Recharge processes and groundwater evolution of multiple aquifers, Beijing, China

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A geological and hydrogeological survey was performed in the upper alluvial and proluvial fan and the northern mountain area of the Chaobai River in Beijing. Samples of local precipitation, surface water and groundwater (including spring discharges, groundwater from the fractured bedrock, and shallow and deep groundwater of the alluvium) were collected and analysed to assemble hydrochemical and isotopic data. Q-mode hierarchical cluster analysis (HCA) was used to classify the groundwater samples from multiple aquifers into objective groups. Two groups and six subgroups with distinct groundwater recharge sources, flowpath histories and geochemical evolution histories were identified. Inverse geochemical modelling was adopted to study the deep groundwater chemical evolution. Hydrochemical data and isotopic data on $^2$H, $^3$H and $^{18}$O were used to evaluate groundwater recharge, flowpath histories and geochemical evolution, and $^{87}$Sr was used to provide further insight into groundwater recharge sources and flow directions. It was found that particularly in areas of groundwater cones of depression, the deep alluvial groundwater may be partly derived from the groundwater of the underlying fractured bedrock. The phreatic, or unconfined, groundwater within the northern area of the alluvial and proluvial fan is sustained mainly by the lateral flow of groundwater from the piedmont regions and by recharge from surface water bodies such as the Miyun reservoir. The shallow alluvial groundwater within the central and southern areas of the alluvial and proluvial fan is recharged primarily by the local precipitation and agricultural irrigation. The deep alluvial groundwater within the central and southern areas of the fan is sustained chiefly by the flow of groundwater from the northern area of the fan or from the underlying fractured bedrock. Methodologies adopted in this work may be useful to future investigation of groundwater in multiple aquifer systems similar to this area.

1. Introduction

Research on recharge processes and geochemical evolution of groundwater is relatively popular (Cronin et al., 2005; Edmunds et al., 2002; Moral et al., 2008; Ortega-Guerrero, 2003). Hydrochemistry of groundwater bodies related to a multiple aquifer system has also been reported (Rosenthal, 1987; Stotler et al., 2011; Yin et al., 2011). However, literatures on studies of recharge processes and groundwater evolution of multiple aquifers are still very limited. This work tries to focus on that issue in relation to multi-isotopes.

Two-thirds of the water consumption in Beijing is currently supplied by groundwater. Long-term groundwater overdraft has caused a continual decrease in groundwater levels. Potentiometric levels of the shallow alluvial groundwater in 2009 were about 20–30 m below those recorded in 1970, while levels in the deeper alluvium were about 30–40 m below those of 1970. Cones of depression in the potentiometric surfaces continue to expand, and reliability of the water supply has become a matter of concern. Research into groundwater recharge and geochemical evolution can provide a theoretical basis for local governments in decision-making, and is an important component of groundwater investigation in the Beijing area.

The alluvial and proluvial fan of the Chaobai River (APFCR) is one of the main river fan deposits in the Beijing area. The Beijing Eighth Waterworks is located in the northern part of the APFCR, and uses groundwater as its main source of water supply. The groundwater within the central and southern areas of the APFCR is also the source of water supply for suburban towns and for agricultural activities. As a consequence of groundwater overdraft, there are several large-scale cones of depression in the APFCR from the north to the south.

However, there is very limited literature on studies of groundwater recharge, circulation and geochemical evolution in the APFCR, especially pertaining to the relationship of groundwater in the Quaternary porous media to the underlying bedrock.
groundwater. Existing publications address the $^2$H, $^3$H and $^{18}$O content in local precipitation (Wei et al., 1982), the sources of major chemical ions of groundwater in the urban region, the macroscopic characteristics of groundwater circulation in the entire basin of the Chaobai River and the annual and inter-annual distribution of Chaobai River runoff. Thus, there is an impending necessity to research recharge processes and groundwater evolution of aquifers in the APFCR.

### 2. Geology and hydrogeology

The APFCR is located in the northeastern Beijing plain with an area of about 1850 km$^2$. Local precipitation occurs largely in summer, which accounts for 70–80% of the annual amount. The average annual precipitation was 585 mm from 1949 to 2009, but only 450 mm between 1999 and 2009. The average annual water-surface evaporation is 1729 mm. In the APFCR, the land surface slopes gently (0.7–0.9‰ gradient) to the southeast. The maximum water storage capacity of the Miyun reservoir, which is within the upstream area of the Chaobai River near the APFCR, is 4.375 × 10$^9$ m$^3$, and the annual average streamflow entering the reservoir is 1.19 × 10$^8$ m$^3$. Since 1981, when the Miyun reservoir stopped discharging downriver, the channel of the Chaobai River within the APFCR has been almost dry on a perennial basis. In 2000, the groundwater yield in the APFCR was about 35% of the city's total amount of groundwater exploitation, and thus Beijing's primary groundwater cones of depression are found in the APFCR.

#### 2.1 Geology

The elevation of the mountainous area upstream of the APFCR is generally from 400 m to 1500 m with several mountaintops exceeding 2000 m, and the extent of the mountainous area is about 4900 km$^2$. Strata of the Archean group, the middle-upper Proterozoic group, the lower Paleozoic group and the Mesozoic group outcrop in the mountainous area (Figure 1). Metamorphic and igneous rocks are the most widespread.

The thickness of the Quaternary strata within the APFCR is generally 200–400 m, but may exceed 500 m locally. The rocks underlying the Quaternary are the middle-upper Proterozoic group, the Cambrian and Ordovician strata, and granite.

#### 2.2 Hydrogeology

The infiltration coefficient of precipitation is about 0.30–0.45 in the area of the Proterozoic and Paleozoic carbonate strata, and about 0.10–0.20 in the area of the metamorphic strata and the igneous rocks. The number of springs in the mountainous area was estimated as 790 in 1982. However, the number and flux of the springs has declined since 1990 as a result of groundwater exploitation and decreased precipitation. In recent years, the annual average streamflow entering the Miyun reservoir has been less than 2 × 10$^8$ m$^3$ due to the decreased precipitation.

In the northern area, the lithology of the Quaternary soils is mainly sand and gravel, with a permeability coefficient of 100 m/d, but in the middle and southern areas, the lithology changes gradually to interbedded sand and clay, with a permeability coefficient of 1–5 m/d. Groundwater in the northern area is unconfined, while in the central and southern areas, groundwater is found under various degrees of confinement.

In this work, groundwater in the Quaternary granular media is termed shallow if it occurs at depths of zero to 150 m below land surface, and is termed deep if found at greater depths. Hydraulic gradients in the groundwater of the Quaternary sediments can reach 0.035 in the northern part of the APFCR, but they decrease to less than 0.005 in the deep groundwater of the middle and southern areas. The larger gradient of the groundwater in the northern area suggests a strong lateral recharge coming from the mountainous area. Flow directions of the groundwater in the APFCR are generally from north and northwest to south and southeast.

### 3. Methodology

The primary methods adopted in this study to investigate groundwater recharge and geochemical evolution include the following: field surveys, sampling, field testing, laboratory experiments, interpretation of hydrochemical and isotopic data in conjunction with basic hydrogeologic background information to generate inferences regarding recharge patterns and geochemical evolution, statistical classification of hydrochemical data using the method of Q-mode hierarchical cluster analysis, study of the spatial distribution and correlation of the classified groups, geochemical modelling, and further insight into deep groundwater geochemical evolution using the distributions of strontium (Sr) and strontium-87 ($^{87}$Sr).

#### 3.1 Sampling and analyses

Field sampling of surface- and ground-waters was performed over the period from May to August 2009 for the groundwater in the Quaternary sediments and for the groundwater in the underlying fractured bedrock within the APFCR, as well as for surface water, spring discharges and groundwater within the fractured rocks in the mountainous area to the north. A total of 154 samples were collected (Figure 2) and analysed through laboratory experiments. Of these, 62 samples (including three surface water samples, four samples of groundwater from the fractured rock, and three samples of spring discharge) were subjected both to hydrochemical and isotopic analyses, while the remaining 92 samples (including five samples of groundwater from the fractured rock) were subjected to hydrochemical analyses alone. Precipitation was sampled monthly from July 2008 to July 2009, and seven of these precipitation samples were obtained for hydrochemical and isotopic measurements.

At every sampling site, seven parameters, including electronic conductivity (EC), oxidation-reduction potential (ORP), dissolved oxygen (DO), pH, total dissolved solids (TDS), water temperature and air temperature were measured in situ. In all cases, the hydrochemical laboratory analyses included determination of the
concentrations of 22 constituents (e.g. primary cations and anions). The laboratory isotopic analyses targeted the isotopes of $^2$H, $^3$H, $^{18}$O and $^{87}$Sr. Analyses for all trace elements were also carried out on the samples separated for isotopic analysis.

The in situ measured parameters were acquired with a multi-parameter water meter (Thermo CyberScan PCD650). Methodologies of sample analysis followed the China national standard of Methods for Examination of Drinking Natural Mineral Water (GBT 8538–2008). The isotopes of $^2$H, $^{18}$O and $^{87}$Sr were analysed at the Chinese Academy of Geological Sciences, and the isotope of $^3$H was measured at the Institute of Geology, China Earthquake Administration. The $^2$H and $^{18}$O compositions were reported in ‰ notation calibrated against the Vienna standard mean ocean water (V-SMOW). The $^3$H concentration was analysed with the electrolytic enrichment and liquid scintillation counting method, and reported as tritium units (TU). The $^{87}$Sr was measured with the MAT-262 isotope mass spectrometer. The average $^{87}$Sr/$^{86}$Sr ratio of standard NBS987 was 0.710242 ± 0.000012 (2 standard deviations), and the strontium isotope fractionation effect was corrected with $^{88}$Sr/$^{86}$Sr = 8.37521. The trace elements were analysed with an inductively coupled plasma mass spectrometry (ICP-MS).

3.2 Q-mode hierarchical cluster analysis
The Q-HCA allows convenient investigation of the geochemical evolution of different clusters of groundwater samples, and provides insights regarding the recharge sources for the ground-
Figure 2. Sampling sites and elevation contour lines of groundwater level in July 2008. Standard deviation (σ) of the average isotope points is shown by error bars.
water samples of each cluster, while at the same time providing a classification of groundwater compounds to support geochemical modelling (Kebede et al., 2005; Meng and Maynard, 2001; Omorabor et al., 2008; Ragno et al., 2007; Swanson et al., 2001). The methods and preconditions for application of the Q-HCA have been discussed in detail by many authors (e.g. Barbieri et al., 2001; Cloutier, 2004; Cloutier et al., 2008; Tempel et al., 2008).

The Q-HCA was applied to the 144 groundwater and springflow samples collected in this study. The three surface water samples and seven precipitation samples were excluded. Ten variables were selected for the Q-HCA. The variables include K$^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, HCO$_3^-$, SO$_4^{2-}$, Cl$^-$, F$^-$, NO$_3^-$ and TDS. Euclidian distance was adopted to calculate the similarities among the samples. The selected variables are normalised by logarithm transform and standard deviation transform.

### 3.3 Inverse geochemical modelling

Inverse geochemical modelling has been widely applied in studies of groundwater geochemical evolution (Andre et al., 2005; Dai et al., 2006; Edmunds, 2009; Gi-Tak et al., 2006; Maliknecht et al., 2003; Mukherjee and Fryar, 2008; Sharif et al., 2008). In the inverse modelling approach, the geochemical and isotopic compounds within the initial and final members are used to deduce the chemical reactions and mass transformations that have taken place during the process of geochemical evolution from an initial member to a final one. The PHREEQC 2-15 computer code (Parkhurst and Appelo, 1999) was used in this study. The initial and final waters were selected according to the results of the Q-HCA. Selection of the mineral phases is discussed in the following sections.

### 4. Results

#### 4.1 Water chemical compositions and their indications for groundwater recharge sources

The main chemical compositions of the local precipitation, surface water, springs and groundwater are shown in Table 1.

In the northern part of the APFCR, the groundwater is a Ca-Mg-HCO$_3$ type water. This is consistent with the chemical quality of the spring discharges in the mountainous area, and may indicate that the groundwater in the northern area is recharged in part by lateral runoff of the groundwater in the mountains. However, the average contents of K$^+$, Na$^+$, SO$_4^{2-}$, Cl$^-$ and TDS of the groundwater in the unconsolidated sediments are obviously higher than those of the spring discharges. This suggests that other sources, in addition to the precipitation and the piedmont groundwater, may contribute to the alluvial aquifer in the north. Of the possible source in the northern region, the Miyun reservoir exhibits concentrations of K$^+$, Na$^+$, SO$_4^{2-}$, Cl$^-$ and TDS that are relatively close to those of the alluvial groundwater in the north. This suggests that the Miyun reservoir may also contribute recharge to the alluvium, possibly by flow through the strata under the dam.

In the central area of the APFCR, Na$^+$ concentrations range from 58 to 120 mg/l in the deep groundwater and from 21 to 90 mg/l in the shallow groundwater. These results suggest flow into the deeper zone from or through a region of high-sodium water. The groundwater in the fractured bedrock underlying the deeper alluvium is in fact Na-HCO$_3$ type water, and its content of Na$^+$ reaches 123 mg/l. The data thus suggest upward flow from the underlying bedrock into the deeper alluvium of the central and southern areas of the APFCR. This conclusion is consistent with the available hydraulic data. According to the existing limited observation data of groundwater in the underlying fractured bedrock, potentiometric levels in the underlying bedrock were originally 8–10 m below those in the deeper alluvium. However, as the cones of depression in the potentiometric levels of the deep alluvium (Figure 2) developed in response to pumping, water levels in the alluvium decreased by 30–40 m from their original levels, reversing the vertical head gradients and causing water levels in the deep alluvium to fall below those in the underlying bedrock. Moreover, there is no consistent or extensive aquiclude or aquitard between the alluvium and the underlying bedrock. Thus groundwater in the underlying fractured rock can flow upward readily in response to lower heads in the alluvium, causing the Na$^+$ content of the alluvial groundwater to increase.

In the southern part of the APFCR, the groundwater in the deeper alluvium is closer in chemical composition to the groundwater of the fractured bedrock (Table 1). As in the central area, there are cones of depression in the potentiometric surface of the deep

<table>
<thead>
<tr>
<th>Sample type</th>
<th>K$^+$</th>
<th>Na$^+$</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>HCO$_3^-$</th>
<th>SO$_4^{2-}$</th>
<th>Cl$^-$</th>
<th>NO$_3^-$</th>
<th>TDS</th>
<th>Groundwater type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation</td>
<td>0.50</td>
<td>0.94</td>
<td>4.86</td>
<td>0.64</td>
<td>9.49</td>
<td>8.80</td>
<td>2.93</td>
<td>6.31</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>Surface water</td>
<td>2.65</td>
<td>11.97</td>
<td>38.70</td>
<td>20.60</td>
<td>155.80</td>
<td>54.27</td>
<td>18.07</td>
<td>5.44</td>
<td>308</td>
<td></td>
</tr>
<tr>
<td>Springs</td>
<td>0.70</td>
<td>2.63</td>
<td>41.20</td>
<td>18.85</td>
<td>207.50</td>
<td>14.40</td>
<td>5.00</td>
<td>3.00</td>
<td>290</td>
<td></td>
</tr>
<tr>
<td>Northern area GW</td>
<td>1.39</td>
<td>9.19</td>
<td>54.83</td>
<td>19.49</td>
<td>220.20</td>
<td>27.08</td>
<td>14.61</td>
<td>19.49</td>
<td>367</td>
<td>Ca-Mg-HCO$_3$</td>
</tr>
<tr>
<td>Central area GW</td>
<td>3.56</td>
<td>58.85</td>
<td>57.99</td>
<td>18.17</td>
<td>334.63</td>
<td>32.05</td>
<td>19.05</td>
<td>8.02</td>
<td>428</td>
<td>Ca-Na-HCO$_3$(deeper GW)</td>
</tr>
<tr>
<td>Southern area GW</td>
<td>1.37</td>
<td>78.34</td>
<td>53.63</td>
<td>20.95</td>
<td>339.28</td>
<td>47.81</td>
<td>30.00</td>
<td>2.55</td>
<td>491</td>
<td>Na-HCO$_3$(deeper GW)</td>
</tr>
<tr>
<td>GW of fractured bedrock</td>
<td>3.85</td>
<td>132.0</td>
<td>12.0</td>
<td>6.40</td>
<td>256.30</td>
<td>24.00</td>
<td>52.5</td>
<td>0.05</td>
<td>493</td>
<td>Na-HCO$_3$</td>
</tr>
</tbody>
</table>

Table 1. Average chemical composition of surface water and groundwater (GW): mg/l
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4.2 Spatial variation of isotopes and their indications for groundwater recharge sources
Isotopes of $^2$H and $^{18}$O are commonly used to evaluate recharge processes and geochemical evolution of groundwater (Barth, 2000; Hildenbrand et al., 2005; O’Driscoll et al., 2005; Plummer et al., 2001). In the Beijing area, the local meteoric water line (LMWL) is usually adopted as $\delta^2$H = 7.3$\delta^{18}$O + 9.7 (Wei et al., 1982), which was based on $^2$H and $^{18}$O data in precipitation during 1979–1980. The $^2$H and $^{18}$O data of the precipitation obtained in this study were added into the series of 1979–1980, and a new LMWL was acquired as $\delta^2$H = 6.93$\delta^{18}$O + 3.93 (Figure 3) with $R^2 = 0.849$, which is adopted in this paper. The global meteoric water line (GMWL) was selected as Craig’s $\delta^2$H = 8$\delta^{18}$O + 10 (Craig, 1961).

The $\delta^{18}$O and $\delta^2$H of the surface water and the groundwater are generally (−7.1)–(−11.9) and (−51)–(−84). These are much closer to those of the rainy season precipitation (−6.8)–(−11.4) and (−55)–(−82) than to those of the non-rainy season precipitation (−2.3)–(−4.7) and (−15)–(−38). These results indicate that the surface water and the groundwater in the APFCR are recharged primarily by rainy season precipitation.

The average $\delta^{18}$O and $\delta^2$H of the alluvial groundwater of the northern APFCR are −7.84 and −55.9, and plot among the points of the precipitation (−7.85 and −58.5 on average), the surface water and the piedmont bedrock groundwater (−9.2 and −58.0). Thus the sources of the northern area alluvial groundwater may be related to the latter three as end-members. The average $\delta^{18}$O and $\delta^2$H of the central shallow groundwater are −8.58 and −64.0, which are close to those of the southern area shallow groundwater, −8.74 and −63.82. This indicates that they have almost the same sources, which are primarily precipitation and agricultural irrigation according to field surveys and the general hydrogeologic setting.

The $\delta^{18}$O and $\delta^2$H of the deep groundwater decrease slowly from the northern area to the southern area of the APFCR. In the central and southern areas, there are the two most depleted $\delta^{18}$O and $\delta^2$H centres of the deep alluvial groundwater (Figure 4) occurring within the potentiometric cones of depression of the central and southern areas of the APFCR. This indicates that the water being pumped from the deep alluvium is derived at least partially from the underlying bedrock, where the groundwater is characterised by depleted $\delta^{18}$O and $\delta^2$H. This confirms the flow relationships indicated by the analysis of relative water levels, that is, upward flow from the bedrock to the deep alluvium must occur within the cones of depression. In turn this may help explain the high yield per foot of drawdown of the deep alluvium, which exceeds that predicted by theoretical analyses that do not take into account flow from the underlying bedrock.

According to the tritium ($^3$H) dating, the age of the alluvial groundwater in the northern part of the APFCR is less than 10 years, implying modern water recharge and a rapid renewal rate. The age of the shallow groundwater in the central and southern areas is commonly 30–40 years, and also shows modern water recharge,
but with a relatively slower renewal rate. The age of the deep alluvial groundwater in the central and southern areas is generally 40–50 years, except in the areas of the potentiometric cones of depression, where the $^3$H content is less than 3 TU. This suggests that the deeper alluvial groundwater in these areas is a mixture of modern water and the older water derived from the fractured bedrock. Carbon-14 data have indicated that the age of groundwater in the fractured bedrock in the central area exceeds 8600 years, and that the ages of the deep alluvial groundwater and the groundwater in the fractured bedrock in the southern area of the APFCR are respectively 2100 and 21 000 years. Thus, the groundwater of the fractured bedrock in these areas is the oldest in age, is of the Na-HCO$_3$ chemical type, and exhibits depleted $\delta^{18}$O and $\delta^2$H.

### 4.3 Groundwater hierarchical clusters and their hydrogeological meanings

Classified groups of the groundwater samples can be selected visually from the dendrogram (Figure 5), an output by the Q-HCA codes. According to the dendrogram, the 144 groundwater samples can be classified into two major groups and six subgroups by choosing a similarity index of 0.17. The two major groups and the subgroups are different in their average compositions (Table 2) and hydrochemical characteristics. Each subgroup is defined by distinct hydrochemical characteristics and corresponds to a clear region of distribution (Table 3).

The central area shallow groundwater (subgroup II) and the southern area shallow groundwater (subgroups I and III) belong to the shallow groundwater group and the deep groundwater group in the dendrogram of the Q-HCA. This may indicate that they have similar recharge sources, which would include precipitation and agricultural irrigation. The northern area groundwater (subgroup IV), the central area deep groundwater (subgroup V) and the southern area deep groundwater (subgroup VI) belong to the deep groundwater group, which may imply that they are correlated in terms of recharge and discharge.

The shallow groundwaters of the central and southern areas (subgroups II and III) differ in chemical composition and chemical type from the northern area groundwater (subgroup IV). These differences suggest that the shallow groundwater in the central and southern areas may be derived from sources other than groundwater flow from the northern area.

In one local area situated in the southwestern part of the southern area of the APFCR, the shallow groundwater displays a high TDS, as well as relatively high levels of its primary cations and anions. The NO$_3^-$ content in this area is as high as 30-2 mg/l. The shallow groundwater samples of this area were segregated as subgroup I in the Q-HCA. The high NO$_3^-$ of the shallow groundwater in this local area is attributed to anthropogenic activities, especially agricultural irrigation and fertilisation.

The groundwater of the northern area (subgroup IV), and the deep groundwater of the central and southern areas (subgroups V and VI), all belong to the deep groundwater group, are close to one another in average TDS and have the same primary anion, HCO$_3^-$. However, they also display slight differences in evolution of chemical types (Table 3).

### 4.4 Inverse geochemical modelling and groundwater chemical evolution

Three applications of inverse geochemical modelling were carried out in this study. One addressed the chemical evolution of the deep alluvial groundwater of the central area, one that of the deep alluvial groundwater of the southern area, and one the chemical evolution of seepage from the Miyun reservoir, which is believed to occur primarily through the strata underlying the dam. The
The shallow groundwater group

The deep groundwater group

Members of the subgroups

Subgroup I: 7 members from T135 to T62
Subgroup II: 23 members from S78 to S103
Subgroup III: 24 members from T127 to C132
Subgroup IV: 33 members from J23 to S99
Subgroup V: 29 members from S85 to S108
Subgroup VI: 28 members from J76 to C133

Figure 5. Dendrogram of Q-mode hierarchical cluster analysis. The left-hand samples are interlaced for clarity. The dashed line shows the Sr concentration of 0.527 mg/l. Sr content of the shallow groundwater ranges generally from 0.527 mg/l to 1.33 mg/l, while that of the deep groundwater (including that of the northern area phreatic groundwater) ranges commonly from 0.149 mg/l to 0.527 mg/l. This may indicate a difference between the recharge sources of the shallow groundwater and those of the deep groundwater.
inverse modelling provided further insights into the geochemical evolution processes affecting this resource. In the same way, seepage from the Miyun reservoir is a matter of primary interest to water supply planners, both in terms of the quality of the northern area groundwater, and in terms of the performance of the reservoir itself. The inverse modelling similarly provided insights into these issues. The flow under the dam is referred to in this paper as the river valley underflow.

The chemical compositions of the initial and final waters (Table 4) were assigned according to Table 2 and the results of the hydrochemical experiments on the respective samples. The mineral phases were selected based on (a) the saturation indices of the minerals in the initial and final waters deduced by the PHREEQC code, (b) the primary mineral phases in the rocks of the upstream mountainous area (Bao, 1996) and (c) the primary mineral phases were selected based on (a) the saturation indices of the minerals in the initial and final waters deduced by the PHREEQC code, (b) the primary mineral phases in the rocks of the upstream mountainous area (Bao, 1996) and (c) the primary mineral phases in the rocks of the Quaternary soils in the downstream plain (Ye et al., 2008). The selected mineral phases vary with the different selected paths and are presented in the results of the inverse geochemical modelling.

<table>
<thead>
<tr>
<th>Subgroup</th>
<th>pH</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Na⁺</th>
<th>HCO₃⁻</th>
<th>SO₄²⁻</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>F⁻</th>
<th>TDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>7.5</td>
<td>1.57</td>
<td>77.57</td>
<td>139.17</td>
<td>133.01</td>
<td>535.44</td>
<td>177.91</td>
<td>227.19</td>
<td>30.19</td>
<td>0.82</td>
<td>1201.00</td>
</tr>
<tr>
<td>II</td>
<td>7.9</td>
<td>4.88</td>
<td>23.01</td>
<td>77.10</td>
<td>45.25</td>
<td>318.12</td>
<td>58.96</td>
<td>29.85</td>
<td>17.47</td>
<td>0.34</td>
<td>516.30</td>
</tr>
<tr>
<td>III</td>
<td>7.8</td>
<td>1.52</td>
<td>32.48</td>
<td>82.15</td>
<td>55.99</td>
<td>423.83</td>
<td>46.35</td>
<td>36.78</td>
<td>4.87</td>
<td>0.47</td>
<td>604.75</td>
</tr>
<tr>
<td>IV</td>
<td>7.8</td>
<td>1.54</td>
<td>19.77</td>
<td>57.17</td>
<td>16.99</td>
<td>228.60</td>
<td>25.92</td>
<td>13.64</td>
<td>11.38</td>
<td>0.27</td>
<td>337.88</td>
</tr>
<tr>
<td>V</td>
<td>8.1</td>
<td>2.51</td>
<td>14.34</td>
<td>42.84</td>
<td>69.63</td>
<td>347.72</td>
<td>10.70</td>
<td>10.48</td>
<td>0.53</td>
<td>0.58</td>
<td>358.03</td>
</tr>
<tr>
<td>VI</td>
<td>8.2</td>
<td>1.24</td>
<td>11.08</td>
<td>29.18</td>
<td>97.50</td>
<td>266.81</td>
<td>49.06</td>
<td>24.19</td>
<td>0.57</td>
<td>0.94</td>
<td>394.43</td>
</tr>
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</table>

Table 2. Average value of chemical composition in groundwater subgroups: mg/l

<table>
<thead>
<tr>
<th>Subgroup</th>
<th>Distributing regions and hydrochemical characteristics</th>
</tr>
</thead>
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<tr>
<td>I</td>
<td>Having a smaller amount of samples, and situated in a small area of farmlands and vegetable fields in the southwestern part of the southern area of the APFCR. This subgroup belongs to the shallow groundwater distributing at a depth of 0–100 m, and is alkalescent Ca-Mg-Na-HCO₃ type water with relatively high TDS and NO₃⁻. Molar percentages of the Ca²⁺, Mg²⁺ and Na⁺ are 37%, 32% and 27% respectively of the total cations, and those of the HCO₃⁻ and Cl⁻ are 49% and 32% of the total anions.</td>
</tr>
<tr>
<td>II</td>
<td>Distributing in the shallow aquifers (&lt;150 m) of the central area and representing the central area shallow groundwater. The molar percentage of Na⁺ exceeds that of Mg²⁺, and it is alkalescent Ca-Na-HCO₃ type water with a relatively high TDS and K⁺. Molar percentages of the Ca²⁺ and Na⁺ are 47% and 28% of the total cations, and the HCO₃⁻ percentage is 69% of the total anions.</td>
</tr>
<tr>
<td>III</td>
<td>Distributing in the shallow aquifers (&lt;150 m) of the southern area of the APFCR and representing the southern area shallow groundwater, it is alkalescent Ca-Mg-Na-HCO₃ type water with a relatively high TDS and Cl⁻. The molar percentages of the Ca²⁺, Mg²⁺ and Na⁺ are 44%, 29% and 26% respectively of the total cations, and that of the HCO₃⁻ is 77% of the total anions.</td>
</tr>
<tr>
<td>IV</td>
<td>Distributing in the northern area of the APFCR and including all the samples of the phreatic groundwater, the groundwater of the piedmont fractured rock, and the springs. Every main composition therein is relatively low and it is alkalescent Ca-Mg-HCO₃ type water with a low TDS and F⁻. The molar percentages of the Ca²⁺ and Mg²⁺ are 54% and 32% of the total cations, and that of the HCO₃⁻ is 75% of the total anions.</td>
</tr>
<tr>
<td>V</td>
<td>Distributing in the deep alluvial aquifers (&gt;150 m) of the central area of the APFCR and representing the central area deep groundwater. Its Ca²⁺ molar percentage decreases compared to that of subgroup IV, but its molar percentages of Na⁺ and HCO₃⁻ increase largely. It belongs to an alkalescent Na-Ca-HCO₃ type water with a low TDS and SO₄²⁻. The molar percentages of the Ca²⁺ and Na⁺ are 34% and 46% of the total cations, and that of the HCO₃⁻ is 91% of the total anions.</td>
</tr>
<tr>
<td>VI</td>
<td>Distributing in the deep alluvial aquifers (&gt;150 m) of the southern area of the APFCR and representing the southern area deep groundwater. It belongs to an alkalescent Na-HCO₃ type water with a low TDS and a high F⁻. Its Na⁺ molar percentage is 63% of the total cations and that of the HCO₃⁻ is 72% of the total anions.</td>
</tr>
</tbody>
</table>

Table 3. Distributing regions and hydrochemical characteristics of subgroups classified by Q-HCA
The sample of the river valley underflow (M39) was acquired from a well with a depth of 58 m, which is downstream of the Miyun reservoir (Figure 2) and penetrates a single stratum of pebbles and sands. The chemical type of the groundwater in the well is Ca-HCO₃ type, while that of the Miyun reservoir water is Ca-Mg-HCO₃ type. The results of the inverse geochemical modelling show that dissolution of carbonate minerals (dolomite and calcite), quartz, trace mica and gaseous carbon dioxide, and precipitation of gypsum and silicate minerals (feldspar), are required to satisfy the simulation of the river valley underflow.

The possible recharge sources of the central area deep alluvial groundwater are the northern area phreatic water, the central area shallow groundwater and the central area underlying bedrock water. The results of the inverse geochemical modelling show that, in the solution fractions of the initial waters, the northern area phreatic water is dominant, the central area underlying bedrock water is secondary, and the central area shallow groundwater is very small. These results suggest that the shallow groundwater played a minor role in the geochemical evolution of the central area deep alluvial groundwater.

The possible sources of the southern area deep alluvial groundwater include central area deep alluvial groundwater, the southern area shallow groundwater and the southern area underlying bedrock water. However, the results of the inverse geochemical modelling show a small solution fraction for the southern area shallow groundwater among the initial waters, and dominant fractions for the central area deep alluvial groundwater and the central area underlying bedrock water. Thus the results suggest that the shallow groundwater may have had a limited effect on the geochemical evolution of the deep alluvial groundwater.

The above results of the inverse geochemical modelling indicate that the deep alluvial groundwater may have a limited recharge from the shallow groundwater, and the main recharge sources of the two types of groundwater may be different from each other. That difference in recharge sources is also supported by the mentioned differences in the isotopic distributions of ²H and ¹⁸O, and in the ages of the shallow groundwater and the deep alluvial groundwater.

### 4.5 Sr evidence of groundwater recharge and chemical evolution

The ⁸⁷Sr/⁸⁶Sr ratio of the groundwater mirrors that of the rocks through which the groundwater has flowed (Uliana et al., 2007). The ⁸⁷Sr/⁸⁶Sr ratio can be used to investigate the geochemical evolution and flow path of the groundwater (Armstrong and Sturchio, 1998; Barbieri et al., 2005; Gosselina et al., 2004; Negrel, 2006), and to study the relationship between surface water and groundwater (Ojiambo et al., 2003). The presence of ⁸⁷Sr in rocks is caused mainly by the radioactive decay of the ⁸⁷Rb (87-Rubidium) isotope, and groundwater which is in chemical equilibrium with rocks rich in the Rb isotope commonly has a high ⁸⁷Sr/⁸⁶Sr ratio. A high ⁸⁷Sr/⁸⁶Sr ratio indicates feldspar, mica, clay minerals and igneous rocks (Armstrong and Sturchio, 1998; Banner and Hanson, 1990).

In this study, based on the distributions of the Sr element and the ratios of ⁸⁷Sr/⁸⁶Sr and ⁸²Rb/Sr, the groundwater recharge and geochemical evolution were analysed further.

### 4.5.1 Sr and ⁸⁷Sr evidence for groundwater recharge

The Sr content of the shallow groundwater in the APFCR is obviously different from that of the deep alluvial groundwater (Figure 6). The former ranges generally from 0.527 mg/l to 1.33 mg/l with an average of 0.705 mg/l, while the latter (including that of the northern area phreatic groundwater) is commonly less than 0.527 mg/l with a range of 0.149–0.527 mg/l and an average of 0.351 mg/l. This indicates a difference between the recharge sources or prior pathways of groundwater flow between the shallow groundwater and those of the deep alluvial groundwater. Three samples (S102, T73 and T58) of the deep groundwater have a high Sr content, which may be caused by mixing with the shallow groundwater. The Sr content of the shallow alluvial groundwater in the central and southern areas disagrees with that of the phreatic groundwater in the northern area, as well as with that of the springs and the mountainous surface water.
This is a further indication that the shallow groundwater in the APFCR has little direct recharge or groundwater flow relationship with those waters. According to the field survey and the apparently prevailing hydrogeologic conditions, the recharge sources of the shallow groundwater are mainly local precipitation, agricultural irrigation and the limited seasonal surface water.

The $^{87}$Sr/$^{86}$Sr ratios of the shallow alluvial groundwater converge on a range of 0.709463 to 0.709765, and show little variation with $^{85}$Rb/$^{86}$Sr ratios (Figure 7(a)). However, the $^{87}$Sr/$^{86}$Sr ratios of the northern area phreatic groundwater and of the deep alluvial groundwater vary generally with the $^{85}$Rb/$^{86}$Sr ratios (Figure 7(b)). These results suggest that the $^{87}$Sr of the shallow groundwater comes mainly from non-radiogenic sources, and that the increased $^{87}$Sr in the deep groundwater may be related to a radiogenic source. The difference in the apparent $^{87}$Sr sources between the shallow groundwater and deep groundwater of the central and southern areas further supports the hypothesis of different recharge sources and different isotopic evolutions between them. According to the field survey and the apparent hydrogeologic conditions, the deep alluvial groundwater and the northern area phreatic groundwater are sustained primarily by groundwater flow from the fractured rock of the piedmont, by the river valley underflow from the Miyun reservoir, and by groundwater flow from the underlying fractured bedrock in the APFCR. The isotopic work done in this study indicates that the influence of downward groundwater flow from the shallow alluvium to the deep alluvium is relatively limited in the APFCR, which is consistent with the results of the isotopic analysis and the inverse geochemical modelling.

4.5.2 Sr isotope geochemistry, deep groundwater recharge and geochemical evolution

Although the Sr content of the water samples varies from the northern area to the southern area, a main evolution path (MEP)
of Sr from the northern area phreatic groundwater to the southern area deep groundwater can be inferred (Figure 8). The MEP actually reflects also the overall direction of groundwater flow and the geochemical evolution path of the deep groundwater, in that the sampling locations near the MEP almost on the longitudinal midline of the APFCR, and the location and direction of the MEP are consistent with the main flow path of the deep groundwater according to the elevation contour lines of the potentiometric surface (Figure 2). These results suggest further that the northern area groundwater and the deep alluvial groundwater are sustained largely by the flow of groundwater from the fractured rock of the mountainous area, by recharge from surface water bodies of that area, and by groundwater flow from the fractured bedrock underlying the alluvium. These results further suggest that the primary direction of groundwater flow and the primary path of geochemical evolution coincide with the Sr MEP.

In Figure 8, the variance of Sr content along the MEP suggests the existence of various secondary flow paths in the APFCR. At the starting point of the MEP, the samples are primarily those of surface water from the mountain areas, and of spring discharges, both of which show relatively low Sr content. The Sr content of the groundwater increases gradually from a point about 20 km downstream from the start of the MEP. This appears to be due to mixing with Sr-rich groundwater (M2 and M41) from a northeast tributary river valley, and to groundwater inflow (H46) from the northwest mountains, which shows a Sr content similar to that near the MEP starting point. From a point about 40 km downstream from the start, the Sr content of the groundwater increases further due to an input of Sr-rich groundwater from the southwest mountains. Over approximately the same interval, groundwater inflow from the underlying Proterozoic and Paleozoic Sr-rich carbonates in the central and southern areas of the APFCR acts to maintain the Sr content of the deep alluvial groundwater. However, the input of groundwater from the fractured bedrock of the eastern mountains (J4) has a relatively low Sr content, and apparently because of this the downstream groundwater (S99, T78 and X70) also exhibits relatively low Sr levels. Therefore, it is reasonable to infer that a secondary flow path exists in the east. This eastern flow path would mingle with the primary flow path at a point about 80 km downstream from the start of the MEP, accounting for the decrease in Sr content of the groundwater from its highest high level.

The distribution of the $^{87}$Sr/$^{86}$Sr ratios along the main flow path shows a very similar pattern to that of the Sr content, although typically the samples with high Sr content have a low $^{87}$Sr/$^{86}$Sr ratio. The distribution of the $^{87}$Sr/$^{86}$Sr ratio suggests the same primary and secondary groundwater flow paths, recharge sources and pathways of geochemical evolution as are indicated by Figure 8 and by general inferences based on hydrogeologic conditions.

The above distributions of Sr and $^{87}$Sr/$^{86}$Sr indicate further that the northern area phreatic groundwater and the deep alluvial groundwater are sustained primarily by recharge from surface water sources in the mountain areas, by inflow of groundwater from the fractured rock of the mountains, and by inflow of groundwater from the fractured bedrock underlying and bordering the alluvium in the central and southern areas of the APFCR. This is supported by the mentioned results of the isotopic analysis and the inverse geochemical modelling.

5. Conclusions

The alluvial groundwater within multiple aquifers in the APFCR can be classified into two major groups: the shallow groundwater group (<150 m) and the deep groundwater group (>150 m). The shallow groundwater group can be classified further into three subgroups: the central area shallow groundwater, the southern area shallow groundwater and the shallow groundwater in a local area strongly affected by agricultural activities such as irrigation.
and fertilisation. The deep groundwater group includes also three subgroups: the northern area phreatic or unconfined groundwater, the central area deep alluvial groundwater and the southern area deep alluvial groundwater. Every subgroup has its own hydrochemical characteristics, different from those of the other subgroups, has a clear area of geographical distribution and supports explicit hydrochemical interpretations.

According to the hydrochemical and isotopic data developed in this study, and to inferences based on the general characteristics of the hydrogeologic setting, both the surface water of the mountain areas and the groundwater of APFCR depend ultimately on rainy season precipitation. The impact of non-rainy season precipitation on either resource is limited. The shallow groundwater appears to be recharged primarily by local precipitation, drainage from agricultural irrigation, and a limited amount of seasonal surface water. The deep groundwater (including the phreatic groundwater of the northern area) is sustained by recharge from surface water bodies of the mountain areas, by groundwater inflow from the fractured rock of the mountain areas, by groundwater inflow from the fractured bedrock underlying the alluvium in the central and southern areas of the APFCR, and to a very limited extent by downward seepage of the shallow groundwater.

The distributions of Sr and $^{87}$Sr/$^{86}$Sr indicate that the primary flow path of the northern area phreatic groundwater and the deep alluvial groundwater are generally accordant with the longitudinal midline of the APFCR and run towards the south. At the starting point of the main flow path, the groundwater is recharged mainly by seepage from surface water bodies of the mountain area (primarily the Miyun reservoir). Along the primary flow path, it is continuously recharged by groundwater inflow from the fractured rock of the mountain areas to the east and west of the APFCR. In the central and southern areas of the APFCR, inflow from the fractured bedrock underlying the alluvium acts to replenish the alluvial groundwater. Under the joint action of recharge and water–rock interactions along the various flow pathways, the chemical composition and isotope content of the shallow groundwater and the deep groundwater have undergone different evolutions.

The data obtained and the major conclusions found in this work will help to reassess future targets for studying groundwater supply in a related area. The methodologies adopted in this paper to investigate recharge processes and geochemical evolution of groundwater within multiple aquifers may be useful for similar work in other areas.

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