Spatial geochemical and isotopic characteristics associated with groundwater flow in the North China Plain

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Abstract:

The North China Plain (NCP) is an important agricultural area in China and has a high population density. Serious water shortages have occurred in this region over the last 20 years. Water transfer from the Yangtze River (the east route) was initiated in the year 2002 to provide water for the major cities of the NCP. This study was carried out before the implementation of the water transfer project, focusing on the spatial integration of the groundwater flow system and geochemical characteristics, which are mainly controlled by tectonics, geomorphology, and lithology. The field survey and the geochemical analyses of the groundwater samples indicated that the groundwater in the NCP has a two-layer structure, with a boundary at a depth of about 100–150 m. The two layers differ in pH, concentrations of SiO2 and major ions, and isotopes (18O, deuterium and tritium (T)). Chemical components in the upper layer showed a wider range and higher variability than those in the lower layer, indicating the impact of human activity. The flow direction of the groundwater in the upper layer was examined in detail in two profiles, showing that the upper layer flows east towards the Cangzhou–Daming fault, while the groundwater in the lower layer flows northeast towards Tianjin. Three hydrogeological zones are identified: recharge (Zone I), intermediate (Zone II), and discharge (Zone III). The recharge zone was found to be low in chloride (Cl−) but high in T. The discharge zone was found to be high in Cl− and low in T. This may be due to the difference in groundwater age. The discharge zone was subdivided into two sub-zones, Zone III1 and Zone III2, by considering the effects of human activities. Zone III2 was strongly affected by water diversions from the Yellow River. As groundwater flows from the recharge zone to the intermediate and discharge zones, chemical patterns evolve in the order: Ca-HCO3 > Mg-HCO3 > Na-Cl + SO4. Copyright © 2004 John Wiley & Sons, Ltd.

KEY WORDS hydrogeological zoning; geochemical characteristics; stable isotopes; groundwater flow; human activity; North China Plain

INTRODUCTION

The North China Plain (NCP) is located in the eastern part of China between 36°00' and 40°00'N and between 114°00' and 118°00'E (Figure 1). The NCP is an important region of agriculture in China, with an area of about 13,600 km² and a population of around 112 million. Bounded by Taihang Mountain to the west, Yanshan Mountain to the north, the Bohai Sea to the east, and the Yellow River to the south, the plain is a fault-subsidence basin with Quaternary sediment about 400–600 m thick. Rivers include the Yellow River and the
Haihe River and its main tributaries (Figure 1). Swells (uplifts) and depressions alternate with one another from the west to the east of the NCP. There is also a fault from Cangzhou to Daming, and a deep-seated fault from Haixing to Ningjin (Xu et al., 1996).

There are four main geomorphological units in the NCP: mountains and piedmont plain, alluvial fan plain, flood plain, and coastal plain (Wu et al., 1996). The four geomorphological units are closely associated with groundwater flow zones. The mountain and the piedmont plain correspond to the recharge zone, with downward-flowing groundwater. The coastal plain and part of the flood plain correspond to the discharge zone, with upward-flowing groundwater. The alluvial fan plain and part of the flood plain correspond to the intermediate zone, where groundwater passes through from the recharge to the discharge zone with movement either upwards or downwards. Since groundwater of the discharge zone in both the flood plain and the coastal plain are highly salinized (Rozelle et al., 1997), the Yellow River has been diverted to the flood plain since 1972 to reclaim this area for agriculture. Impacts of the diversion on the local groundwater quality and flow system ought to be considered (Ouyang et al., 1998; Chen et al., 2001).

Geochemical characteristics change from recharge, intermediate, to discharge zone according to the regional groundwater flow system (Stuyfzand, 1999; Toth, 1999). Chemical processes may provide evidence for groundwater flow. The chemical composition of surface water and groundwater can be used as a tracer for hydrograph separation of base flow and direct runoff, and for the identification of groundwater flow paths.

Figure 1. Location map of sampling sites in the NCP. Grand Canal is the boundary between the intermediate and the discharge zone.
(Eshleman et al., 1994; O’Brien, 1994; Katz et al., 1997; James et al., 2000). Surface water usually has an isotopic signature resulting from evaporation. Interactions in the semi-arid plain are not as active as those in headwater wetland or karst areas, where the surface water–groundwater head difference is significant (Devito et al., 1996; Devito and Hill, 1997). However, the use of the geochemical method to estimate groundwater flow rates and mixing ratios is effective for the NCP (Cheng, 1988; Chen et al., 2002; Shimada et al., 2002).

The groundwater age from wells of 150–250 m and 341–456 m depths in the Cangzhou area were estimated using 36Cl to be 250,000 years and 300,000 years respectively (Zhou et al., 2001), but the upper layer was found to be much younger using 14C and stable isotopes (Zhang et al., 2000; Chen et al., 2003). Climate change and human activity can also be interpreted by isotopic features and/or pollen data (Liu, 1996; Yi et al., 2002).

Since serious water shortages have occurred in the last 20 years, three schemes were planned to divert water from the Yangtze (Changjiang) River to the NCP, with design diversion capacities of 8.85 × 10^9 m³ year⁻¹, 2.3 × 10^10 m³ year⁻¹, and 2.0 × 10^10 m³ year⁻¹ (Liu and He, 1996; Wang and Ma, 1999; Qiang and Zhang, 2001). The eastern route was initiated in 2002. Impacts associated with the diversions on local ecology and environment are anticipated.

The aim of this study is to examine the geochemical characteristics and groundwater flow system of the NCP, with an emphasis on relating geochemical characteristics to factors such as tectonics and geomorphology. The study involves field survey, groundwater sampling and laboratory analysis, and provides a hydro-chemical background for possible environmental change due to the diversion project from the Yangtze River. Reasons for groundwater salinity in the eastern part of the NCP are also discussed.

### MATERIAL AND METHODS

Field surveys were carried out from 1998 to 2001 in the NCP, and 20 springs and 350 wells with depths ranging from 0 m (springs) to 550 m were surveyed (Figure 1). About 500 groundwater samples were collected. Electrical conductivity (EC) and pH were measured in situ. Chemical composition of NO₃⁻, Cl⁻, and SO₄²⁻ were analysed by ion chromatography, Na⁺, K⁺, Mg²⁺, Ca²⁺, SiO₂ by inductively coupled plasma A atomic emission spectronetry (AES), HCO₃⁻ by titration, and stable isotopes (₁⁸O and deuterium (D)) by a Delta S mass spectrometer. Tritium was analysed by the Institute of Hydrogeology and Engineering Geology, Chinese Academy of Geological Sciences, Zhengding. Basic information such as groundwater usage, well and screen depth, and land use were acquired from well managers or farmers.

δD and δ¹⁸O are expressed as the per mill (‰) difference of the isotope ratios of a sample (sp) and a standard (std), referred to as standard mean ocean water (SMOW) for D and ¹⁸O. They are defined as follows:

\[
\delta^{18}O(\delta D)_{‰} = \left( \frac{R_{sp} - R_{std}}{R_{std}} \right) \times 10^3
\]

where \( R \) is the ratio of the heavy to the light isotope, i.e. \( R = (^{18}O/^{16}O) \) or (D/H). Tritium is expressed as TU, i.e. one atom of tritium in 10¹⁸ atoms of hydrogen.

### RESULTS AND DISCUSSION

#### Hydrogeological zoning

Three hydrogeological zones (recharge (Zone I), intermediate (Zone II) and discharge (Zone III)) were delineated according to the tectonic structure and geomorphologic units. The discharge zone was subdivided into two sub-zones by taking the effects of human activities into account (Figure 1). The discharge zone in the coastal area (Zone III₁), to the east of the Cangzhou–Daming fault, is a relatively independent zone influenced by the Bohai Sea. Zone III₂ is affected by the Yellow River, as the water level of this river is higher than...
that of the local groundwater. The piedmont boundary, with an altitude of about 50 m above seawater level and regarded as the hydrogeological boundary of Zone I and Zone II, was delineated mainly based on the geomorphological map of the NCP (Wu et al., 1996). This line is close to the middle diversion route for the water transfer project from the Yangtze River to the NCP (Wang and Ma, 1999). Environmental impacts are to be expected on the regional groundwater flow in these two zones.

**Vertical layering of regional groundwater**

As mentioned above, a thick sedimentary sequence has been deposited in the NCP, with a depth of 500–600 m in depressions, 350–450 m in uplift areas, and 150–300 m around the piedmont (Zhou et al., 2001). These sediments of the Quaternary layer are composed of four layers: an unconfined layer of fine sand and silt to 40–60 m depth; a confined layer of sand and gravel to 100–150 m depth; a confined layer of course sand and gravel to 250–350 m depth; and a confined layer of fine sand and gravel to bedrock at 400–600 m depth (Yang et al., 2001).

Average pH, SiO$_2$, EC, HCO$_3^-$, $\delta^{18}$O, and $\delta D$ of the groundwater in the NCP are given in Figure 2. The groundwater was found to have a vertical two-layer structure with a boundary at about 100–150 m depth, with Layer I (upper) and Layer II (lower). The main characteristics of the groundwater of these two layers are shown in Table I. All these chemical parameters, except pH, decrease as the depth increases in Layer I, whereas those for Layer II were found to be relatively constant. The boundary of about 100–150 m depth between these two layers corresponded to the bottom depth of the confined layer of sand and gravel mentioned above. According to the data set of EC, $\delta^{18}$O and $\delta D$ (Figures 2 and 3), different water sources can clearly be indicated, such as enriched isotopes in Layer I and depleted isotopes in Layer II, reflecting a change in climate and environment (Chen et al., 1998, 2003; Yi et al., 2002) and human activities (Liu, 1996; Liu et al., 2001). The layer of 400–550 m depth indicates a possible association with seawater, since the isotopic values are increased and the pH is close to 8–4, the average for seawater. Several seawater intrusions have occurred in the NCP during Holocene (Zhang et al., 2000).

The two-layer structure for the groundwater in the NCP was confirmed by the vertical distribution of tritium, which showed that Layer I was affected by thermonuclear bomb fallout (tritium value more than 10 TU), whereas Layer II was less affected (tritium value less than 10 TU; Figure 4). Groundwater is widely used for irrigation in the NCP, especially in piedmont regions. The return flow of irrigation, mixing with rainfall affected by thermonuclear bomb fallout, recharges the aquifer. A wide range of tritium, of about 10–40 TU, for Layer I indicated mixture of water types, whereas a narrow range in Layer II indicated little mixing. The tritium concentration decreased exponentially with depth. The groundwater at depth 125 m, with an estimated tritium of 10 TU, was estimated to have a groundwater age of about 50 years (Shimada et al., 2002). Vertical groundwater movement was calculated thereby to be about 2.5 m year$^{-1}$ in the NCP. Lowering of the water table due to overexploitation of groundwater for irrigation (Liu et al., 2001) exaggerates the mixture of tritium-free Pleistocene and some tritium-containing Holocene waters. The width of the data scatter could be a reflection of the mixture and the complicated tritium input function (Clark and Fritz, 1997).

<table>
<thead>
<tr>
<th>Layer</th>
<th>pH</th>
<th>EC (mS m$^{-1}$)</th>
<th>SiO$_2$ (mg l$^{-1}$)</th>
<th>HCO$_3^-$ (mg l$^{-1}$)</th>
<th>$\delta^{18}$O (%)</th>
<th>$\delta D$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>I 7.6</td>
<td>177.8</td>
<td>11.0</td>
<td>506.7</td>
<td>$-8.3$</td>
<td>$-65.3$</td>
</tr>
<tr>
<td></td>
<td>II 8.0</td>
<td>107.7</td>
<td>9.4</td>
<td>290.5</td>
<td>$-10.1$</td>
<td>$-78.3$</td>
</tr>
<tr>
<td>Range (min/max)</td>
<td>I 6.4/8.7</td>
<td>40/970</td>
<td>1.83/25</td>
<td>161/1287</td>
<td>$-10.6/-3.6$</td>
<td>$-81.8/-41.4$</td>
</tr>
<tr>
<td></td>
<td>II 7.0/9.4</td>
<td>19/314</td>
<td>0.73/25.8</td>
<td>48.8/939.7</td>
<td>$-11.2/-7.8$</td>
<td>$-87.0/-55.5$</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>I 0.363</td>
<td>172.22</td>
<td>4.09</td>
<td>219.9</td>
<td>0.89</td>
<td>6.15</td>
</tr>
<tr>
<td></td>
<td>II 0.494</td>
<td>60.37</td>
<td>4.63</td>
<td>193</td>
<td>0.73</td>
<td>5.75</td>
</tr>
</tbody>
</table>

Table I. Geochemical and isotopic statistics for the two layers of groundwater in the NCP
Zhang et al. (2000) indicated that groundwater older than 10,000 years in the NCP has a $\delta^{18}O$ value of less than $-9\%e$, whereas that younger than 10,000 years has a value greater than $-9\%e$. Groundwater age in the upper layer is thus estimated to be younger than 10,000 years, whereas that in the lower layer is estimated to be older than 10,000 years, with the exception of that in the recharge zone (Zone I).

**Areal distribution of geochemical and isotopic characteristics**

The main geochemical and isotopic characteristics of groundwater in Layer I and Layer II are given in Table II. Among the major ions measured, chloride (Cl$^-$) has the lowest selectivity coefficient for ion exchange, due to its ionic charge and size, and, therefore, is used as a conservative tracer to identify the groundwater flow path. Areas of high Cl$^-$ concentration for Layer I include: 37.5–38.5°N and 115.5–116.5°E; and 36.5–37.0°N and 116.5–117.0°E (Figure 5). The Cangzhou–Daming fault serves as the eastern boundary of
Figure 3. Diagram of $\delta^{18}$O and EC in relation to Layer I and II

Figure 4. Distribution of tritium versus well depth

Table II. Average geochemical and isotopic compositions of the hydrogeological zones in the NCP

<table>
<thead>
<tr>
<th>Zone</th>
<th>Layer</th>
<th>pH</th>
<th>EC (mS m(^{-1}))</th>
<th>SiO(_2) (mg l(^{-1}))</th>
<th>HCO(_3) (mg l(^{-1}))</th>
<th>$\delta^{18}$O (‰)</th>
<th>$\delta$D (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone I</td>
<td>I</td>
<td>7.6</td>
<td>78.4</td>
<td>16.6</td>
<td>318</td>
<td>-8.28</td>
<td>-69.6</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>7.9</td>
<td>56.4</td>
<td>13.2</td>
<td>279</td>
<td>-8.51</td>
<td>-67.76</td>
</tr>
<tr>
<td>Zone II</td>
<td>I</td>
<td>7.5</td>
<td>160</td>
<td>10.9</td>
<td>447</td>
<td>-8.31</td>
<td>-64.5</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>8.1</td>
<td>89</td>
<td>8.86</td>
<td>238.5</td>
<td>-10.32</td>
<td>-79.6</td>
</tr>
<tr>
<td>Zone III(_1)</td>
<td>I</td>
<td>7.5</td>
<td>314</td>
<td>8.29</td>
<td>554</td>
<td>-8.38</td>
<td>-65.3</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>8.2</td>
<td>181</td>
<td>9.25</td>
<td>481</td>
<td>-9.9</td>
<td>-77.2</td>
</tr>
<tr>
<td>Zone III(_2)</td>
<td>I</td>
<td>7.7</td>
<td>216</td>
<td>9.54</td>
<td>650</td>
<td>-8.44</td>
<td>-64.11</td>
</tr>
</tbody>
</table>

the concentration zone, preventing groundwater from flowing to the east. The existence of a relatively high Cl\(^-\) concentration in the zone 36.5–37.0°N, 116.5–117.0°E indicates the impacts of the Haixing–Ninjin fault. The impedance to groundwater flow and enforced discharge due to the faults and swell is considered to be the main reason for the wide distribution of alkaline land in the NCP, which corresponds well to the distribution of high Cl\(^-\) concentration in the groundwater. Groundwater was expected to move to the east and/or the northeast due to the potential gradient. It was estimated to flow eastward at a rate of 4 m day\(^{-1}\) (around 1.5 km year\(^{-1}\)) in the Hutuo basin, based on analysis of tritium (Shimada et al., 2002). High Cl\(^-\) concentration would be flushed to the Bohai Sea if the Cangzhou–Daming fault did not exist.
For Layer II, two areas of high Cl\(^-\) concentration occurred, one in the coastal area and the other following a belt along 38°N. These two areas are perpendicular to each other and intersect at Cangzhou, indicating the impact of the Cangzhou–Daming fault on the groundwater flow in the deep layer. High Cl\(^-\) concentration for both layers between 37.5 and 38.5°N and between 115.5 and 116.5°E confirmed the impedance of the Cangzhou–Daming fault on the groundwater flow in the whole Quaternary layer to about 400–500 m depth.

Figure 6 shows that the main enriched centre of δ\(^{18}\)O for Layer I was kept in the western side of the Cangzhou–Daming fault, i.e. groundwater was prevented from passing through the fault. The δ\(^{18}\)O composition for rainfall, which was measured at Luancheng Station in the range of −4.8 to −9.4‰, with an average of
—7.33‰ (Cheng, 1988), confirmed the mixture of groundwater and modern recharge. The occurrence of the other enriched centre of about —7.5‰ near Dugai River was the result of water diversion from the Yellow River since the 1970s (Chen et al., 2001, 2002).

An isotopically depleted centre of —10.6‰ in the middle part of the NCP for Layer II indicates the phenomenon of water stagnation in front of the Cangzhou–Daming fault. In the juncture area of the Hutuo River and the Fuyang River, δ18O decreases gradually from the Taihang Mountain to the east, indicating the direction of groundwater flow. In the coastal area, δ18O becomes enriched closer to the seashore.

Geochemical and isotopic profiles

Two cross-sections, AA′ and BB′ (Figure 1), were selected to examine the groundwater flow in more detail based on geochemical and isotopic characteristics.

Figure 7 shows that groundwater moves to the east in the upper layer from 100 to —50 m a.m.s.l., and the front of this flow occurs at about 116.5°E, which is the location of the Cangzhou–Daming fault. Cl− in this layer is high at around 0 m a.m.s.l., with a concentration of more than 300 mg l−1. Enriched δ18O and high tritium at this depth imply that the groundwater here is relatively new compared with the water at about —400 m a.m.s.l., where a Cl− concentration of more than 700 mg l−1 and low δ18O and tritium were found. Groundwater in the deep layer (lower than —50 m a.m.s.l.) moves mainly downward, as indicated by the arrows in the profile of tritium. It also shows that the Cangzhou–Daming fault at 116.5°E serves as the boundary of groundwater flow, at least for the layer from the ground surface to —400 m a.m.s.l. As the groundwater moves along the flow path, δ18O changes in the upper layer due to the mixing of groundwater and modern recharge, whilst it remains stable in the lower layer. Cl− concentration increases along the flow path, corresponding to the pattern given by Toth (1999).

Figure 8 shows that the groundwater flow from ground surface to —50 m a.m.s.l. on the west side and —150 m a.m.s.l. on the east side was greatly affected by the downward groundwater flow from the Daqing
Figure 8. Profiles of tritium values (TU), $\delta^{18}$O (‰) and Cl$^-$ concentration (mg l$^{-1}$) in relation to the depth of aquifer (m a.m.s.l.) for the cross-section BB$^\prime$.

River and the Yongding River. About 200 km from Shijiazhuang City, two groundwater flows, one from Taihang Mountain to the east and the other from the Yanshan Mountain to the south, merge near the fault. The collision of the two flows slowed the flow of both surface and groundwater, leading to the occurrence of an enriched $\delta^{18}$O centre in this area. Because of this collision and the stagnation of water flow, the Cl$^-$ concentration in the groundwater increases to as high as 750 mg l$^{-1}$. The deep layer of lower than $-50$ m a.m.s.l. on the west side and $-150$ m a.m.s.l. on the east side has a groundwater flow path as indicated by the arrow along this cross-section.

Based on the profiles, it was concluded that groundwater from Taihang Mountain in the NCP flowed mainly to the east in the upper layer (greater than $-100$ m a.m.s.l.), and to the north-northeast in the lower layer (less than $-100$ m a.m.s.l.), due to the effect of the Cangzhou–Daming fault and the collision of groundwater. Groundwater flow in the upper layer is very active and groundwater age is in the order of tens to hundreds of years. Conversely, groundwater flow is relatively stable in the lower layer, with groundwater age in the order of thousands of years.

**Ionic and isotopic relationships associated with hydrogeological zones**

Relatively high Cl$^-$ and $\text{SO}_4^{2-}$ concentrations were found in Zone III$_1$, whereas low Cl$^-$ and sulphate ($\text{SO}_4^{2-}$) concentrations of less than 100 mg l$^{-1}$ and 200 mg l$^{-1}$ respectively were found in Zone I (Figure 9). A wide range of about 10–800 mg l$^{-1}$ for both Cl$^-$ and $\text{SO}_4^{2-}$ were found for Zone III$_2$. The mixture of local groundwater and the diverted water from the Yellow River was regarded as the main reason for this (Chen et al., 2002). Figure 9 also indicates that Cl$^-$ has an increasing trend along the flow path. The Cl$^-$ concentration in Zone III$_1$ is generally higher than that in Zone III$_2$. 

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Figure 9. Relationship between Cl\(^-\) and SO\(_4^{2-}\) concentration for the four zones delineated in the NCP

Figure 10. Relationship between $\delta^{18}O$ and tritium values

Three delineated zones (tritium was not measured for Zone III\(_2\)) in the NCP can be separated as shown in Figure 10 using the relationship of tritium value and $\delta^{18}O$. The recharge zone has high tritium levels of more than 10 TU, with $\delta^{18}O$ greater than $-10\%_c$, and the coastal zone (Zone III\(_1\)) has a low tritium value.
of less than 5 TU, with δ18O greater than −10·4‰ except for shallow wells of less than 20 m depth. The intermediate zone was less affected by thermonuclear bomb fallout in the lower layer, where low tritium values of <10 TU and depleted δ18O of less than −10‰ were found. A narrow range of δ18O from −10‰ to −8‰ and a wide range of δD, either very enriched or depleted, were found in groundwater samples in the recharge zone (Figure 11). The enriched δD in springs or wide-open wells of the recharge zone agrees well with the global meteoric line given by Craig (1961a, b), implying that modern rainfall is the dominant component for such groundwater. The depleted δD locations were mainly found to be at wells near the Hutuo River, which is supplied principally by the outflow from the Huangbizhuang reservoir. Though relatively enriched δ18O and δD were found for Zone I and III2, it was difficult to separate these zones based on the δ18O–δD relationship (Figure 11). The most depleted δ18O and δD were found for the lower layer of the intermediate zone.

Chemical type and evolution following the groundwater flow system

Groundwater in Zone I is distinctive in its low concentration of Na+ and high concentrations of Ca2+ and Mg2+, and is readily classified as Ca–Mg–HCO3 type as shown in the Piper diagram (Figure 12). In contrast to Zone I, groundwater in Zone III1 is high in Na+ concentration and low in Ca2+ and Mg2+. Since the intermediate zone (Zone II) incorporates both a transitional area and a local discharge area, a high variation in chemical pattern is found for the groundwater of this zone. As Zone III2 is affected by the Yellow River, the chemical type of the groundwater, either Ca–Mg–HCO3 or Ca–Mg–Cl, is related to the distance from the river (Chen et al., 2001).

Both Layer I and Layer II showed a similar geochemical evolution pattern for the regional groundwater flow system in the NCP, in an order as indicated by the arrow in Figure 12, Ca–HCO3 > Mg–HCO3 > Na–Cl + SO4.
CONCLUSIONS

A vertical two-layer structure with the boundary at 100–150 m depth was found for the groundwater in the NCP. The upper layer, having δ18O of less than −9‰ and an estimated groundwater age of less than 10,000 years, shows a high variation of ionic concentrations and isotopic values, which indicates mixing of groundwater and modern recharge due to irrigation. The vertical flow velocity was estimated at 2.5 m yr⁻¹ using tritium data. The Cangzhou–Daming fault has controlled the groundwater flow path by preventing groundwater from flowing eastward to the sea as indicated by the profiles of Cl⁻, δ18O, and tritium. The groundwater in the upper layer flows mainly eastward until it reaches the Cangzhou–Daming fault, resulting in a wide distribution of alkaline land in the NCP. The groundwater in the lower layer flows mainly to the northeast.

Four hydrogeological zones were delineated based on hydrogeological conditions: recharge (Zone I), intermediate (Zone II), discharge in the coastal area (Zone III₁), and discharge in the lower reach of the Yellow River (Zone III₂). The zones vary in chemical content of major ions and isotopic features, and chemical patterns evolve from the recharge to the discharge zone in the order: Ca–HCO₃ > Mg–HCO₃ > CaMg–Cl + SO₄ > Na–Cl + SO₄.

It is concluded from this study that geochemical characteristics, including isotopic features, are associated with the regional groundwater flow system and are affected by human activities.
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