Q1: The introduction should be rewritten, and a brief introduction of the work whether has been done or not should be written thus highlighting the necessity and importance of this work.

A1: The introduction part has been rewritten, and key sentences have been added to address the importance and specific objectives of this project, which could be referred to lines 63-70.

Q2: References are mostly Chinese literatures, it is recommended to add some English literatures.

A2: Although most references in this paper are written by Chinese, the majority are published in top journals using English. Only two of them are in Chinese and have been labeled in the reference section. Also, we added several related literatures written by other countries' scholars to give a broader context of this topic.

Q3: It is suggested to modify the references format.

A3: The format of reference has been modified.

Q4: It is suggested to add the study area's location on the map of China in figure 1.

A4: We have demonstrated the location of Weihe river in the text. What we showed in Fig. 1 is the specific location of the study area in Weihe River basin, and the distribution of sampled sections, which are considered as more essential information.

Q5: TH in Table 1 is not described in the text, which can be deleted.

A5: Revised. The column of TH has been deleted.

Q6: The translation of name in figure 4 should be confirmed, which are Evaporation-crystallization dominance, Rock weathering dominance, Atmospheric precipitation dominance.

A6: The captain of Fig 4 has been revised.

Research on Hydrogeochemical Characteristics and Transformation Relationships between Surface Water and Groundwater in the Weihe River

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Abstract: The transforming relationship between surface water and groundwater as well as their origins are the basis for studying the transport of pollutants in river-groundwater systems. ~~A t~~Typical sections of the river were~~was~~ chosen to sample the surface water and shallow groundwater. Then, a Piper trilinear diagram, Gibbs diagram, ratios of major ions, factor analysis, cluster analysis and other methods were ~~used~~ applied to investigate the hydrogeochemical evolution of surface water and groundwater and determine the formation of hydrogeochemical components in different water bodies. Based on the distribution characteristics of hydrogen and oxygen stable isotopes δD and $\delta^{18}O$ and discharge hydrograph separation methods, the relationship between surface water and groundwater in the Weihe River was analyzed. The results ~~indicated~~ reveal that the river water is a SO_4 Cl—Na type and ~~that~~ the groundwater hydrogeochemical types are not the same. The dominant anions are HCO_3^- in the upstream reaches and ~~are~~ SO_4^{2-} and Cl^- in downstream reaches. Hydrogeochemical processes include evaporation and concentration, weathering of rocks, ion exchange, and dissolution infiltration reactions. The δD and $\delta^{18}O$ of surface water change little along the river and are more enriched than are those of the groundwater. With the influences of precipitation, irrigation, river recharge and evaporation, the δD and $\delta^{18}O$ of shallow groundwater at different sections are not the same. It could be established that surface water recharges groundwater at 5 sections along the Weihe River, and each section has unique recharge intensity and relationship due to its specific hydraulic environment. ~~There is a close relationship between the surface water and groundwater.~~ Surface water supplies the groundwater, which provides the hydrodynamic conditions for the entry of pollutants into the aquifer.

Keywords: hydrogeochemical characteristics; hydrogen and oxygen stable isotopes; surface water-groundwater system; cycle and transformation

1. Introduction

The regularity of the water cycle and the conversion between surface water and groundwater is the basis for the study of pollutant transport in river-groundwater systems (Lu et al., 2016a; Shang et al., 2017). Different water bodies have specific ~~different~~ hydrogeochemical characteristics and isotopic signatures ~~because of~~due to ~~their~~ different ~~sources of~~ recharge sources, environments and circulation conditions. Hence, hydrogeochemical characteristics are ~~the ideal tracers~~used for displaying~~tracking~~ water circulation processes and~~.~~ a~~A~~nalysi~~e~~s of hydrogeochemical and isotopic characteristics~~ of rivers and groundwater~~ can effectively reveal the ~~relationship in the~~ transformation of river water to groundwater (Kanduč et al., 2014). An integration of the hydrogeological and isotopic data could be more reliable and meaningful (Matiatos et al., 2014).

A series of mathematical methods are employed and combined to process the measured data. Descriptive statistics, graphic analysis and multivariate statistical analysis methods are used to determine~~analyze~~ the hydrogeochemical characteristics (Lu et al., 2015). ~~Graphic methods include the~~ Durov diagram (1948), Stiff diagram (1951), Piper diagram (1944) and Gibbs diagram (1970) belong to graphical methods (Rekha et al., 2013). Common multivariate statistical analysis methods include factor analysis (Keesari et al., 2016), principal component analysis (Chattopadhyay and Singh, 2103) and cluster analysis (Zhang et al., 2012). Stable isotopes of δD and δ^{18}O are considered as ideal tracers for tracking various hydrogeochemical processes (Liu et al., 2014). The surface-ground water transformation mechanism is a worldwide topic, about which researches were conducted on many regions via the above methods. Dogramaci et al. (2012) investigated~~studied~~ the hydrogeochemical and isotopic characteristics of the Hamersley Basin in northwestern Australia and provided a theoretical basis for the sustainable development of local water resource utilization. A series of methods, such as t~~T~~he descriptive statistical method, the Piper diagram and the main ion component proportion coefficient and the factor analysis method, were employed~~used~~ to study hydrogeochemical characteristics of groundwater in the Sara Wusu aquifer system in the Ordos Basin (Yang et al., 2016). Fuzzy mathematics and multivariate statistical methods were used to study the quality characteristics of surface water and groundwater in the Songnen plain (Zhang et al., 2012). Zeng et al. (2013) investigated~~studied~~ the spatial distribution of hydrogeochemical and isotopic characteristics of different water bodies in Tajikistan, including spring water, river water and lake water~~, in different parts of Tajikistan~~ and discussed their origins and environmental significance. ~~Although there are many studies related to the chemical and isotopic characteristics of groundwater and surface water, the relationship between surface water and groundwater transformation is still a prevalent topic in hydrology and water resource studies (Wang et al., 2016; Lu et al., 2016b), hydrogeochemistry, biogeochemistry, and ecohydrology.~~ Hydrogen and oxygen stable isotopes (δ^{18}O and δD) and electrical conductivity (EC) as typical parameters were adopted~~ used~~ to represent~~study~~ the mutual relationship among precipitation, river water and groundwater in Taiwan Douliushan (Peng et al., 2014). Meanwhile, ~~M~~multivariate statistical analysis ~~methods~~ and isotopic~~e~~ analysis methods were used to study the hydraulic linkage between surface water and ~~ground water~~groundwater and their temporal and spatial variations in the Condamine River in Australia (Martinez et al., 2015). Hydrogen and oxygen isotopes were used to study the relationship of recharge and discharge between the various water bodies on the Portuguese island of Madeira, from which a hydrogeological conceptual model of Madeira Island was established (Prada et al., 2016). By analyzing the hydrogeochemical characteristics of surface water and groundwater in the Heihe River Basin, Nie et al. (2005) identified the transformation relationship between groundwater and surface water in the main stream of Heihe River. ~~Hydrogen and oxygen isotopes and water chemistry were used to investigate the relationship between surface water and groundwater of the Second Songhua River, and t~~Except for the common relationship determination, ~~he end element method was used to quantitatively calculate~~ a conversion proportion between surface water and groundwater of the Second Songhua River was also calculated quantitatively through the end element method (Zhang et al, 2014). Although many studies related to the chemical and isotopic characteristics of groundwater and surface water have been conducted recently, the relationship between surface water and groundwater transformation is still a prevalent and essential topic in hydrology and water resource studies, hydrogeochemistry, biogeochemistry, and ecohydrology (Wang et al., 2016; Lu et al., 2016b).

The surface water of Weihe River in this paper is seriously polluted and has become a major pollution source for nearby shallow groundwater. This seriously affects the exploitation, utilization and protection of groundwater resources and endangers the ecological safety and the health of the residents (Lu et al., 2016c). This present study has three main objectives as follows: (1) To investigate the hydrogeochemical components formation of surface water and groundwater through the samples taken from~~The surface water and groundwater were sampled in~~ several typical sections of the Weihe River Basin; (2) To ~~to study~~determine the recharge~~conversion~~ relationship between surface water and groundwater based on the hydrogeochemical and isotopic characteristics; (3)~~and~~ T~~t~~o provide ~~a~~the systematic~~–~~ methods for hydrogeochemical analysis including Piper trilinear diagram, Gibbs diagram, factor analysis and cluster analysis.~~basis for groundwater protection, restoration and management.~~

2. Materials and methods

2.1 Study area

The Weihe River Basin~~, which is~~ with the length of 344.5 km ~~long~~ and ~~has~~ a basin area of 14970 km^2, is located in the northern part of the Henan Province, south of the North China Plain. It is the main tributary to the Zhangweinan Canal, which is ~~a~~ tributary to the Haihe River. The Weihe River Basin has a typical warm, temperate, continental monsoon climate. It is cold and dry~~, with minor rain~~ in the winter~~,~~ hot and rainy in the summer, and the average annual precipitation in the basin is 608 mm (Zhu et al., 2006). The influence of river pollutants on groundwater is mainly banded and has a relatively small range~~area of influence~~. Considering the shallow groundwater along both sides of the river, a~~A~~ 26.67-km-long segment of the Weihe River between Xizhangzhuang village of Xiaohe Town and Dongwangqiao village of Liyang Town~~, considering the shallow groundwater along both sides of the river,~~ was selected as the study area~~. This is an area~~ of approximately 160 km^2 (as shown in Fig. 1). The Weihe River Basin is closely related to groundwater, and the polluted river water of the Weihe River is a pollution source of groundwater on both sides of the river. The groundwater is mainly supplied by atmospheric precipitation, lateral seepage, piedmont lateral runoff and canal leakage, and drainage is dominated by artificial extraction and evaporation. Groundwater flows from the southwest to the northeast, which is generally consistent with the topography. The average hydraulic gradient is 1/3000.

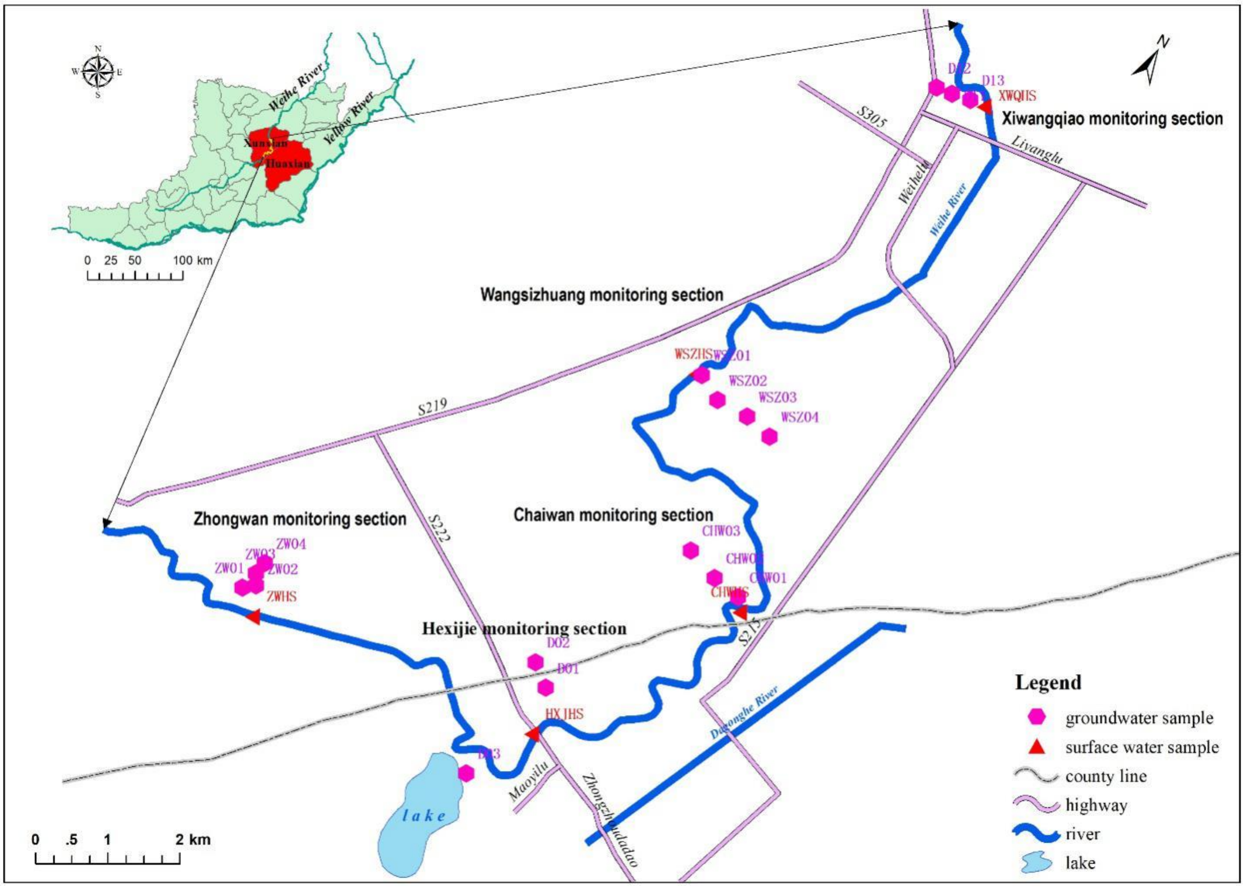


Fig. 1 The location of the study area and the distribution of sampling~~ed~~ sections

2.2 Sample collection

~~According to the goals of the study, t~~The surface water sampling sites were chosen parallel to the direction of river flow, ~~and~~ while the groundwater sampling sites were ~~chosen~~ perpendicular to the river flow. There were 5 sections sampled from upstream to downstream between Xiaohe Town and Liyang Town along the Weihe River (i.e., the Zongwan sample section, Hexijie sample section, Chaiwan sample section, Wangsizhuang sample section and Xiwangqiao sample section). A total of 5 surface water samples and 17 groundwater samples were collected in May 2016. Among them, ZWHS, HXJHS, CHWHS, WSZHS and XWQHS were surface water sampling sites, and the others were groundwater sampling sites. ~~The samples were collected in May 2016.~~ The sampling sites encompassed the band of influence of pollutants from the Weihe River on groundwater. The locations and types of the sampling sites ~~and the types of water samples~~ are shown in Figure 1.

Groundwater was sampled mainly from irrigation wells and drinking wells. Prior to sampling, wells ~~were~~ should be pumped for more than 20 min until the temperature, electrical conductivity (EC), and pH ~~were~~ become stable. Surface water samples were collected from the river bank at a depth of more than 50 cm and kept~~. Samples were collected~~ in 500 ml polyethylene bottles, which were ~~cleaned~~ washed with sample water at least three times ~~prior to~~before ~~sampling~~. ~~When~~ After sampling work having been finished~~each sample was collected~~, it should be confirmed that no bubbles were left in the bottle, and the outer cap was sealed with sealant to prevent air exchange. Samples were ~~brought back to the laboratory and~~ stored in a refrigerated container at 0 to 4 ℃.

2.3 Stable hydrogen and oxygen isotopes and hydrogeochemical analysis

Hydrogen and oxygen isotopes were measured in the laboratory of groundwater science and engineering of the Ministry of Land and Resources of the Institute of Hydrogeology and Environmental Geology at the Chinese Academy of Geological Sciences. Analysies were conducted using wavelength scanning-optical cavity ring down spectroscopy. The ratio of hydrogen and oxygen isotopes (δ) is expressed as the deviation relative to Vienna VSMOW (Zhao, et al, 2015):

$$\delta(‰) = \frac{R_{sp} - R_{st}}{R_{st}} \times 1000 \tag{1}$$

where R_{sp} and R_{st} refer to the ratio of D/H (or $^{18}O/^{16}O$) in samples and VSMOW, respectively. When δD and $\delta^{18}O$ are positive, the samples are enriched with D and ^{18}O compared to the VSMOW standard; when they are negative, the two isotopes are diluted compared to the VSMOW standard (Zhang et al., 2006).

Analysies of water chemical~~stry~~ components was~~ere~~ conducted ~~completed~~ in the laboratory of hydrogeology at the North China University of Water Resources and Electric Power, ~~. The analyses~~ including~~ed~~ Cl^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Mg^{2+}, HCO_3^-, CO_3^{2-} and Ca^{2+}. Among these ions, HCO_3^- and CO_3^- were detected using acid-base indicator titration, Ca^{2+} and Mg^{2+} were tested via ~~detected using~~ EDTA titration, and the other ions were through ~~detected using~~ ion chromatography. ~~pH~~PH, total dissolved solids (TDS), rugged dissolved oxygen (RDO), conductivity, redox potential and other indicators were detected *in situ* with a PX.68-smarTROLL MP hand-held multi-parameter water quality detector.

2.4 Conversion ratio of surface water to ~~ground water~~groundwater

The stable hydrogen and oxygen isotope method can determine the sources of runoff, the division of river runoff and the conversion of surface water and groundwater. The principle of division is based on the law of mass conservation of isotopes (Song et al., 2007), in which the sum of two runoff components is equal to the total flow ~~of the resultant runoff~~, and the sum of ~~the tracer flow of~~ the two tracer ~~runoff~~ components ~~is~~ equals to the sum of the tracer of synthetic runoff (Fig~~ure~~. 2). The ~~calculations~~ basic equations are as follows:

$$Q_t = Q_u + Q_v \tag{2}$$

$$Q_t \cdot C_t = Q_u \cdot C_u + Q_v \cdot C_v \tag{3}$$

$$f = \frac{Q_v}{Q_t} = \frac{C_t - C_u}{C_v - C_u} \tag{4}$$

where Q is the flux, C is the isotope– concentration~~component~~, t and u ~~are~~ – indicate surface water, and v represents~~is~~ –groundwater. f is the ratio of surface ~~river~~ water to ~~ground water~~groundwater and is calculated with δD as a standard.

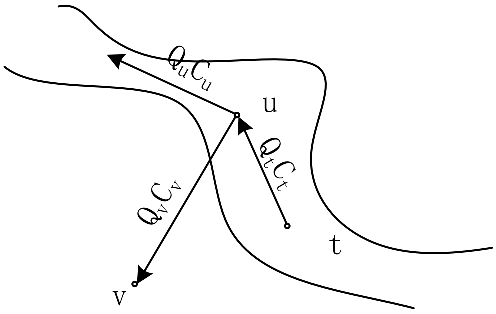


Fig. 2 Principle diagram of the discharge hydrograph separation methods

3. Results and discussion

3.1 Characteristics of main hydrogeochemical components

The water composition results are shown in Table 1. The groundwater pH ~~in the study~~of the sampling area was ~~near~~ close to neutral, ranging from 6.83 to 7.81. The TDS ~~ranged from~~values were between 564.66 and~~to~~ 1747.84 mg/L, ~~and the TDS of~~ all 17 groundwater samples of which exceeded the World Health Organization (WHO) drinking water ~~standard~~ threshold of 500 mg/L. As illustrated in Table 1,~~The relationship between~~ the average concentrations of groundwater anions were~~as~~ sorted as $HCO_3^->SO_4^{2-}>Cl^-$. ~~The concentration of HCO_3^- ranged from 461.75 mg/L to 735.15 mg/L, with an average concentration of 635.88 mg/L. The concentration of SO_4^{2-} ranged from 116.11 mg/L to 833.33 mg/L, with an average concentration of 307.52 mg/L. The concentration of Cl^- ranged from 102.17 mg/L to 640.13 mg/L, with an average concentration of 275.24 mg/L.~~ The relationship of the average concentrations of the cations was $Na^+> Ca^{2+}> Mg^{2+}>K^+$. Na^+ and Ca^{2+} were dominant, and their concentrations ranged from 74.21 mg/L to 272.00 mg/L and 64 mg/L to 268.80 mg/L, respectively, with average values of 182.78 mg/L and 121.69 mg/L.

The pH of the Weihe River in the study area ranged from 8.03 to 8.22, which ~~and~~ was ~~therefore~~ weakly alkaline. The TDS ~~ranged from 1401.32 to 1518.71 mg/L~~with an average value of 1473.74~~, which~~ is generally higher than that of groundwater. The sorting results of ~~relationships between~~ the concentrations of anions and cations in surface water were $SO_4^{2-}> Cl^-> HCO_3^-$ and $Na^+> Ca^{2+}> Mg^{2+}>K^+$, respectively. The concentration of SO_4^{2-} in the river water ranged from 627.07 mg/L to 664.06 mg/L, with an average value of 647.12 mg/L. The concentration of Cl^- ranged from 325.95 mg/L to 391.57 mg/L, with an average concentration of 365.89 mg/L. The concentrations of Na^+ and Ca^{2+} ranged from 294.47 mg/L to 314.27 mg/L and 94.40 mg/L to 115.20 mg/L, respectively, and their mean values were 305.58 mg/L and 107.52 mg/L. As seen in Table 1, there is no significant change in the ion concentration between the upstream and downstream parts of the Weihe River.

According to WHO ~~standard of~~ drinking water standards, except for K^+ and pH, the other measured components of surface water and groundwater all exceeded the maximum acceptable values in the study area. ~~As such~~Under such conditions, both surface water and groundwater along the Weihe River could not be considered as ~~are not~~ suitable drinking water sources.

Table 1 Analytical results of water quality in the study area

Ion content/（mg.L^{-1}）		pH	TDS	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
Groundwater (17)	Minimum	6.73	564.66	74.21	6.20	57.76	64.00	102.17	116.11	461.75
	Maximum	7.81	1747.84	272.00	34.26	162.38	268.80	640.13	833.33	735.15
	Average	7.30	1170.00	182.78	16.58	110.23	121.69	275.24	307.52	635.88

Surface water (5)	Minimum	8.03	1401.32	294.47	24.23	49.90	94.40	325.95	627.07	282.52
	Maximum	8.22	1518.71	314.27	28.35	59.54	115.20	391.57	664.06	385.80
	Average	8.11	1473.74	305.58	26.40	53.79	107.52	365.89	647.12	350.56
WHO drinking water standards		6.5～8.5	500	200	100	30	75	200	200	200
Over-standard rate of groundwater (%)		0	100	47	0	100	70	70	65	100
Over-standard rate of surface water (%)		0	100	100	0	100	100	100	100	100

3.2 Hydrogeochemical characteristics

The Piper diagram is widely ~~one of the most commonly used~~applied as graphical method~~s~~ for settling ~~interpreting~~ hydro-geological problems. According to the analytical results, the Piper diagram of the hydrogeochemical compositions of all water samples in the study area is shown in Fig. 3. The results illustrate~~indicate~~ that the chemical type of surface water ~~in the study area~~ is ~~the~~ SO_4·Cl—Na~~ type~~, indicating that the surface water is uniform across the study ~~area~~region. From upstream to downstream along the Weihe River, the water ~~chemistry~~ chemical type of each groundwater section is as follows: The Zong Wan section and Hexijie section are mainly HCO_3--Mg·Na types, the Chaiwan section is mainly the SO_4·Cl—Mg·Na type, the Wangsizhuang section is mainly the HCO_3·SO_4·Cl--Mg·Na type, and the Xiwangqiao section is mainly the HCO_3·Cl—Mg·Ca·Na type. From the recharge area to the discharge area,~~Usually,~~ the chemical types of groundwater usually~~,~~ ~~from the recharge area to the discharge area,~~ change in the following ways: HCO_3^- —SO_4^{2-} —Cl^-. ~~Considering~~ Based on the results of groundwater chemical types~~ of groundwater of each section~~, it could be concluded that HCO_3^- is dominant in groundwater on both sides of river in the upstream section, whereas SO_4^{2-} and Cl^- are dominant in the middle and lower reaches. The ~~type of water chemistry~~water chemical types can indirectly verify that the groundwater flow on both sides of river.

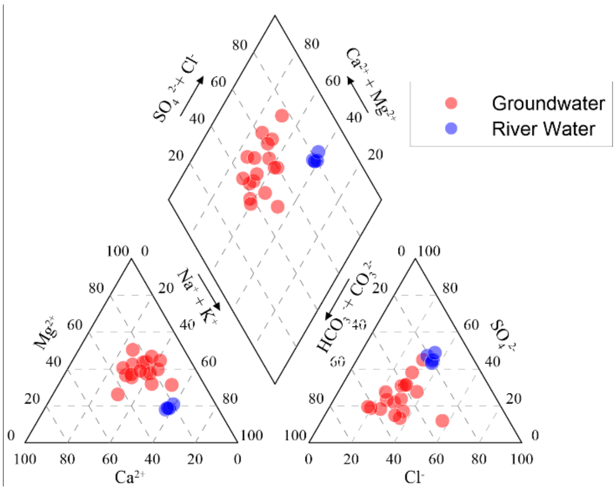


Fig. 3 Piper diagram of water chemical components~~stry~~ for surface and groundwater in the study area

3.3 Analysis of formation function of water chemical compositions

3.3.1 Analysis of formation function based on the Gibbs diagram

The Gibbs diagram can clearly indicate whether the chemical components of river and groundwater are the precipitation dominance type, rock dominance type or evaporation crystallization dominance type. It is an efficient ~~important~~ way to qualitatively determine the effects of regional rocks, atmospheric precipitation, and evaporation concentration on river water components (Wang et al., 2010). Generally, samples with low TDS and high $Na^+/(Na^++Ca^{2+})$ or $Cl^-/(Cl^-+HCO_3^-)$ ratios (close to 1),~~ are~~ mainly distributed in the lower-right corner, ~~indicating~~ indicate precipitation dominance. Samples with slightly high TDS and $Na^+/(Na^++Ca^{2+})$ or $Cl^-/(Cl^-+HCO_3^-)$ ratios of approximately 0.5 or less than 0.5~~ are~~, mainly distributed in the middle zone, ~~indicating~~ indicate rock dominance. Samples with very high TDS and large $Na^+/(Na^++Ca^{2+})$ or $Cl^-/(Cl^-+HCO_3^-)$ ratios,~~ are~~ mainly distributed in the upper-right corner, indicate~~ing~~ evaporation crystallization dominance type, reflecting the influence of evaporation on~~in~~ arid areas (Sun et al., 2014).

The ion concentrations of the 5 river surface ~~ground~~water samples and 17 groundwater samples from the study area are shown on a Gibbs diagram in Fig. 4. Apparently, ~~It is apparent that~~ the surface water samples~~ in the study area~~ are~~is~~ distributed~~located~~ the upper-right corner of the diagram with a $Na^+/(Na^++Ca^{2+})$ or $Cl^-/(Cl^-+HCO_3^-)$ ratio greater than 0.5 and~~ with~~ a high content of TDS, which means~~indicating~~ that surface water has an evaporation crystallization dominance origin. The groundwater samples differing in the two criterions ~~figures but~~ are mainly distributed in the evaporation crystallization dominance region, slightly towards to the rock dominance region, indicating that the chemical composition of water is both controlled by evaporation crystallization and rock weathering.

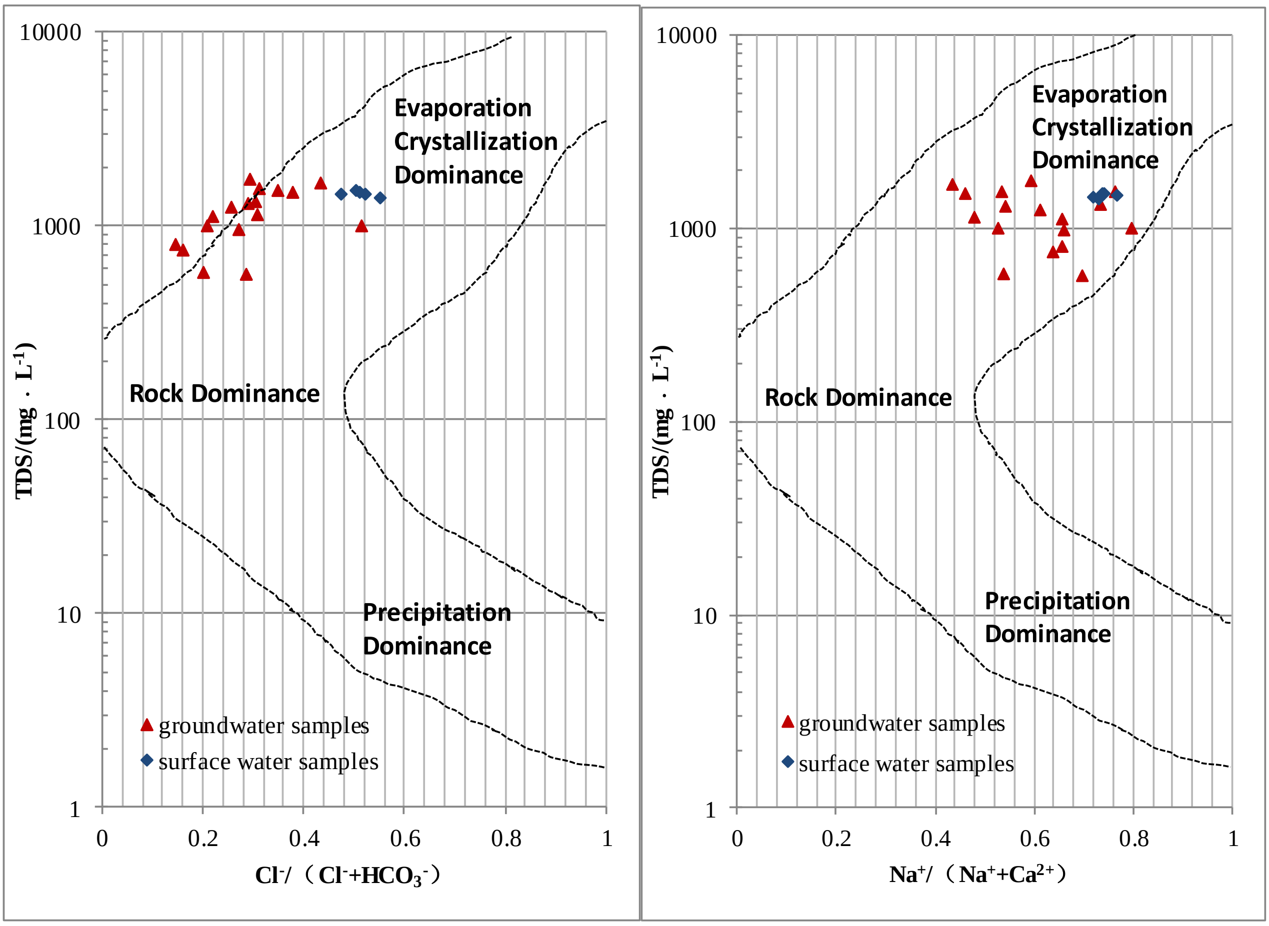


Fig. 4 Gibbs plots of the ~~surface~~ river and groundwater chemistry in the study area, confirming the type of evaporation-crystallization dominance, rock weathering dominance and precipitation dominance.

3.3.3 Analysis of formation function based on multivariate statistics

To further analyze the hydrogeochemical formation functions, factor analysis and R cluster analysis were conducted~~performed~~ on surface and ground water~~water~~ samples using TDS, Cl$^-$, SO$_4^{2-}$, HCO$_3^-$, Na$^+$, K$^+$, Ca^{2+}, and Mg^{2+} as the original parameters. ~~Seventeen groups of groundwater samples and 5 groups of surface water samples were calculated. After the calculation, t~~The initial KMO value of the groundwater samples was 0.596. According to the KMO test standard, ~~when 0.5<KMO<0.6,~~ the original variable is barely suitable for factor analysis when 0.5<KMO<0.6. According to the ~~calculation~~ results shown in ~~(~~Table 2~~)~~, the formation function of the groundwater chemical compositions ~~can~~could be summarized in 3 factors, and the cumulative contribution rate of ~~the~~ all 3 factors is 75%. The Ca^{2+}, Cl$^-$, SO$_4^{2-}$ and TDS of factor 1 have higher positive loads and the coefficient of Ca^{2+} and SO$_4^{2-}$ is large, indicating that there may be weathering of calcium feldspar, dissolution of gypsum, or oxidation of pyrite. A large coefficient of Cl$^-$ ~~indicates~~ suggests that there may be leaching of halite. The Na$^+$, Mg^{2+} and HCO$_3^-$ of factor 2 have higher positive loads, which indicates possible weathering of carbonate or silicate. The alternating adsorption of cations between Na$^+$ and Ca^{2+} causes the content of Na$^+$ to increase. The K$^+$ content of factor 3 is large, which indicates~~ possible~~ weathering of feldspar. Meanwhile, s~~S~~urface water samples can be summarized in 2 factors with~~, and~~ the contribution rate of~~ the 2 factors is~~ 91%. The K$^+$, HCO$_3^-$ and TDS of factor 1 have higher positive loads, indicating the possible weathering of carbonate and feldspar. The Mg^{2+}, Na$^+$ and Cl$^-$ of factor 2 have ~~a~~ higher positive loads, which indicates the possible dissolution of halite and the alternate adsorption of cations between Na$^+$ and Ca^{2+}~~, which~~ causes the content of Na$^+$ to increase.

Cluster analysis can be simplified as the identification of the relationship between large-scale samples. R cluster analysis is used to classify variables, while~~and~~ Q cluster analysis is used to classify samples (Sun and Gui, 2013). The results of the R cluster analysis are shown in Fig.~~ure~~ 5. The groundwater components can be divided into 3 groups, which is totally consistent with the results of the factor analysis. ~~The first group includes Ca^{2+}, Cl$^-$, SO$_4^{2-}$ and TDS. The second group includes Na$^+$, Mg^{2+} and HCO$_3^-$. Finally, the third group includes K$^+$.~~ Surface water ions can be divided into 2 groups which differ from the results of factor analysis. The first group includes TDS, Cl$^-$, HCO$_3^-$, Na$^+$, K$^+$ and Mg^{2+}, and the second group includes Ca^{2+} and SO$_4^{2-}$,~~. This~~ indicating~~es~~ the presence of gypsum dissolution~~, which differs from the results of factor analysis~~.

In summary, a variety of complex hydrogeochemical processes may have occurred in the study area, such as concentration through evaporation, rock weathering, cation alternate adsorption, oxidation and dissolution.

Table 2 Factor analysis composition coefficient of ground and surface water

Parameter variable	Groundwater			Surface water	
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2
Ca^{2+}	0.889	-0.083	0.339	0.206	-0.970
Na$^+$	0.261	0.799	-0.041	0.650	0.738
K$^+$	0.061	0.081	0.916	0.783	0.540
Mg^{2+}	0.298	0.702	0.265	0.106	0.986
Cl$^-$	0.735	0.259	0.323	0.479	0.817
SO$_4^{2-}$	0.760	0.299	-0.046	-0.883	0.351
HCO$_3^-$	-0.004	0.915	0.010	0.812	0.151
TDS	0.762	0.197	-0.208	0.972	0.200
Characteristic value	3.472	1.492	1.037	4.856	2.446
Contribution rate%	43.394	18.649	12.965	60.704	30.578
Cumulative contribution rate	43.394	62.043	75.008	60.704	91.282

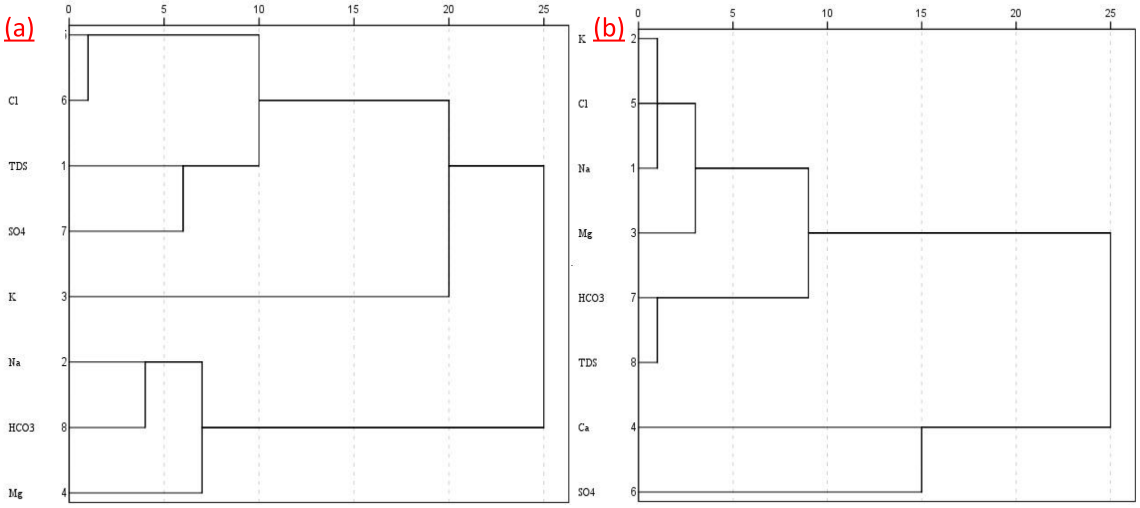


Fig. 5 R type cluster analysis. (a) groundwater variables; (b) surface water variables.

3.4 Isotopic characteristics and transformation relationships of surface water and groundwater

3.4.1 Isotopic variation characteristics

δD and δ^{18}O of surface water and groundwater and the *d* value of deuterium excess in the study area are listed in Table 3, ~~in which~~where d=δD-8δ^{18}O.

As seen in Table 3, δD and δ^{18}O of surface water are more enriched than ~~in~~those of groundwater. The variation ~~in~~ in δD and δ^{18}O of~~for~~ surface water~~ from the Weihe River~~ is relatively small. δ^{18}O ranges from -7.8‰ to -7.6‰ with an average value of -7.7‰, and δD ranges from -59‰ to -57‰ with an average value of -58‰. The range of δ^{18}O for shallow groundwater is from -9.4‰ to -7.7‰, with an average value of -8.55‰; the range of δD is from -59‰ to -69‰, with an average value of -63.3‰. The *d* value of deuterium excess ~~of water~~ is positive and less than 10 of the atmospheric precipitation intercept. The value~~at~~ of surface water is less than that of shallow groundwater, indicating that the recharge sources of surface water and groundwater are subject to evaporation effects but ~~that~~ shallow groundwater is less influenced~~ by evaporation effects~~.

Generally, the isotopic ~~characteristics~~ concentrations of river water bodies increase from upstream to downstream because of the isotopic fractionation~~ that is~~ caused by the evaporation of water. The fractionation effect on the isotopes could be greater as the location is c~~The c~~loser to the lower reaches of the river~~, the greater the fractionation effect is on the isotopes~~ (Liu et al., 2014).~~ Figure 6 shows the variation in δD and δ^{18}O in river water.~~ As shown in Fig. 6, i~~I~~t is apparent that δD and δ^{18}O become more enriched as the river flows downstream, in which δ^{18}O declines in HXJHS, probably because there is a lake in the vicinity of the upstream reaches and river water supplies the lake.

For groundwater, the values of δD and δ^{18}O in the Zongwan section, Hexijie section and Xiwangqiao section become more depleted as the distance between sampling points and Weihe River increases. ~~The closer~~As the sample location is closer to the river, ~~the closer~~ the δD and δ^{18}O values are more similar to the surface water, reveal~~indicat~~ing that the influence of surface water on groundwater decreases with increasing distance. In contrast, the influence of precipitation and irrigation infiltration recharge on groundwater is enhanced. The values of δD and δ^{18}O for the Chaiwan section and the Wangsizhuang section become enriched as the distance between the sampling points and the Weihe River increases. The reason is probably that ~~This is likely because~~ the farmland in the Chaiwan section and the Wangsizhuang section is mainly irrigated using Weihe River water, and the infiltration of irrigation water causes the enrichment of hydrogen and oxygen isotopes in the groundwater. The hydrogen and oxygen isotope characteristics are more similar to those of the Weihe River. The CHW02 and CHW03 sampling points in the Chaiwan section are located in an area affected by river irrigation, and CHW01 is a household well. ~~As such, t~~The hydrogen and oxygen isotope values are CHW03≥CHW02>CHW01. Similarly, WSZ02, WSZ03 and WSZ04 in the Wangsizhuang section are located in an area affected by river irrigation, and WSZ01 is a household well. Thus, the hydrogen and oxygen isotope values are WSZ04≥WSZ03≥WSZ02> WSZ01.

Table 3 δD, $\delta^{18}O$ and *d* values of water samples in study area

Water sample type	No.	δ D/‰	$\delta^{18}O$/‰	*d*/‰	*f*/%
Surface water	ZWHS	-59	-7.7	2.6	
	HXJHS	-58	-7.8	4.4	
	CHWHS	-58	-7.7	3.6	
	WSZHS	-58	-7.7	3.6	
	XWQHS	-57	-7.6	3.8	
	average	-58	-7.7	3.6	
Shallow groundwater	ZW01	-62	-8.6	6.8	33.3
	ZW02	-63	-8.6	5.8	25
	ZW03	-63	-8.6	5.8	25
	ZW04	-69	-9.4	6.2	10
	D01	-65	-8.7	4.6	14.3
	D02	-66	-8.9	5.2	12.5
	D03	-60	-8	4	50
	CHW01	-63	-8.6	5.8	20
	CHW02	-62	-8.4	5.2	25
	CHW03	-62	-8.3	4.4	25
	WSZ01	-68	-9.2	5.6	10
	WSZ02	-63	-8.6	5.8	20
	WSZ03	-63	-8.5	5	20
	WSZ04	-63	-8.5	5	20
	D11	-59	-7.7	2.6	50
	D12	-62	-8.4	5.2	20
	D13	-63	-8.4	4.2	16.7
	Average	-63.3	-8.55	5.1	

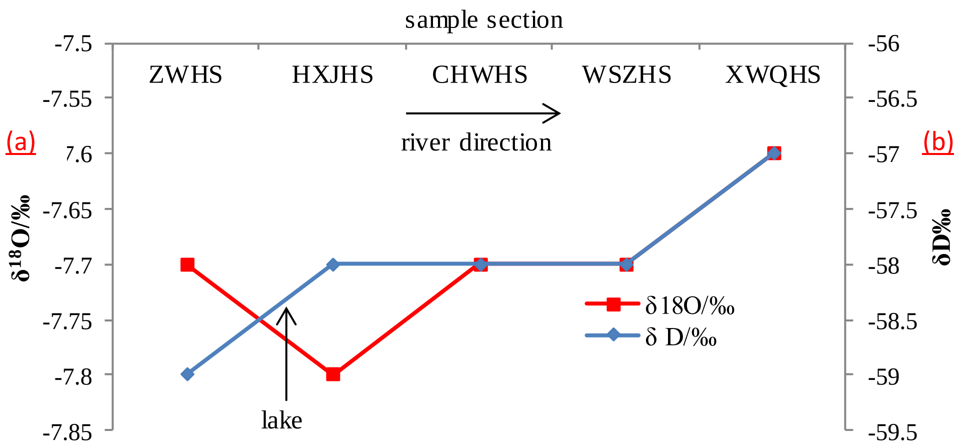


Fig. 6 Isotopic variation of surface water. (a) δ^{18}O; (b) δD

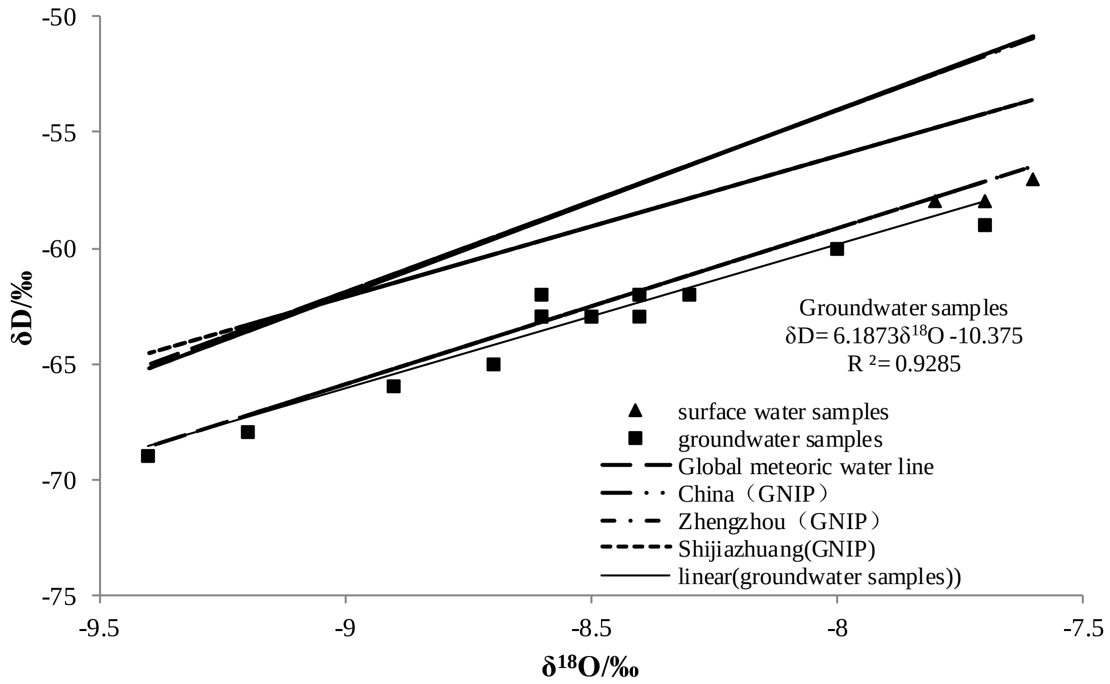


Fig. 7 Relationship between δD and δ^{18}O of surface water and groundwater

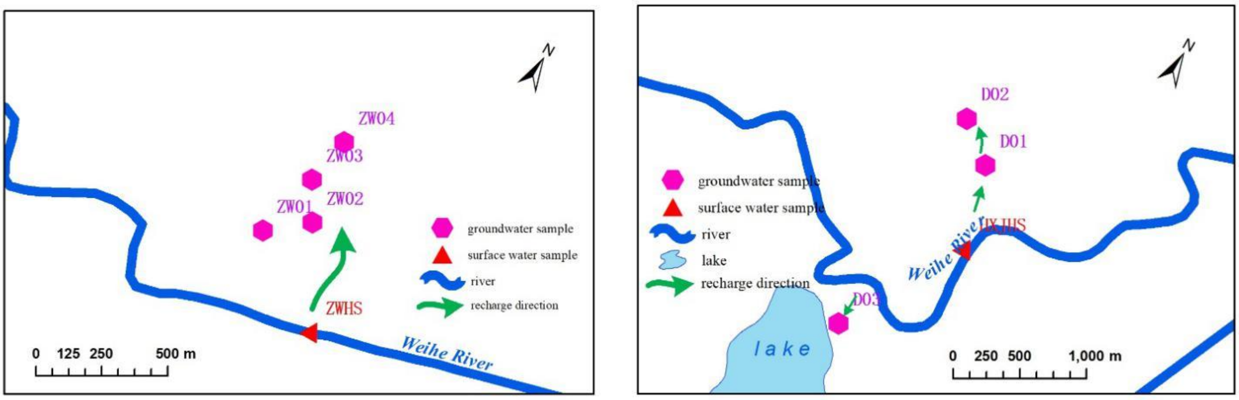
According to the 27 Global Network of Isotopes in Precipitations (GNIPs) set up in China by the International Atomic Energy Association (IAEA), the monitoring sites that could be considered as substitutes for~~are closest to~~ the study area are at Shijiazhuang and Zhengzhou (IAEA/WMO, 2015; Zhang and Wang, 2016). The meteoric water line of $\delta D=6.75\ \delta^{18}O-5.12$ in Zhengzhou is close to the characteristic line for hydrogen and oxygen isotopes of samples in ~~the~~ this study ~~area~~ region (Fig.~~ure~~ 7), ~~so the meteoric water line in Zhengzhou~~which is taken as~~assumed to be~~ the local meteoric water line (LMWL). When the compositions of δD and δ^{18}O ~~of water samples~~ are compared to the meteoric water line, the source of the local river water and shallow groundwater and their mutual transformation relationship can be distinguished. ~~From d~~From~~rawing~~ the trend line ~~between~~ of the ~~underground water~~groundwater sample points, the relationship between δD and δ^{18}O is $\delta D=6.1873\delta^{18}O-10.375$~~, and the~~ with a correlation coefficient of~~is~~ 0.9285. From ~~drawing~~ the trend line ~~between~~ of the ~~the~~ groundwater and surface water sample points, the relationship between δD and δ^{18}O is fitted with $\delta D=6.19328\delta^{18}O-10.321$~~, and~~ and the correlation coefficient is~~is~~ 0.9585. The two trend lines are ~~basically the~~

~~same~~extremely close with ~~, and~~ the high related coefficient ~~is very high~~. The surface water sample points are located in the direction of the groundwater trend line that extends to the right. δD and δ^{18}O are relatively enriched, indicating that the sources of surface water and groundwater are the same and that there is a hydraulic connection~~.~~ ~~The hydraulic connection between the two is~~, i.e. a single-line infiltration of the surface river water into groundwater. The trend line is close to the local meteoric water line (LMWL) and the slope is small, which means~~indicating~~ that surface water and groundwater are recharged from meteoric water but ~~are~~ also subject to the evaporation, resulting in the enrichment of hydrogen and oxygen isotopes.

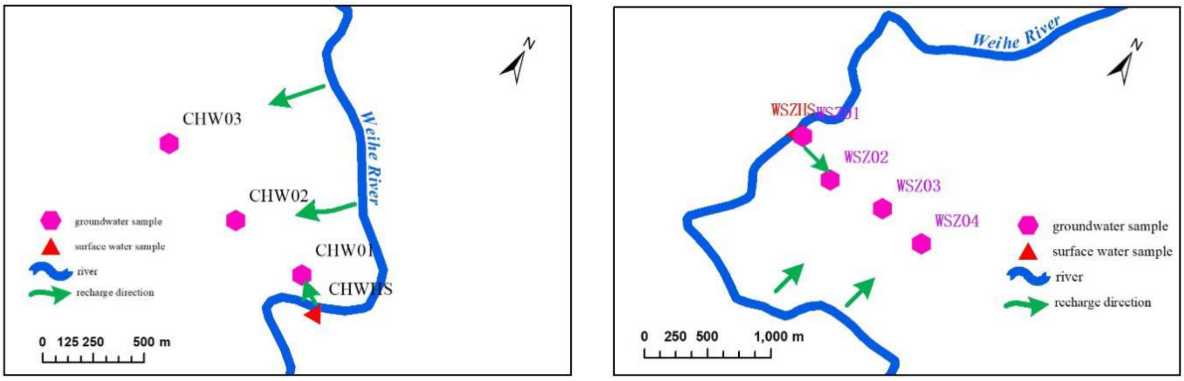
3.4.2 Estimation of recharge capacity of river water to groundwater

According to the stable isotope signatures of the water samples, the calculated results of ratio *f* of groundwater recharge to river water are shown in Table ~~4~~3. As illustrated in Fig. 8, except for regular pattern, t~~T~~he ratio *f* of surface water infiltration to recharge groundwater in each observation section also shows ~~has a~~ differen~~t~~ce~~t, but regular, pattern, and the results are shown in Figure 8~~.

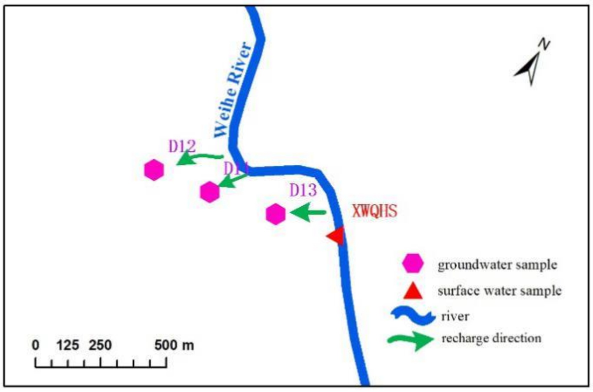
In the Zongwan section (Fig.~~gure~~ 8a), as the distance between groundwater sampling sites and the river increased (ZW01 toward ZW04), the ratio of surface water infiltration to groundwater recharge (*f*) decreased from 33.3% to 10%, confirming ~~indicating~~ that the river water recharges groundwater in this section and the direction of groundwater flow is from ZW01 toward ZW04. The infiltration rates at D01 and D02 in the Hexijie section (~~Figure~~ Fig. 8b) are 14.3% and 12.5% ~~,~~ respectively, and~~with~~ from the~~a~~ decreasing trend, it can be deduced~~indicating~~ that there is a small amount of river water recharging groundwater in that section, with a direction of groundwater flow from D01 toward D02. The ratio of surface water infiltration to groundwater at D03 is as high as 50%, ~~indicating~~ which means that the river mainly recharges the artificial lake that exists near D03 in the Hexijie section. The ratio of surface water infiltration to groundwater in the Chaiwan section (Fig.~~ure~~ 8C) increases from 20% to 25% as the distance increases between groundwater sampling sites and the river, whereas it increases from 10% to 20% in the Wangsizhuang section (~~Figure~~ Fig. 8D). This may be associated with the unique river trend of the two sections. The Chaiwan section and the Wangsizhuang section are located near the right corner of the river, where the influence of ~~the~~ river water on groundwater is complicated, but the river is the main supply ~~ier~~ of groundwater. The groundwater flow line is an~~the~~ enclosed space where there~~water~~ is no water~~not~~ exchange~~d~~ with the outside ~~world~~. I~~Some i~~nput values like δD and δ^{18}O remain constant along the entire streamline~~, such as δD and δ^{18}O~~, inferring~~. Therefore, it is possible to interpret~~ that WSZ01, WSZ02, and WSZ03 are on the same streamline. At the same time, because farmland is primarily irrigated by ~~water from~~ the Weihe River, irrigation water infiltrates the soil to recharge groundwater, resulting in the enrichment of hydrogen and oxygen isotopes. For the Xiwangqiao section (Fig.~~ure~~ 8e), the ratio of river water infiltration to groundwater at D11 is close to 50%, whereas it is 20% and 16.7% at D12 and D13, respectively. This is primarily because D11 is located in the convexity of the river, where it is significantly eroded with a large amount of infiltration.



(a) Zongwan section (b) Hexijie section



(c) Chaiwan section (d) Wangsizhuang section



(e) Xiwangqiao section

Fig. 8 ~~Relationships between~~Recharge directions between surface water and~~and~~ groundwater at all sampling sections

4. Conclusions

This paper provides systematical methods for hydrogeochemical components analysis which could contribute to the relationship of surface water and groundwater. The main results are concluded as follows:

(1) The surface water components of Weihe River ~~display~~ have no significant spatial variations, but the ion concentrations of groundwater samples from 5 sections are different. The cation concentrations of surface water and groundwater are consistent~~,~~ with $Na^+>Ca^{2+}>Mg^{2+}>K^+$. The relative concentrations of anions in groundwater are $HCO_3^->SO_4^{2-}>Cl^->NO_3^-$, whereas the relative concentrations of anions in the surface water are $SO_4^{2-}> Cl^->$

HCO$_3^-$>NO$_3^-$. The surface water in all sections of the Weihe River is the SO$_4$ Cl—Na type, whereas the hydrogeochemical types of groundwater are not the same ~~different~~. HCO$_3^-$ dominates in the groundwater in the upper reaches of the river, ~~and~~ while SO$_4^{2-}$ and Cl$^-$ dominate in the middle and lower reaches.

(2) ~~By using~~Based on a Gibbs diagram, factor analysis and cluster analysis, we established that the geochemical processes of the Weihe River Basin include concentration by evaporation, rock weathering, cation alternate adsorption and dissolution. Because surface water is an open system, the source of ions in a water body is greatly influenced by human activity and atmospheric precipitation, whereas the factors contributing to the formation of water chemistry are more complex.

(3) The isotope results show that δD and δ^{18}O of the surface water in the Weihe River of small variations ~~varies little~~ are~~and is~~ more enriched than those of the groundwater~~ is~~. Affected by rainfall, irrigation, river recharge and evaporation, t~~T~~he shallow groundwater at different sections ~~is affected by rainfall, irrigation, river recharge and evaporation, resulting in~~have different δD and δ^{18}O values. By analyzing hydrogen and oxygen isotopic characteristics of surface water and groundwater in different sections and using the segmentation of flow duration curve, it was established that surface water recharges groundwater at 5 sections along the Weihe River, and each section has unique recharge intensity and relationship due to its specific ~~unique~~ hydraulic environment.

However, d~~D~~ue to the lack of local isotope monitoring data for meteoric water, the Zhengzhou meteoric water line was used to analyze the isotopic characteristics of surface water and groundwater. The existing household wells~~, were~~ used as groundwater sampling points, ~~. Because they~~ are affected by towns and villages surrounding the Weihe River, causing that groundwater sampling points cannot be fully symmetric and isometric relative to the Weihe River. ~~As such, t~~The research results need to be improved by sufficient ~~monitoring more~~ local measured ~~complete~~ data in future research. Moreover, the methods conducted in this paper could offer efficient ways of research on surface water and groundwater, and the specific results could also provide valuable information for the local water groundwater protection, restoration and management.

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