DE GRUYTER Open Geosciences 2020; 12: 1421–1429

Research Article

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# Hydrochemical differences between river water and groundwater in Suzhou, Northern Anhui Province, China

https://doi.org/10.1515/geo-2020-0203
received August 07, 2020; accepted October 09, 2020

**Abstract:** Understanding hydrological process of surface water and groundwater is significant for the management of urban water resources. In this study, a total of thirty-seven water samples have been collected from the river (RW, 15 samples), shallow aquifer (SG, 12 samples), and deep aquifer (DG, 10 samples) in Suzhou, Northern Anhui Province, China, and their major ion concentrations and stable H–O isotopes have been measured. The results revealed that $Na^+$ and $HCO_3^-$ were the dominant cation and anion, respectively, and most of the water samples are classified to be Na-$HCO_3$ type, to a lesser extent, Mg-$HCO_3$ type. K-mean and Q-type clustering analyses ruled out the hydrological relationship between river and groundwater, but there was a significant connectivity between shallow and deep groundwater, which was further confirmed by the hydrogen and oxygen isotopes. The relationship between $\delta^2H$ and $\delta^{18}O$ has shown that precipitation was the main source of the groundwater in the study area. Furthermore, the values of deuterium excess (d-excess) in different water bodies suggested that the groundwater has not been affected by evaporation, which was the main process controlling the isotopic composition of river water.

**Keywords:** river water, groundwater, major ions, stable isotopes, hydrochemistry

## 1 Introduction

Water resources, including the surface water and groundwater, are important for human survival and social development. However, with the development of the economic, as well as the ecological fragility of the surface water, the groundwater has become more and more important for households, agriculture, and industry in many regions, especially in North China [1]. However, a series of studies revealed that the groundwater is not separated from other hydrological systems, but can be influenced by surface water deposits, climate change, and human factors [2–5]. Therefore, understanding the relationship between surface water and groundwater is of great significance for the protection and management of water resources [6,7].

At present, as an effective tool, hydro-geochemistry has long been used to study the relationships between two or more water bodies, especially major ions and stable H–O isotopes [7–9]. For example, the hydraulic relationship and evolution of surface water and groundwater in the Songnen Plain, southwestern Heilongjiang province, China, have been analyzed by major ions and stable isotopes, and the results provided theoretical guidance for the water resources management in saline-alkali land [7]. The stable isotopes of precipitation, river water, and groundwater in Zagreb, northwestern Republic of Croatia, have been analyzed and the results showed that the Sava River was the main source recharging the aquifer in the region [8]. Similarly, the recharge mechanism between surface water and groundwater in the Al-Khazir Gomal Basin, northern Iraq, has been identified by means of water chemistry and stable isotopes [9]. These studies revealed that hydro-geochemistry is effective for identifying sources of groundwater and relationship between different water bodies.

Water resource is important for the Suzhou City, northern Anhui Province, China, because the city has a large number of population and agriculture is the main industry in the area. However, a series of studies revealed

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that the surface water has been polluted with different degrees in the region [10,11], and therefore, groundwater has become more and more important as it is the only source of water supply for domestic purpose recently, which should be paid more attention to. Given the condition of the pollution of surface water, getting the information about the relationship between the surface water and groundwater is therefore becoming more and more important, as the quality of the groundwater might be affected by the surface water.

Therefore, a total of thirty-seven river water and groundwater samples have been collected, and their major ion concentrations and stable H–O isotopic compositions have been analyzed for getting the following information: (1) the characteristics of major ion concentrations and stable H–O isotopic compositions; (2) the relationships between river water and shallow and deep groundwater; and (3) the recharge of groundwater.

# 2 Methods

## 2.1 Study area

Suzhou is located in the north of Anhui Province, China, (Figure 1a) with longitude between 116°50′18″ and 117°08′ 24″ and latitude between 33°31′28″ and 33°48′47″. The area has warm temperate and belongs to semi-humid monsoon climate, with hot summers, dry and cold winters, and distinct four seasons. The study area is in a plain landform with elevations ranging from 20 to 30 m. The annual average temperature of the area is 14.4°C, with relative humidity near 70%. The average annual precipitation and evaporation are 858.1 and 1589.4 mm, respectively, and the precipitation is mainly concentrated in June to August (Figure 1b). All climate information (including temperature, humidity, precipitation, and evaporation) was provided by the Suzhou Water Conservancy Bureau.

The surface water system is relatively developed in Suzhou, and there are many rivers in the area, the largest one is the Xinbian River, followed by Tuo River. Xinbian River is a large-scale artificial river with a total length of 127 km and width of 90–115 m. Tuo River is a main tributary of Huai River, with a total length of 75.1 km and width of 20–60 m. During the wet season, the flow of the Xinbian River and the Tuo river is 90 and 50 $m^3/s$, respectively, while during the dry season, due to evaporation and irrigation pumping, they decrease to 30 and 18 $m^3/s$, respectively. The groundwater in the area is mainly from the Quaternary loose layer aquifer system, which can be subdivided into four aquifers from shallow to deep: the first aquifer (groundwater from it has been called SG), the second aquifer (groundwater from it has been called DG), the third, and fourth aquifers. The clay minerals, sandstone, mudstone, and gravel are the main rock types in the loose layer aquifer system. The first and second aquifers can recharge from precipitation in some areas and are highly water-rich. Due to the effect of aquiclude, the third and fourth aquifers are mainly interstitial recharge and have poor water quantity. Over the years, groundwater from the second aquifer is the main source of urban water supply. The depth of first and second aquifers is 0–30 and 30–100 m, respectively.

## 2.2 Sampling and analyses

A total of thirty-seven river water and groundwater samples have been collected on October 5–6, 2019, including the river water (RW, 15 samples), the shallow groundwater (SG, 12 samples), and the deep groundwater (DG, 10 samples). The sampling site of the river and groundwater are shown in Figure 1c, and the direction arrows indicate the order of sample numbers. The locations of samples are shown in Figure 1c. Before sampling, the two liters of polyethylene bottle have been rinsed three times with distilled water. The river water samples were collected directly, and the groundwater samples were extracted from the well through pump. After sampling, the samples were stored in refrigerator at 4°C; the major ions and stable hydrogen and oxygen isotopes have been measured within one week. All of the experiments were completed in the Key Laboratory of Mine Water Resource Utilization of Anhui Higher Education Institute, Suzhou University, China.

Cations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$) and anions ($Cl^-$, $SO_4{}^{2-}$) were determined by ion chromatography (ICS-600-900, Thermo Fischer Scientific, USA). Moreover, the contents of $HCO_3{}^-$ and $CO_3{}^{2-}$ are measured by acid-base titration. The relative standard deviation is less than 5%. The value of $\delta^{18}O$ and $\delta^2H$ was analyzed by liquid water isotope analyzer (LGR, LICA United Technology Limited, CAN), and the measurement accuracy was ±0.1 and ±0.5‰ for $\delta^{18}O$ and $\delta^2H$, respectively. The final analytical results are

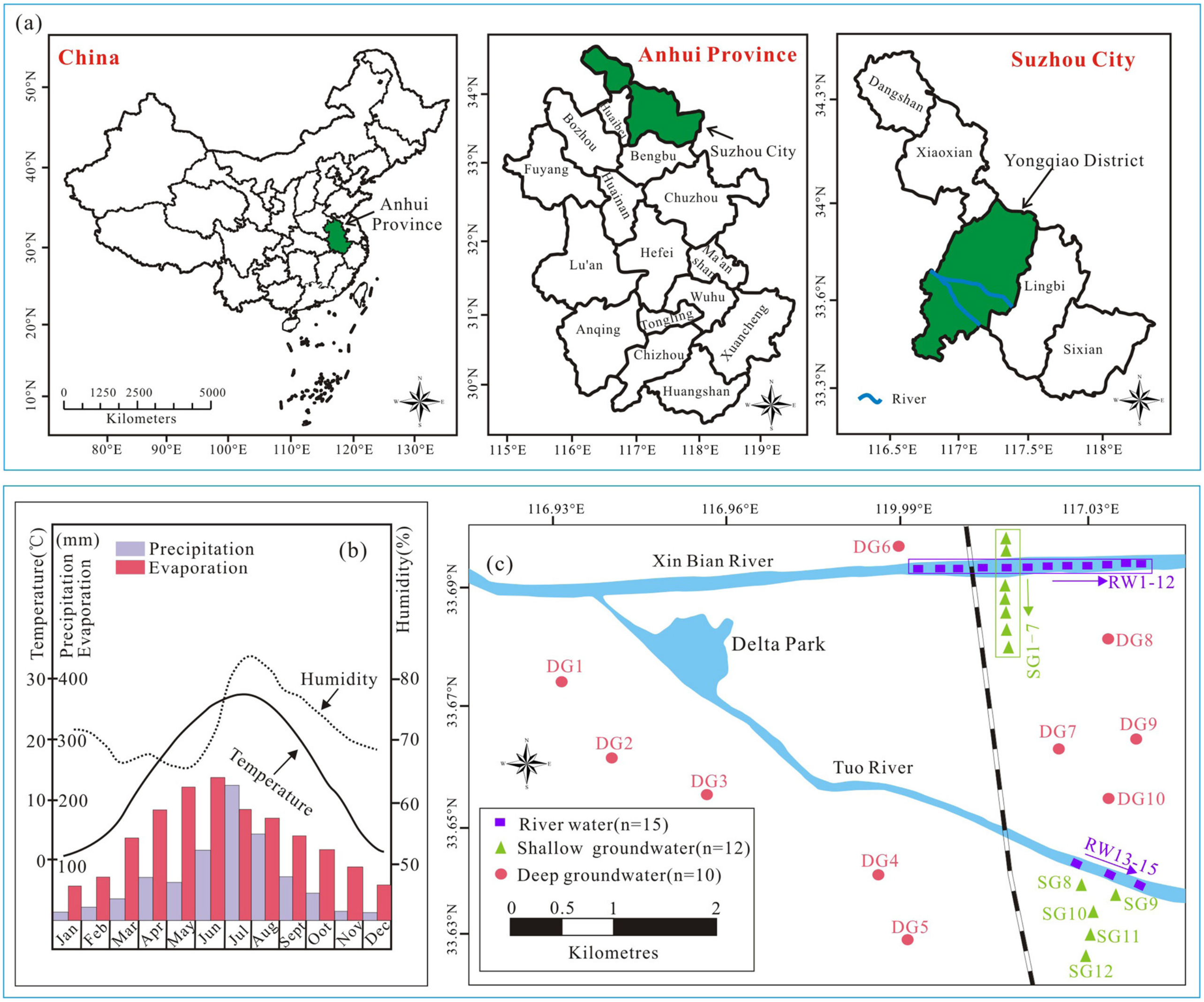

**Figure 1:** (a) Location of the study area. (b) Annual average of temperature, precipitation, evaporation, and humidity from January to December in Suzhou. (c) Sampling location of surface water and groundwater.

expressed in δ-notation (‰) relative to the Vienna Standard Mean Ocean Water (V-SMOW) [12]:

$$\delta^{2}\mathrm{H}\ (‰) = \left[({}^{2}\mathrm{H}/{}^{1}\mathrm{H})_{\mathrm{sample}}/({}^{2}\mathrm{H}/{}^{1}\mathrm{H})_{\mathrm{V\text{-}SMOW}} - 1\right] \times 1{,}000$$

$$\delta^{18}\mathrm{O}\ (‰) = [({}^{18}\mathrm{O}/{}^{16}\mathrm{O})_{\mathrm{sample}}/({}^{18}\mathrm{O}/{}^{16}\mathrm{O})_{\mathrm{V\text{-}SMOW}} - 1] \times 1{,}000$$

## 2.3 Data treatment

To be a powerful mathematical statistical analysis method, cluster analysis has been widely used in ecology, geochemistry, medicine, and other fields [13–15]. In the study of hydro-geochemistry, cluster analysis has often been used for the evaluation of the hydraulic connection between different water bodies [16–19]. In this study, two types of clustering methods (k-means and Q-type) based on factoextra and igragh packages in RStudio have been chosen for calculation [20].

K-means clustering algorithm is a kind of iterative clustering analysis algorithm. The first and foremost steps are to select k objects as the initial clustering center, then calculate the distance between each object and each seed clustering center, and assign each object to the nearest clustering center [21]. In this study, average silhouette width method was used to determine the optimal number of clusters (i.e., $K$ value) and the calculation formula is as follows:

$$S(i) = [b(i) - a(i)]/\max[a(i),\ b(i)]$$

where $a(i)$ is the measuring similarity within a group, $b(i)$ is the measuring similarity between groups, the value of $S(i)$ ranges from −1 to 1, and the larger the value, the higher the intragroup anastomosis and the farther the group spacing, which means that the larger the average silhouette width, the better the clustering effect.

Different from K-means clustering, the calculation principle of Q-type cluster analysis is as follows: first, each sample is classified into one category by itself, and at this time, the distance between the categories is equal to the distance between the samples; then, the two categories with the smallest distance are combined to form a new category, and the distance between the new category and other categories is calculated, and then the two categories with the closest distance are combined, and this step is repeated to all samples put it in one category [22]. In this study, "Euclidean" was used as the distance measurement standard, and the sum of squares of deviations ("Ward") was selected as the merging method to get the best grouping [23].

# 3 Results

## 3.1 Major ion concentrations

As can be seen from the data in Table 1, the average concentrations of $Na^+$, $K^+$, $Mg^{2+}$, $Cl^-$, and $SO_4^{2-}$ in RW are higher than the SG and DG, and the major ion concentrations of RW have the following order: $HCO_3^-$ (307.3 mg/L) > $SO_4^{2-}$ (173.9 mg/L) > $Na^+$ (156.4 mg/L) > $Cl^-$ (121.5 mg/L) > $Mg^{2+}$ (44.7 mg/L) > $K^+$ (24.4 mg/L) > $Ca^{2+}$ (16.9 mg/L) > $CO_3^{2-}$ (0 mg/L). Comparatively, the SG samples have the lowest and highest average concentrations of $Na^+$ and $HCO_3^-$ relative to RW and DG, respectively. The average values in decreasing order are $HCO_3^-$ (404.4 mg/L), $Na^+$ (87.7 mg/L), $SO_4^{2-}$ (59.7 mg/L), $Cl^-$ (40.7 mg/L), $Mg^{2+}$ (40.6 mg/L), $Ca^{2+}$ (31 mg/L), $CO_3^{2-}$ (7.1 mg/L), and $K^+$ (6.1 mg/L). The DG samples have lower contents of $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, and $SO_4^{2-}$, but higher $CO_3^{2-}$ relative to RW and SG, and their mean major ion concentrations are $HCO_3^-$ (381.5 mg/L) > $Na^+$ (106 mg/L) > $Mg^{2+}$ (32.3 mg/L) > $CO_3^{2-}$ (25.3 mg/L) > $Cl^-$ (25 mg/L) > $SO_4^{2-}$ (19 mg/L) > $Ca^{2+}$ (9.1 mg/L) > $K^+$ (2.3 mg/L). In general, the major ion concentrations of shallow groundwater are similar to the deep groundwater, but are different from the river water.

Previous studies revealed that the major anion in water will change from $HCO_3^-$ to $SO_4^{2-}$ and then to $Cl^-$ from the recharge zone to the discharge zone [24,25]. Therefore, the classification of hydrochemical types is of great significance for the study of groundwater evolution [26]. In this study, the Piper diagram (Figure 2) was adopted to help understand the hydrochemical facies [27]. It can be seen from the figure that $HCO_3^-$ and $Na^+$ are the dominant anion and cation, respectively, and all of the river water, 67% of the shallow groundwater, and 80% of the deep groundwater samples are classified to be Na-$HCO_3$ type. Moreover, the remaining groundwater samples (33 and 20% of the shallow groundwater and deep groundwater samples) are classified as Mg-$HCO_3$ type. These hydrochemical types are closely related to water rock interactions, such as the weathering and dissolution of silicate minerals, montmorillonite and illite, which are abundant in the loose layer aquifer and can release $Na^+$, $Mg^{2+}$, $Ca^{2+}$, and $HCO_3^-$ into the water.

## 3.2 Hydrogen and oxygen isotopes

The results of hydrogen and oxygen isotopes are shown in Table 1. As can be seen from the table, the mean values of $\delta^2H$ for the RW, SG, and DG are −42.9, −52.97, and −55.4‰, respectively. And for $\delta^{18}O$, the mean value in RW, SG, and DG is −5.3, −7.7, and −7.8‰, respectively. It can be achieved from the Table 1 and Figure 3 that the $\delta^2H$ and $\delta^{18}O$ values in the RW are significantly different from the other two groups, indicating that the river water is under the condition different from the groundwater and indirectly suggesting that there is no direct relationship between them.

# 4 Discussion

## 4.1 The evolution of hydrogen and oxygen isotopes

In 1961, Craig discovered that there was a linear relationship between $\delta^2H$ and $\delta^{18}O$ in water which has not been over-evaporated and further fitted the function of Global Meteoric Water Line Equation (GMWL, $\delta^2H = 8 \times \delta^{18}O + 10$) [28]. Moreover, Dansgaard founded that the stable H—O isotopic composition in precipitation was affected by many factors such as temperature, altitude, latitude, etc., and these factors lead to the variations of the H–O isotopic compositions of the atmospheric precipitation in different regions [29]. Therefore, local meteoric water line

**Table 1:** Hydrochemical compositions of water samples from different water bodies

| Sample | $\delta^2H$ (‰) | $\delta^{18}O$ (‰) | d-excess (‰) | $Na^+$ (mg/L) | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Cl^-$ | $SO_4^{2-}$ | $HCO_3^-$ | $CO_3^{2-}$ | TDS | Water type |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RW1 | −42.3 | −5.5 | 1.5 | 156.7 | 27.0 | 20.9 | 52.9 | 132.2 | 220.0 | 321.6 | 0.0 | 770.5 | Na-$HCO_3$ |
| RW2 | −43.9 | −5.3 | −1.8 | 156.4 | 26.9 | 21.0 | 52.8 | 129.9 | 211.6 | 311.2 | 0.0 | 754.1 | Na-$HCO_3$ |
| RW3 | −43.5 | −5.5 | 0.4 | 156.0 | 26.8 | 20.9 | 52.7 | 133.1 | 209.1 | 325.2 | 0.0 | 761.1 | Na-$HCO_3$ |
| RW4 | −44.9 | −5.0 | −4.5 | 166.0 | 24.4 | 14.0 | 40.0 | 122.3 | 167.7 | 291.1 | 0.0 | 679.9 | Na-$HCO_3$ |
| RW5 | −42.8 | −5.1 | −2.3 | 166.8 | 24.4 | 13.9 | 39.9 | 124.5 | 168.0 | 288.6 | 0.0 | 681.9 | Na-$HCO_3$ |
| RW6 | −43.6 | −5.1 | −2.9 | 167.4 | 24.6 | 13.9 | 40.4 | 129.6 | 173.6 | 306.9 | 0.0 | 703.0 | Na-$HCO_3$ |
| RW7 | −42.0 | −5.3 | 0.2 | 166.7 | 24.4 | 13.9 | 40.0 | 124.5 | 169.9 | 288.8 | 0.0 | 683.8 | Na-$HCO_3$ |
| RW8 | −42.8 | −5.2 | −0.8 | 167.0 | 24.6 | 13.9 | 40.0 | 125.5 | 171.2 | 297.2 | 0.0 | 690.9 | Na-$HCO_3$ |
| RW9 | −43.3 | −5.2 | −1.4 | 166.2 | 24.5 | 13.9 | 40.0 | 125.1 | 169.4 | 286.8 | 0.0 | 682.5 | Na-$HCO_3$ |
| RW10 | −42.6 | −5.0 | −2.3 | 166.4 | 24.7 | 14.0 | 40.0 | 122.5 | 169.2 | 321.6 | 0.0 | 697.4 | Na-$HCO_3$ |
| RW11 | −41.7 | −5.7 | 4.0 | 141.7 | 22.8 | 18.8 | 46.5 | 112.9 | 156.5 | 312.2 | 0.0 | 655.5 | Na-$HCO_3$ |
| RW12 | −43.0 | −5.3 | −0.5 | 141.8 | 22.7 | 18.7 | 46.5 | 110.7 | 155.9 | 306.6 | 0.0 | 649.7 | Na-$HCO_3$ |
| RW13 | −41.7 | −5.7 | 4.1 | 141.7 | 22.7 | 18.6 | 46.3 | 117.6 | 154.1 | 315.8 | 0.0 | 658.8 | Na-$HCO_3$ |
| RW14 | −43.5 | −5.2 | −2.0 | 142.6 | 23.0 | 18.7 | 46.3 | 110.9 | 156.4 | 287.0 | 0.0 | 641.4 | Na-$HCO_3$ |
| RW15 | −41.8 | −5.9 | 5.7 | 142.5 | 22.9 | 18.6 | 46.2 | 101.6 | 155.2 | 349.8 | 0.0 | 662.0 | Na-$HCO_3$ |
| SG1 | −44.5 | −6.7 | 9.3 | 121.4 | 20.6 | 88.1 | 35.2 | 76.3 | 179.9 | 349.6 | 0.0 | 696.3 | Na-$HCO_3$ |
| SG2 | −53.1 | −7.8 | 9.6 | 82.0 | 1.0 | 80.2 | 66.0 | 67.1 | 114.7 | 634.6 | 0.0 | 728.3 | Mg-$HCO_3$ |
| SG3 | −49.5 | −6.6 | 3.2 | 82.3 | 1.6 | 46.2 | 54.2 | 87.1 | 95.0 | 451.5 | 0.0 | 592.1 | Mg-$HCO_3$ |
| SG4 | −44.5 | −6.2 | 5.3 | 51.2 | 7.9 | 15.6 | 26.1 | 70.8 | 74.6 | 126.3 | 0.0 | 309.4 | Na-$HCO_3$ |
| SG5 | −53.4 | −7.5 | 6.2 | 64.0 | 3.0 | 36.8 | 31.4 | 60.9 | 26.7 | 386.6 | 0.0 | 416.1 | Na-$HCO_3$ |
| SG6 | −57.6 | −8.8 | 12.8 | 76.4 | 9.4 | 12.9 | 51.1 | 9.0 | 17.1 | 514.4 | 0.0 | 433.0 | Mg-$HCO_3$ |
| SG7 | −50.1 | −7.3 | 8.3 | 73.1 | 15.0 | 22.1 | 17.3 | 12.4 | 59.1 | 308.7 | 0.0 | 353.4 | Na-$HCO_3$ |
| SG8 | −49.8 | −8.3 | 16.3 | 70.8 | 0.9 | 32.1 | 58.3 | 28.0 | 34.3 | 564.4 | 0.0 | 506.6 | Mg-$HCO_3$ |
| SG9 | −55.1 | −8.4 | 12.0 | 96.2 | 2.2 | 2.2 | 34.8 | 19.4 | 8.1 | 290.4 | 34.2 | 342.4 | Na-$HCO_3$ |
| SG10 | −59.2 | −8.5 | 8.6 | 120.1 | 2.4 | 1.2 | 36.6 | 8.2 | 8.9 | 400.9 | 25.8 | 403.7 | Na-$HCO_3$ |
| SG11 | −57.8 | −8.6 | 11.2 | 127.6 | 2.9 | 4.0 | 35.1 | 8.8 | 38.8 | 421.0 | 18.0 | 445.6 | Na-$HCO_3$ |
| SG12 | −57.4 | −8.0 | 6.5 | 86.9 | 2.0 | 0.7 | 27.9 | 9.0 | 11.5 | 233.7 | 64.2 | 318.9 | Na-$HCO_3$ |
| DG1 | −53.7 | −8.2 | 11.7 | 86.6 | 4.8 | 4.8 | 19.7 | 29.4 | 5.8 | 167.8 | 58.5 | 293.5 | Na-$HCO_3$ |
| DG2 | −55.6 | −7.3 | 2.5 | 157.6 | 2.9 | 4.0 | 32.7 | 28.6 | 16.0 | 402.7 | 46.0 | 489.2 | Na-$HCO_3$ |
| DG3 | −51.4 | −7.4 | 7.8 | 110.9 | 1.9 | 10.0 | 43.0 | 16.1 | 15.7 | 543.1 | 0.0 | 469.1 | Na-$HCO_3$ |
| DG4 | −52.7 | −7.0 | 3.6 | 149.4 | 1.4 | 6.5 | 36.8 | 20.9 | 14.2 | 553.2 | 38.0 | 543.9 | Na-$HCO_3$ |
| DG5 | −49.0 | −7.0 | 7.0 | 95.0 | 2.1 | 2.5 | 17.5 | 23.7 | 25.5 | 238.4 | 46.1 | 331.5 | Na-$HCO_3$ |
| DG6 | −60.3 | −8.4 | 7.2 | 149.5 | 2.0 | 22.5 | 28.9 | 57.2 | 14.0 | 528.8 | 0.0 | 538.5 | Na-$HCO_3$ |
| DG7 | −57.4 | −8.1 | 7.8 | 85.9 | 2.9 | 10.1 | 28.9 | 18.1 | 13.5 | 375.3 | 0.0 | 347.0 | Na-$HCO_3$ |
| DG8 | −56.4 | −8.1 | 8.1 | 127.7 | 1.4 | 27.3 | 47.2 | 37.1 | 68.8 | 543.1 | 0.0 | 581.2 | Na-$HCO_3$ |
| DG9 | −62.7 | −8.9 | 8.4 | 41.4 | 2.3 | 7.2 | 30.4 | 10.9 | 10.3 | 244.1 | 25.5 | 250.1 | Mg-$HCO_3$ |
| DG10 | −54.7 | −7.7 | 7.0 | 75.4 | 1.5 | 4.7 | 42.5 | 23.9 | 13.2 | 366.1 | 0.0 | 344.3 | Mg-$HCO_3$ |

Note: RW, SG, and DG represent river water, shallow groundwater, and deep groundwater, respectively.

(LMWL) can be used to reflect precipitation patterns in different areas. In recent decades, many scholars have carried out a large number of studies on the replenishment and migration mechanism of water-based GMWL and LMWL, which provided theoretical guidance for the evaluation and management of water resources [7,30,31].

In this study, because of the lack of the LMWL of Suzhou, the national meteoric water line of China (NMWL, $\delta^2H = 7.9 \times \delta^{18}O + 8.2$, $n = 101$, $r^2 = 0.977$) [32] has been chosen as the LMWL. The relationship between $\delta^2H$ and $\delta^{18}O$ of river water and groundwater with GMWL and NMWL is summarized in Figure 4. As can be seen from the figure, all of the SG and DG samples are plotted near the GMWL and NMWL, which indicates that the precipitation is the main source of the shallow and deep groundwater. Comparatively, the RW samples were deviated from the GMWL and NMWL significantly, implying that the river water has been significantly influenced by evaporation [7,31,32].

The deuterium excess (d-excess = $\delta^2H - 8 \times \delta^{18}O$, unit: ‰) proposed by Dansgaard can be used to quantify the degree of difference between atmospheric precipitation isotopes in local areas and hydrogen and oxygen stable isotopic fractionation of global atmospheric precipitation [29].

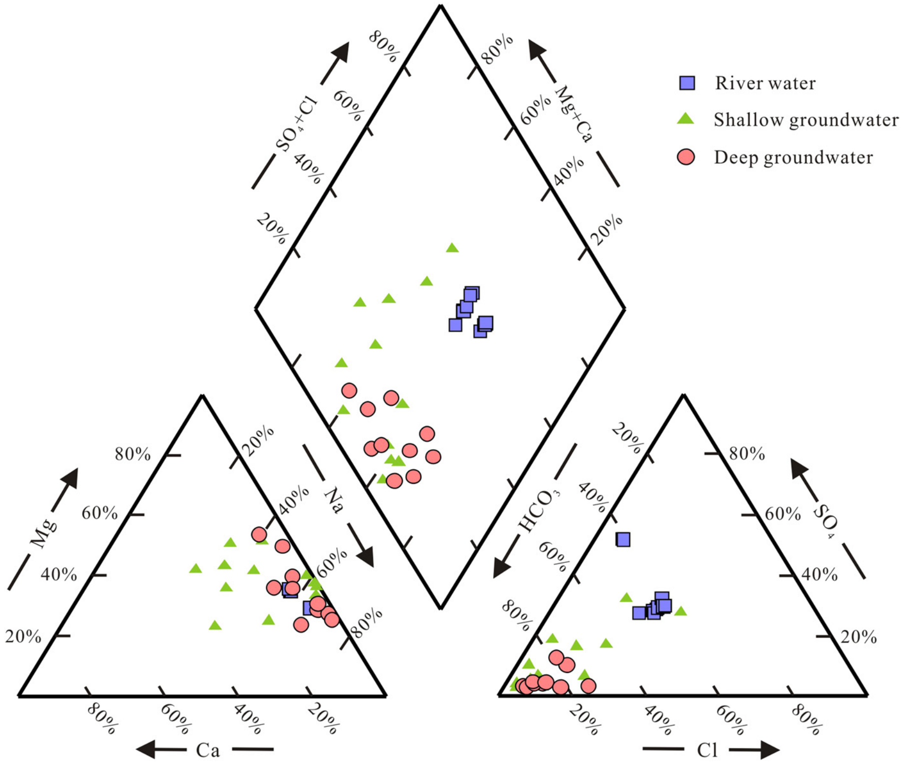

**Figure 2:** Piper diagram.

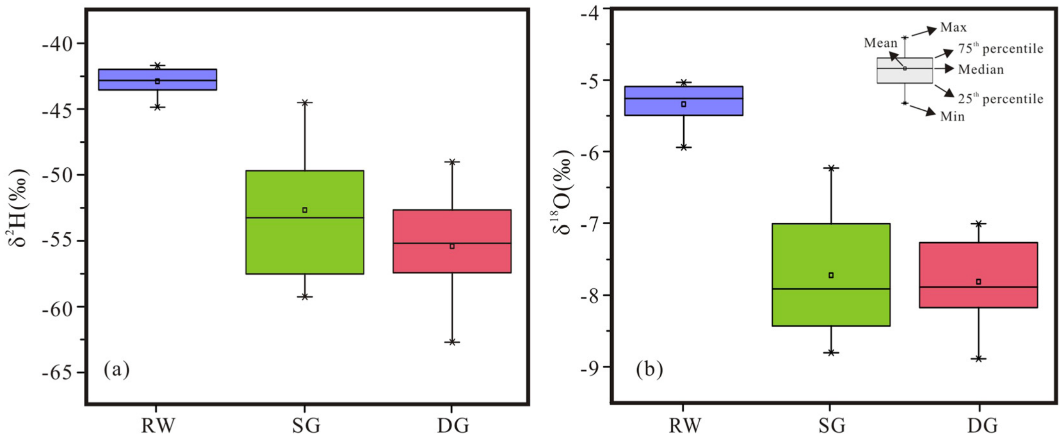

**Figure 3:** Box plot of δ$^2$H and δ$^{18}$O in different water bodies. RW, SG, and DG represent river water, shallow groundwater, and deep groundwater, respectively.

Moreover, several studies have found that evaporation and water rock interaction can increase the δ$^{18}$O in the water, then leading to the decrease of d-excess [33,34]. In this study, the d-excess of RW samples ranges from −4.5 to 5.7‰ (mean = −0.2‰), which is lower than the d-excess value of atmospheric precipitation (Table 1 and Figure 5), and therefore, the river water might have been affected by evaporation. The d-excess of SG and DG samples ranged from −3.2 to 16.3‰ (mean = 9.1‰) and 2.5 to 11.7‰ (mean = 7.1‰), respectively (Table 1 and Figure 8), which confirmed that most of the groundwater samples have not been affected by evaporation, but few ones (SG3, SG8, DG2, and DG4) have been affected by evaporation before infiltration.

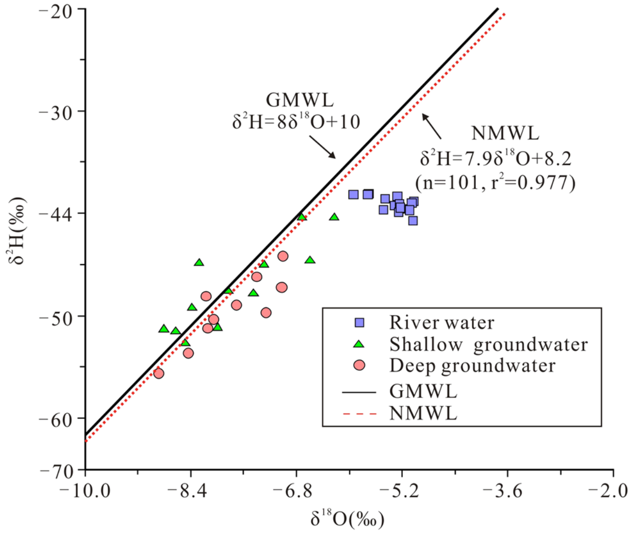

**Figure 4:** The relationship between $\delta^2H$ and $\delta^{18}O$ of river water, shallow groundwater, and deep groundwater, respectively. GWML and NWML represent the global meteoric water line and the national meteoric water line (China), respectively.

## 4.2 The connections between different water bodies

Previous studies have shown that hydrochemistry was a useful tool for identification of the interactions between different water bodies, especially the major ions and stable H–O isotope [4,5,16–19]. As mentioned above, the concentrations of most ions in river water are obviously higher than those in groundwater (such as $Na^+$, $K^+$, $Mg^{2+}$, $Cl^-$, and $SO_4^{2-}$), whereas the shallow and deep groundwater show similar chemical concentrations. Such results rejected the connection between river water and groundwater, but supported the link between shallow groundwater and deep groundwater. Such a consideration can also be supported by the differences of H–O isotopes in river water and groundwater, but similar H–O isotopes of shallow and deep groundwater.

For getting more information about the relationships between the three water bodies, cluster analyses (including k-means and Q-type clustering) have been applied and the results are shown in Figures 6–8. As can be seen from Figure 6, when the number of clusters is set to be 3, the value of average silhouette width gets the peak value, hence *k* = 3 was selected in this study. Then the samples are divided into three categories around the cluster centers (Figure 7): the first category includes 16 water samples (all of the RW samples and one SG sample), the second category possesses 8 water samples (SG and DG samples account for half, respectively), and the third category has 13 water samples (6 and 7 are the SG and DG samples,

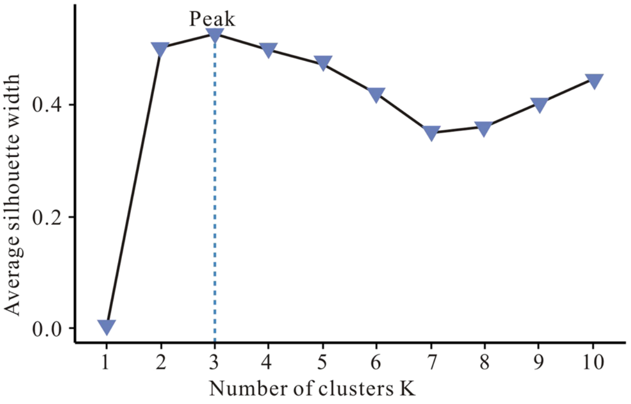

**Figure 6:** Plot of the best choice for the number of cluster centers. The peak value represents that the number of corresponding cluster centers is the best.

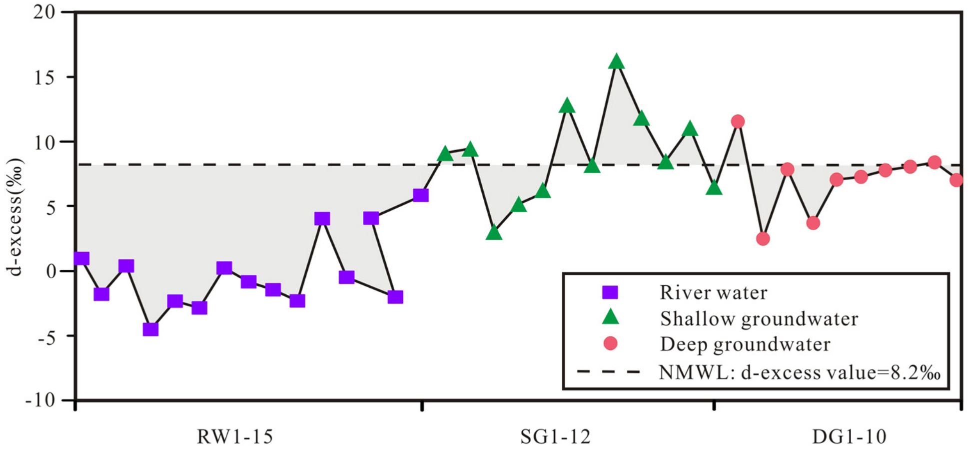

**Figure 5:** d-excess in different water bodies.

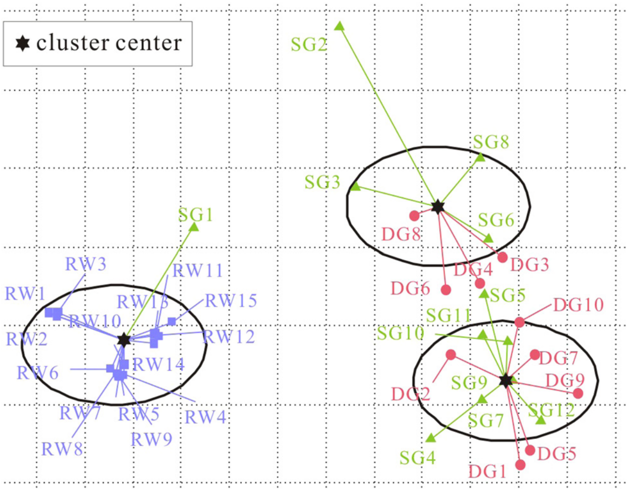

**Figure 7:** Plot of K-mean cluster. RW, SG, and DG represent river water, shallow groundwater, and deep groundwater, respectively.

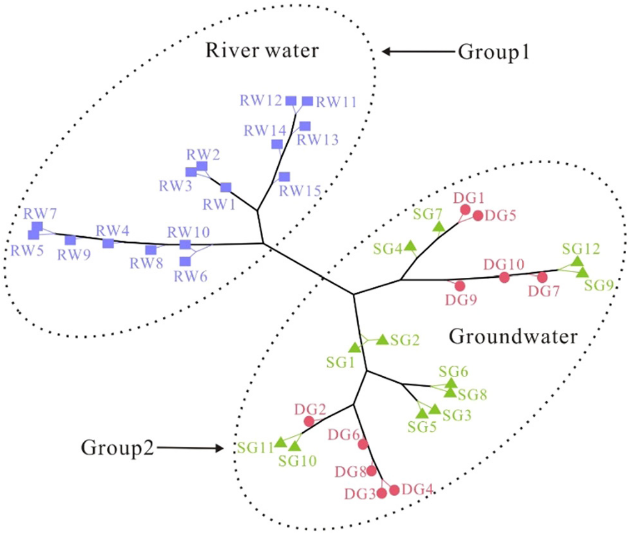

**Figure 8:** Plot of Q-type cluster. RW, SG, and DG represent river water, shallow groundwater, and deep groundwater, respectively.

respectively). Consequently, groundwater and river water can be clearly distinguished (except for SG1). However, it is hard to distinguish SG and DG samples. A similar conclusion can also be achieved by the Q-type cluster analysis, as all of the samples are divided into two main groups (Group 1 and Group 2): Group 1 represents the RW samples, while both the SG and DG samples are contained in Group 2.

The above analyses show that there is no close relationship between river water and groundwater, but the similarity of SG1 and river water should be paid attention to. Moreover, the similarity of groundwater hydrochemistry between shallow and deep groundwater must be noticed, because this might be an indication of the hydro-connection between these two aquifers. Although the main source of water supply in Suzhou is deep groundwater, but if there is connection between the shallow and deep aquifers, the environmental condition of the shallow aquifer should be considered seriously because it is easier to be influenced by human activities.

## 5 Conclusions

Based on the analyses of major ion concentrations and stable H–O isotopes of the river water and groundwater in Suzhou, northern Anhui Province, China, the following conclusions have been made:

(1) In groundwater and surface water, $Na^+$ and $HCO_3^-$ were the dominant cation and anion, respectively, and most of the water samples are classified to be Na-$HCO_3$ type, to a lesser extent, Mg-$HCO_3$ type.

(2) The relationship between $\delta^2H$ and $\delta^{18}O$ has shown that precipitation was the main source of the groundwater in this region. However, in recent years, with the rapid development of urbanization, the asphaltization of the ground has severely restricted the recharge of groundwater, further deepening the contradiction between supply and demand of water resources in Suzhou, which should be paid more attention to.

(3) The values of d-excess in different water bodies suggested that the groundwater has not been affected by evaporation, which was the main process controlling the isotopic composition of river water.

(4) K-mean and Q-type clustering analyses ruled out the hydrological relationship between river and groundwater, but there was a significant connectivity between shallow and deep groundwater. Although deep groundwater is the main source of water supply in Suzhou, the environmental condition of the shallow aquifer should be considered seriously because it is easier to be influenced by human activities.

**Acknowledgments:** This research was supported by the Innovation fund of Anhui University of Science & Technology (2019CX2004) and the Academic Funding for Top-talents in Disciplines of Universities in Anhui Province (gxbjZD48). We sincerely thank the editors and reviewers for their valuable comments that greatly improved this paper.

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