to have undergone extensive organic degradation processes, with very high organic and ammonia content.
For further elucidation of these processes graphs of As vs. Fe(II) and As vs. DOC were plotted (Figure 8 a,b). From Figure 8 (a) As seems to correlate with Fe(II). However, if we see only the plots from the South-zone I (Ha Dinh well-field plus well Y20 and Y22 from Yen Phu well-field) or the South-zone II (Phap Van plus Tuong Mai well-fields), Fe(II) concentration varies irrespective of As concentration in the South-zone I, and vice versa in the South-zone II. Figure 8 (b) indicates a very good correlation between As and DOC in the South-zone II groundwaters, and no correlation in the South-zone I.

From Eq. (1) the ratio of released Fe(II) and HCO₃⁻ is 2. Nickson et al. (2000) found that released HCO₃⁻ was far greater than the concentration predicted by Eq. (1), and they estimated that most of HCO₃⁻ came from simple mineral dissolution. In contrast, our results suggest strong correlation among HCO₃⁻, NH₄⁻, P and other anaerobic degradation products of organic matter. HCO₃⁻ and ammonia have strong correlation and the C/N ratio is 2.3, which is very low in comparison with the C/N ratios of natural organic matter. This result indicates that most HCO₃⁻ came from organic degradation and a significant proportion of HCO₃⁻ was precipitated. These results suggest that there is another anaerobic arsenic release process than the one proposed by Nickson et al. (2000), namely arsenic is released from organic matrices that are undergoing anaerobic degradation.

**Conclusions**

Groundwater samples were taken in Hanoi City in August and December 2000, and analysed for 45 physicochemical parameters including trace metals. Cluster Analysis of the groundwater quality successfully identified three groundwater zones, which were also identified by Piper Diagram. The results of these analyses were consistent with the previously reported groundwater flow charts.

Principal Component Analysis of data on 45 parameters made it possible to separate the mineral dissolution process and anaerobic contamination process. Representative metal traces for the former process are Cd, Co, Mg, Mn and Sr, whereas tracers for the latter are As, B, Ba, Cr, Cs, Fe(II), Mo, P, Pb, Rb, Ti, organic matter and ammonia. Further breakdown of the groundwater contamination processes by PCA and correlation charts shows that there are two processes influencing groundwater contamination: iron reduction and anaerobic organic degradation. Organic matter may also be utilized to reduce ferric iron but bicarbonate released into groundwater is far greater than that estimated from the equation proposed by Nickson et al. (2000). This result, as well as strong association of bicarbonate leaching and other evidences of anaerobic organic degradation, has led us to conclude that arsenic may be also released from anaerobic degradation of organic matrices.
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References