Hydrochemical evolution mechanism of groundwater in the People’s Victory Canal Irrigation District, China

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\textbf{Abstract}

Under the influence of natural factors and human activities, groundwater dynamic field and hydrochemical field in the People’s Victory Canal Irrigation District, a piedmont well irrigation district in the north Henan province, have changed significantly. In this paper, the statistical characteristics of major ions in the groundwater in the People’s Victory Canal Irrigation District were analyzed based on the sampled data in wet season and dry season, and then the main hydrochemical processes in the runoff process of groundwater were discussed using different ion proportionality coefficient method. The results showed that Na\textsuperscript{+} and HCO\textsubscript{3}– were the major cation and anion in the groundwater, respectively. The order of cations in concentration was Na\textsuperscript{+} > Ca\textsuperscript{2+} > Mg\textsuperscript{2+} > K\textsuperscript{+}, and the order of anions in average concentration was HCO\textsubscript{3}– > SO\textsubscript{4}2– > Cl\textsuperscript{–}. The rock weathering and dissolution mainly controlled the hydrochemical evolution of groundwater, as Na\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Cl\textsuperscript{–}, and SO\textsubscript{4}2– in the groundwater were mainly derived from the dissolution of carbonates and sulfates. In addition, they were also derived from the dissolution of aluminum silicate minerals (such as albite). Besides, the hydrochemical process was accompanied by cation-exchange adsorption. The cation exchange between Na\textsuperscript{+} in the groundwater and Ca\textsuperscript{2+} and Mg\textsuperscript{2+} in soil occurred in most of the study area except G-01 area. The chemical constituents of groundwater were not only influenced by natural factors, but also by human activities. Especially in G-01, G-06, and G-08 areas, human pollution influenced the chemical constituents of groundwater obviously. 

\textbf{Keywords:} People’s Victory Canal Irrigation District; Hydrochemical characteristics; Ion proportionality coefficient; Hydrochemical evolution; Groundwater pollution

\section{1. Introduction}

The formation and distribution of the chemical constituents of groundwater are the result of long-term interaction between groundwater and environment, which is influenced by natural factors and human activities [1–3]. The research on the evolution mechanism and inherent law of the chemical constituents of groundwater is of great significance to clarifying the influence mechanisms of natural factors and human activities on groundwater environment, also provides a scientific basis for the prevention of groundwater pollution, having important application value [4–6].

The People’s Victory Canal Irrigation District has been developed from an agricultural gravity irrigation district to a multifunctional district for rural and urban industrial water use as well as domestic water use. However, with the increase of water consumption and decrease of irrigation water quantity from the Yellow River, the groundwater becomes the...
main water supply for the irrigation district. Thus, its mining quantity is increasing, and groundwater depth increases from 2–5 m in the 1950s to 12–20 m, accordingly. And declining trend of groundwater level gradually became obvious, with an average annual decline of about 0.7–0.8 m at present. The change of groundwater dynamic field has affected and continues to influence the evolution of hydrochemical field.

In this paper, based on the analysis of the chemical constituents of groundwater, the causes of formation of groundwater were explored, and then the chemical function of groundwater was analyzed using ion proportionality coefficient method, providing a scientific basis for the evaluation of groundwater resources and prevention of groundwater pollution in the study area.

2. Materials and methods

2.1. The study area

The People's Victory Canal Irrigation District, located in Xinxian city, Henan province, China—the north shore of the Yellow River—is an important grain, cotton, and oil production base in China. Situated at 113°31′–114°25′ of east longitude and 35°0′–35°30′ of north latitude, it stretches across seven counties and one city: Xinxian county, Hua county, Weihui county, Yuanyang County, Yanjin County, Wuzhi county, and Xinxian city, covering a vast area. It is adjacent to the main canal of the Red Flag Canal in Linzhou city in the east, is adjacent to the Communist Canal and Wujia Irrigation District in the west, extends to Yulin town in Yanjin County, Shizhai Town in Yuanyang County, Qizhuang Village in Hua county, and Langgongmiao Town in Xinxian city in the south, and extends to Weihe River in the north [7], as shown in Fig. 1.

2.2. Groundwater sampling and physicochemical analysis

A total of ten typical representative sampling points were selected in the People’s Victory Canal Irrigation District, which are shown in Fig. 1. The groundwater samples were collected once a month in the study area during January to December in 2015. Water samples were collected in 1-L high-density polyethylene bottles with tight fitting plastic caps using Solinst's groundwater sampler (Canada, 425 type). The bottles were washed three or four times with the water to be sampled before taking the sample. All samples were filled to the top to avoid evaporation and exchanges of sample water with atmospheric materials. And the samples were transported immediately to the laboratory of the First Geological Environment Survey Institute, the First Bureau of Geology and Minerals Exploration of Henan Province.

The pH was measured using pH meter. Major cation concentrations (Ca²⁺, Mg²⁺, Na⁺, and K⁺) were analyzed by the atomic absorption spectrometry method. Chloride (Cl⁻) was determined by standard AgNO₃ titration. Carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) were determined by titration with HCl. Sulfate (SO₄²⁻) was measured by spectrophotometer turbidimetry. The total dissolved solids (TDS) were computed by using electrical conductivity meter in dS/m at 25°C. The analytical precision for measurement of ions was determined by calculating the ionic balance error. An error of up to ±3% is tolerable, while every water sample with a calculated error outside this range should be measured again [8]. Approximately 90% of the measured water samples were within this range. This means that the resultant data quality is sufficient for chemical modeling and/or for drawing simple conclusions about water quality.

The sample data in dry season and wet season were selected for comparative study.

3. Results and discussion

3.1. Statistical characteristics of the hydrochemical parameters of groundwater

Descriptive statistical analysis is a basic method in the study on hydrogeochemistry [9-11]. To fully understand the comprehensive characteristics of the chemical constituents of groundwater, a descriptive statistical analysis of the chemical constituents of groundwater was carried out to show the basic features of the chemical constituents of groundwater in certain time and space. Therefore, an analysis of the statistical characteristics of the hydrochemical parameters of groundwater samples in dry season and wet season in 2015 was carried out, as shown in Table 1.

Among cations, Na⁺ showed the highest concentration, with an average concentration of 195.93 mg/L in dry season and 166.41 mg/L in wet season, and the order of cations in concentration was Na⁺ > Ca²⁺ > Mg²⁺ > K⁺. Among anions, HCO₃⁻ showed the highest concentration, with an average concentration of 527.00 mg/L in dry season and 531.29 mg/L in wet season, and the order of anions in concentration was HCO₃⁻ > SO₄²⁻ > Cl⁻. The concentration of Na⁺ and HCO₃⁻ in the groundwater was high, but their variation coefficient was small, indicating that their absolute concentration in the groundwater was high and relatively stable. So they were the major cation and anion in the groundwater in the study area, respectively.

The variation coefficient of K⁺ and SO₄²⁻ was the largest, which was 129.43% and 153.21% in dry season and 139.19% and 161.62% in wet season, while the variation coefficient of the rest ions was below 1, indicating that K⁺ and SO₄²⁻ were more sensitive to hydrological conditions, topography, human activities, and other external influences, and thus
their stability was weak. So they were the important factors influencing the great difference in spatial distribution of the hydrogeochemical properties of groundwater and main variables determining the salinization of groundwater in the irrigation district.

The variation coefficient of Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), HCO\(_3^-\), Cl\(^-\), and TDS was between 14.63% and 82.07%, indicating that their chemical constituents were relatively stable. The little difference between the variation coefficients in dry season and wet season showed that the seasonal variation had little influence on the spatial variability of hydrochemistry.

The pH was between 6.94 and 7.84, with an average pH of 7.47 in dry season and 7.36 in wet season, respectively, indicating that the groundwater was weakly alkaline.

### 3.2. Analysis of the Gibbs graph of groundwater

In 1970, Gibbs designed a semi-logarithmic coordinate graph (Gibbs graph) to compare the chemical constituents and causes of formation of water. The y-coordinate is the logarithmic coordinate of TDS, and the x-coordinate is \(\gamma_{Na}/(\gamma_{Na} + \gamma_{Ca})\) ratio, and the relationship between them reflects the controlling factors of the chemical constituents of water. Three different areas in the Gibbs graph represent three different causes of formation, namely “evaporation concentration,” “rock weathering,” and “precipitation control” [12,13]. In the Gibbs graph, the low-salinity groundwater having large \(\gamma_{Na}/(\gamma_{Na} + \gamma_{Ca})\) ratio (close to 1) is distributed in the bottom right corner, indicating that the groundwater is mainly recharged by atmospheric precipitation. The groundwater with medium dissolved solid content (with TDS content of 70–300 mg/L) having small \(\gamma_{Na}/(\gamma_{Na} + \gamma_{Ca})\) ratio (smaller than 0.5) is distributed in the left middle part, indicating that its chemical constituents are mainly influenced by rock weathering and dissolution. The groundwater with high dissolved solid content having large \(\gamma_{Na}/(\gamma_{Na} + \gamma_{Ca})\) ratio (close to 1) is distributed in the upper right corner, indicating that the region is located in arid areas with strong evaporation. To better reveal the controlling factors of the hydrochemical evolution of groundwater, the tested hydrochemical data of groundwater were substituted into the Gibbs graph, then the causes of formation of groundwater in the study area can be observed intuitively.
3.3. Analysis of the cause coefficient of groundwater

γNa/γCl, called the cause coefficient of groundwater, is a hydrogeochemical parameter characterizing the enrichment of Na⁺ in groundwater. The average γNa/γCl of standard sea water is 0.85, the γNa/γCl of low TDS water is high (γNa/γCl > 0.85), and the γNa/γCl of high TDS water is low (γNa/γCl < 0.85) [14]. The γNa/γCl of groundwater in the study area in dry season (Fig. 3(a)) and wet season (Fig. 3(b)) is shown in Fig. 3.

Most of the sampling points in the study area were above the line 1:1, and their γNa/γCl was greater than 1, indicating that the Na⁺ milligram equivalent concentration was basically greater than Cl⁻ concentration. It was considered that Na⁺ and Cl⁻ were derived from the dissolution of halite, which but was not the only source. The excess Na⁺ may be derived from the weathering and dissolution of albite or sodium montmorillonite or other minerals. In addition, the cation exchange also affected the Na⁺ concentration. In the runoff process of groundwater, the rock minerals were weathered and dissolved by hydrolysis and acid action, thus Na⁺ was released from feldspar, meanwhile, the cation exchange between Ca²⁺ in the groundwater and Na⁺ in soil occurred, so that the Na⁺ concentration was greater than Cl⁻ concentration.

The Na⁺ concentration and Cl⁻ concentration of groundwater in G-06 and G-08 areas in dry season as well as G-06 area in wet season were obviously greater than those in other areas of the study area, and the degree of salinity was abnormally large, which may be due to the influence of human factors.

3.4. Analysis of the ratio of γHCO₃⁻ + γSO₄²⁻ to γCa²⁺ + γMg²⁺ of groundwater

In order to determine the major source of Ca²⁺, Mg²⁺, HCO₃⁻, and SO₄²⁻, a plot of γ(HCO₃⁻ + SO₄²⁻) vs. Γ(Ca²⁺ + Mg²⁺) was plotted as shown in Fig. 4. As we know, Ca²⁺, Mg²⁺, HCO₃⁻, and SO₄²⁻ are mainly from dissoluble rocks, such as calcite, dolomite, and gypsum. And there would be a charge balance among Ca²⁺, Mg²⁺, HCO₃⁻, and SO₄²⁻, if they are derived from simple dissolution of these rocks [17,18]. But in the study area, no matter in dry season or wet season, all the points, except the G-01 in wet season, are plotted above the 1:1 line. It means that HCO₃⁻ and SO₄²⁻ are more than Ca²⁺ and Mg²⁺ except G-01 in wet season. The excess of HCO₃⁻ and SO₄²⁻ must be balanced by Na⁺ and K⁺ in order to keep the charge balance in groundwater. It suggests that aluminum silicate minerals

![Fig. 3. Distribution of the cause coefficient of groundwater in the study area: (a) dry season, (b) wet season.](image1)

![Fig. 4. Relationship between γ(Ca²⁺ + Mg²⁺) and -γ(HCO₃⁻ + γSO₄²⁻) in (a) dry and (b) wet seasons.](image2)
(e.g., albite) dissolution may be the main source of HCO$_3^-$ + SO$_4^{2-}$, which can be explained by the formula as below:

\[
\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_8 + 2\text{CO}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 2\text{Na}^+ + \text{H}_4\text{Al}_2\text{Si}_3\text{O}_8 + 4\text{SiO}_2^-
\]

This formula explains the source of excess HCO$_3^-$ + SO$_4^{2-}$ relative to Ca$^{2+}$ + Mg$^{2+}$, also explains the excess Na$^+$ relative to Cl$^-$. Of course, Na$^+$ can be derived from cation exchange as stated before.

In order to determine the significance cation exchange in controlling the water chemistry, a plot of $\gamma(\text{Ca}^{2+} + \text{Mg}^{2+})$ – $\gamma(\text{HCO}_3^- + \text{SO}_4^{2-})$ vs. $\gamma(\text{Na}^+ – \text{Cl}^-)$ was examined. The $\gamma(\text{Ca}^{2+} + \text{Mg}^{2+})$ – $\gamma(\text{HCO}_3^- + \text{SO}_4^{2-})$ represents the amount of Ca$^{2+}$ + Mg$^{2+}$ gained or lost compared with that provided by calcite, dolomite, and gypsum, while $\gamma(\text{Na}^+ – \text{Cl}^-)$ represents the amount of Na$^+$ lost or relative to that provided by halite [17].

If cation exchange is the main process that controlling the water chemistry, there should be a linear relationship with a slope of -1 between $\gamma(\text{Ca}^{2+} + \text{Mg}^{2+})$ – $\gamma(\text{HCO}_3^- + \text{SO}_4^{2-})$ and $\gamma(\text{Na}^+ – \text{Cl}^-)$. Fig. 5 shows that almost all the points plotted near the 1:1 linear except the point G-06 in dry season, which can be concluded that in the study area, cation exchange is the main function that controlling the groundwater chemistry.

However, how did the cation exchange occur is not clear. As a result, the CAI 1 and CAI 2 were calculated, and are plotted in Fig. 6. CAI 1 represents the ratio of $\gamma(\text{Cl}^-)$ – $\gamma(\text{Na}^+ + \text{K}^+)$ to $\gamma(\text{HCO}_3^- + \text{SO}_4^{2-})$, and CAI 2 represents the ratio of $\gamma(\text{Cl}^-)$ to $\gamma(\text{Na}^+ + \text{K}^+)$ to $\gamma(\text{Cl}^-)$. Based on the former study, negative CAI indicates exchange of Ca$^{2+}$ + Mg$^{2+}$ in groundwater with Na$^+$ in rocks, while positive value represents Na$^+$ in groundwater with Ca$^{2+}$ + Mg$^{2+}$ in rocks. In the study area, except the positive CAI of point G-01 no matter in dry and wet season, CAI of all the other points is negative values. It shows that Ca$^{2+}$ + Mg$^{2+}$ in groundwater exchanges with Na$^+$ in rocks, but in the area near G-01, Na$^+$ in groundwater exchanges with Ca$^{2+}$ + Mg$^{2+}$ in rocks.

### 3.5. Influence of human activities on groundwater hydrochemistry

From Figs. 2–6, we can conclude that anthropogenic activities have affected groundwater chemistry, especially in the area near G-01, G-06, and G-08. In order to confirm anthropogenic influence, the plot of relationship between NO$_3^-$ and Cl$^-$ was examined, as shown in Fig. 7. Distinct positive correlations of NO$_3^-$ and Cl$^-$ in both seasons indicate anthropogenic sources of the ions [17].

Potential sources of NO$_3^-$ and Cl$^-$ are industrial sewage, domestic sewage, pit toilets, etc. In the study area, average concentration of Cl$^-$ is 169.08 and 158.43 mg/L, respectively, in dry and wet season, less than 250 mg/L, which satisfies the III classification of groundwater quality standard in China in 2016. But the concentration of G-06 in dry and wet season and that of G-08 in wet season are all more than 250 mg/L, which means the groundwater cannot be used for domestic use directly. Meanwhile, concentration of NO$_3^-$ is 10.53 and 11.66 mg/L, respectively, in dry and wet season, less than 20 mg/L, and satisfies the III classification of groundwater quality standard in China in 2016. But the concentration of G-06 in dry and wet season and that of G-08 in dry season are all more than 20 mg/L and cannot satisfy the III classification standard according to the groundwater quality standard in China. The remarkably high value of NO$_3^-$ concentration is significantly influenced by anthropogenic activities [19,20].

![Fig. 5. Relationship between $\gamma(\text{Ca}^{2+} + \text{Mg}^{2+})$ – $\gamma(\text{HCO}_3^- + \text{SO}_4^{2-})$ and $\gamma(\text{Na}^+ – \text{Cl}^-)$ in (a) dry and (b) wet seasons.](image)

![Fig. 6. Chlor-alkali index (a) 1 and (b) 2 in groundwater in dry and wet seasons.](image)
and Cl\(^-\), Cl as well as γ(Cl–Mg\(^{2+}\), Mg\(^{2+}\) and HCO\(_3\)–Ca\(^{2+}\), Ca\(^{2+}\)) – γ(HCO\(_3\)–SO\(_4\)\(^{2-}\), SO\(_4\)\(^{2-}\)) confirmed that the cation exchange adsorption occurred in solution of aluminum silicate minerals (such as albite). It also showed that the groundwater were not only derived from the dissolution of carbonates and sulfates, but also derived from the weathering and dissolution of feldspar minerals as well as cation exchange.

The proportionality coefficients γ(HCO\(_3\)–SO\(_4\)\(^{2-}\) and γCa\(^{2+}\) + γMg\(^{2+}\) as well as γ(Ca\(^{2+}\) + Mg\(^{2+}\)) – γ(HCO\(_3\)–SO\(_4\)\(^{2-}\)) and γ(Na–Cl–) showed that the Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Cl\(^-\), and SO\(_4\)\(^{2-}\) in the groundwater were not only derived from the dissolution of carbonates and sulfates, but also derived from the dissolution of alumina silicate minerals (such as albite). It also confirmed that the cation exchange adsorption occurred in the runoff process of groundwater.

The TDS and γNa/γCl, high concentration of NO\(_3\)– and Cl\(^-\) in the groundwater, as well as the relationship between NO\(_3\)– and Cl\(^-\) showed that the chemical constituents of groundwater were not only influenced by natural factors, but also by human activities. Especially in G-01, G-06, and G-08 areas, human pollution influenced the chemical constituents of groundwater obviously.

4. Conclusion

The concentration of Na\(^+\) and HCO\(_3\)– in the groundwater was high, but their variation coefficient was small, so they were the major cation and anion in the groundwater in the study area, respectively. The variation coefficient of K\(^+\) and SO\(_4\)\(^{2-}\) was the largest, so they were the important factors influencing the great difference in spatial distribution of the hydrogeochemical properties of groundwater.

The Gibbs graph of groundwater in the study area showed that the chemical constituents of groundwater were mainly influenced by rock weathering and dissolution. The analysis of the cause coefficient of groundwater showed that Na\(^+\) and Cl\(^-\) were not only derived from the dissolution of halite, but also derived from the weathering and dissolution of feldspar minerals as well as cation exchange.

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References


Fig. 7. Relationship between NO\(_3\)– and Cl\(^-\) in dry and wet seasons.