



# Hydrological characteristics and water quality change in mountain river valley on Qinghai-Tibet Plateau

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## Abstract

Management and protection of regional water resources requires an understanding of the hydrological characteristics and water quality changes. In this study, we combined isotopic, geochemical and hydrometric measurements to investigate hydrological characteristics and water quality changes during the interactions between surface water and groundwater in mountain river valley. Our results showed that the stable isotope values in most of the groundwater and river water samples were located above the middle of the local meteoric water line in a mountain river valley. The hydrochemical types of most of the groundwater and river water samples were Ca–Mg–HCO<sub>3</sub> and were primarily dominated by rock weathering. The hydrochemical compositions of groundwater and river water were mainly affected by carbonate dissolution and cation exchange, but influences of saltwater intrusion and human activity were found at the lakeside. Precipitation was the main factor affecting the changes in hydrological processes at these groundwater and river water sites and they were also affected by meltwater, soil water and the interaction between groundwater and surface water. The water level of the river increased, and the recharge of the groundwater by river water increased in river valley during the rainy season, which led to an increase runoff path in groundwater. The interaction between the river water and groundwater was affected by the rainfall frequency and intensity, the recharge time of the soil water and the pressure of the river on both sides of the river channels. Additionally, our results indicated that the flow of groundwater into the river will lead to water quality deterioration. The increasing pressure of the river on the groundwater will cause the deterioration of groundwater quality, which will also be affected by saltwater intrusion and human activity. Our results detailed the hydrological characteristics, water quality changes and main influencing factors of the interaction between surface water and groundwater of river valley in mountain, which will be beneficial to promote the reasonable protection of water resources under climate change in the future.

**Keywords** Groundwater-surface water · Water quality · Stable isotopes · Hydrochemistry · River valley

## Introduction

Water is the most precious resource, along with land and energy, for human survival and socioeconomic development (Howells et al. 2013; Mas-Pla and Menció 2019; Ma et al. 2020; Ondrasek et al. 2021; Wada et al. 2014). However,

water shortages are an emergent issue worldwide for several reasons (e.g., climate change, population growth, irrigated croplands, economic development and population) (Florke et al. 2013; Foster and MacDonald 2014; Haddeland et al. 2014; Posthuma et al. 2019; Vorosmarty et al. 2000). Today, more than 1.2 billion people live under water shortages (Howells et al. 2013), and two-thirds of the world's population will live under water stress by 2025 (UN 2015). Therefore, the global shortage of water poses a serious challenge to sustainable development, but the efficient management of water may alleviate this emergency.

The United Nations reports that more than 1.7 billion people live in river basins (UN 2015) because river water provides freshwater, and freshwater is critical for human production and life. However, the utilization of river water is limited in semiarid and arid regions (e.g.,

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India, Pakistan, northwestern China, the Middle East and North Africa) because of lower precipitation (Wade et al. 2014). In these regions, groundwater is extracted for sustainable food production and economic development. However, the storage and quality of groundwater are rapidly deteriorating due to overexploitation and population, which has caused widespread international concern (Aeschbach-Hertig and Gleeson 2012; Feike et al. 2017; Jia et al. 2019; Mariangela et al. 2019; Zaidi et al. 2015). Reasonable exploitation and utilization of surface water and groundwater resources may be the key to promoting sustainable development of water. Therefore, understanding the transport processes and the effects of the interaction between surface water and groundwater on the water environment is crucial for the comprehensive utilization of surface water and groundwater.

Mountains are core components of the global water supply (Somers and McKenzie 2020). The substantial capacity of groundwater storage and discharge is vital to buffer the streamflow during dry periods in mountain watersheds (Liu et al. 2004; Soulsby et al. 2000; Uhlenbrook et al. 2002). As the global climate changes, temperature changes will dramatically alter mountain hydrological conditions through permafrost degradation, increasing evapotranspiration and reducing water storage in glaciers (Barnett et al. 2005; Immerzeel et al. 2010). Permafrost degradation will deepen the underground runoff path and increase the amount of permafrost meltwater infiltration (Frampton et al. 2013; Ge et al. 2011; Wellman et al. 2013). Focusing on the interaction between groundwater and surface water is beneficial for predicting the change in water under climate change in mountainous areas and formulating timely and effective water resource utilization measures.

The stable isotope ratio ( $\delta^{18}\text{O}/\delta^{16}\text{O}$  and  $\delta^2\text{H}/\delta^1\text{H}$ ) and hydrochemical ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{NO}_3^-$ ) of water allow the tracing of recharge sources, evolution and flow paths of groundwater and the interaction of surface water and groundwater (Li et al. 2021; Martinez et al. 2015; Rodgers et al. 2005). The integrated application of isotopes and hydrochemical ions is an effective method to reveal hydrological processes, especially the interaction between surface water and groundwater (Cui and Li 2014; Gibson et al. 2005; Raghavendra and Deka 2015). Dogramaci et al. (2012) determined the processes that control surface water and groundwater recharge and quantified the sources of major recharge. Yuan et al. (2020) found that the interaction between rivers and groundwater was completely changed by water transfer by using stable isotopes and hydrochemistry. Zhang et al. (2021) investigated the transport processes between surface water and groundwater in selected tributaries of the Wei River (China).

In this study, stable isotopes and hydrochemical ions from 273 samples were tested and analysed from March 2019 to January 2020 to (1) investigate the spatial and temporal isotopic, geochemical and hydrometric characteristics of precipitation, river water, groundwater and lake water in a river valley, (2) reveal the hydrological characteristics, water quality changes and main influencing factors during the interaction between surface water and groundwater.

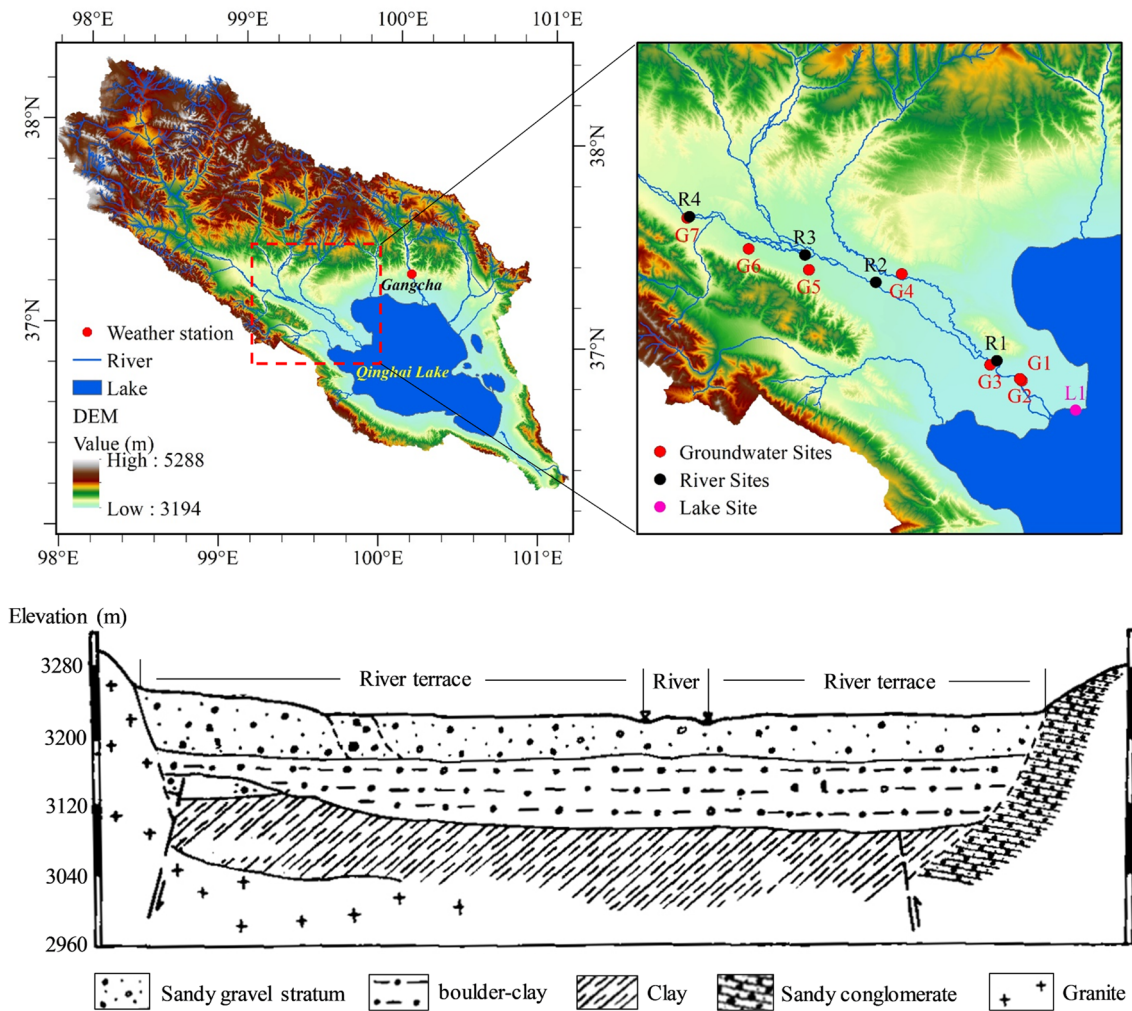
## Study area

The Qinghai Lake Basin ( $36^\circ 15' - 38^\circ 20' \text{N}$ ,  $97^\circ 50' - 101^\circ 20' \text{E}$ ) is the largest inland saline lake watershed on the northeastern Tibet Plateau in China, with an area of 29,661 km<sup>2</sup> (Fig. 1). The lake is surrounded by the Datong Mountains, Qilian Mountains, Riyue Mountains and Qinghai Nan Mountains (Dong et al. 2019; Fan et al. 2021). The Qinghai Lake Basin lies in a critical transitional zone (Li et al. 2018a, b) that is affected by the East Asian Monsoon in summer (June–August) and the Westerly Circulation in winter (September–May) (Cui et al. 2021; Dong et al. 2019). The three largest rivers in the Qinghai Lake Basin are the Buha River, Shaliu River, and Haergai River, which account for 75% of the surface water inflow into Qinghai Lake.

The Buha River is the largest of these rivers, located in the western Qinghai Lake Basin (Fig. 1). The annual runoff is  $7.84 \times 10^6 \text{ m}^3$  and the average annual flow is  $24.85 \text{ m}^3 \text{ s}^{-1}$ . The flood period is from June to September (the flood peaks in July), and the dry period is from December to March. The maximum and minimum flows are  $81.33 \text{ m}^3 \text{ s}^{-1}$  and  $2.38 \text{ m}^3 \text{ s}^{-1}$ , respectively. The width and altitude of the Buha Valley plain are 6–10 km and 3200–3400 m above sea level (m a.s.l.), respectively. The Buha River Valley is wide and flat, and the river terraces are mainly composed of sandy gravel stratum, boulder-clay, clay, sandy conglomerate and granite (Fig. 1).

## Sampling and analytical methods

Precipitation samples were collected by using samplers during every precipitation event from March 2019 to February 2020 at the Gangcha meteorological station (3301.5 m a.s.l.) (Fig. 1). Samplers were placed in an open area over 1.5 m aboveground. In total, 142 precipitation samples were collected. Groundwater and surface water (river and lake water) samples were collected once a month from 12 sites from March 2019 to January 2020 (Fig. 1). A total of 131 samples of groundwater and surface water were collected (77 groundwater samples, 43 river water samples, and 11 lake water samples). Groundwater samples were collected after the water conductivity stabilized after 3–5 min of well



**Fig. 1** Locations of the study area and sampling sites and a geological sketch

pumping. River water samples were collected 20 cm below the flowing water surface, and lake water samples were collected 50 cm below the water surface. All samples were filtered using 0.45 μm filters and stored in 50 ml bottles for isotopic analyses. In addition, water samples were stored in 100 ml acidified and not-acidified bottles for cation and anion analyses, respectively. All samples were sealed with sealing film (Parafilm 996, America) and stored in refrigerators (4 °C).

Stable isotopes were measured using a Los Gatos Research (IWA-45-EP) isotopic water analyser. Cations ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ ) were measured using an inductively coupled plasma emission spectrometer (Optima -8000). Anions ( $Cl^-$ ,  $SO_4^{2-}$  and  $NO_3^-$ ) were measured using ion chromatography (ICS -2000).  $CO_3^{2-}$  and  $HCO_3^-$  were measured in situ using direct titration with phenolphthalein ( $5\text{ gL}^{-1}$ ), methyl orange ( $1\text{ gL}^{-1}$ ), and sulfuric acid ( $0.01\text{ molL}^{-1}$ ). The locations of the sampling sites were acquired using a global positioning system (GPS). The electrical conductivity, total

dissolved solids (TDS), temperature and pH of the groundwater were measured in situ by a handheld metre. The water level and temperature of the groundwater were acquired using a water level logger-titanium (ONSET HOBO). Water level and runoff data for the Buha River were downloaded from the Qinghai hydrological information website (<http://www.qhsw.org.cn/qhsq.php>). Daily precipitation data from the Gangcha weather station were downloaded from the China Meteorological Data Service Centre (<http://data.cma.cn/>).

The hydrochemical characteristics and evolution of groundwater were revealed using a Piper diagram and the boomerang envelope model (Gibbs 1970; Li et al. 2021; Piper 1944). Piper (1944) drew two triangles on behalf of the cations and anions in order to reflect the main water composition. The apexes of the cation plot are  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Na^+ + K^+$ . The apexes of the anion plot are  $SO_4^{2-}$ ,  $Cl^-$  and  $CO_3^{2-} + HCO_3^-$ . A hydrogeochemical categorization of the groundwater, river water, and lake water was carried out

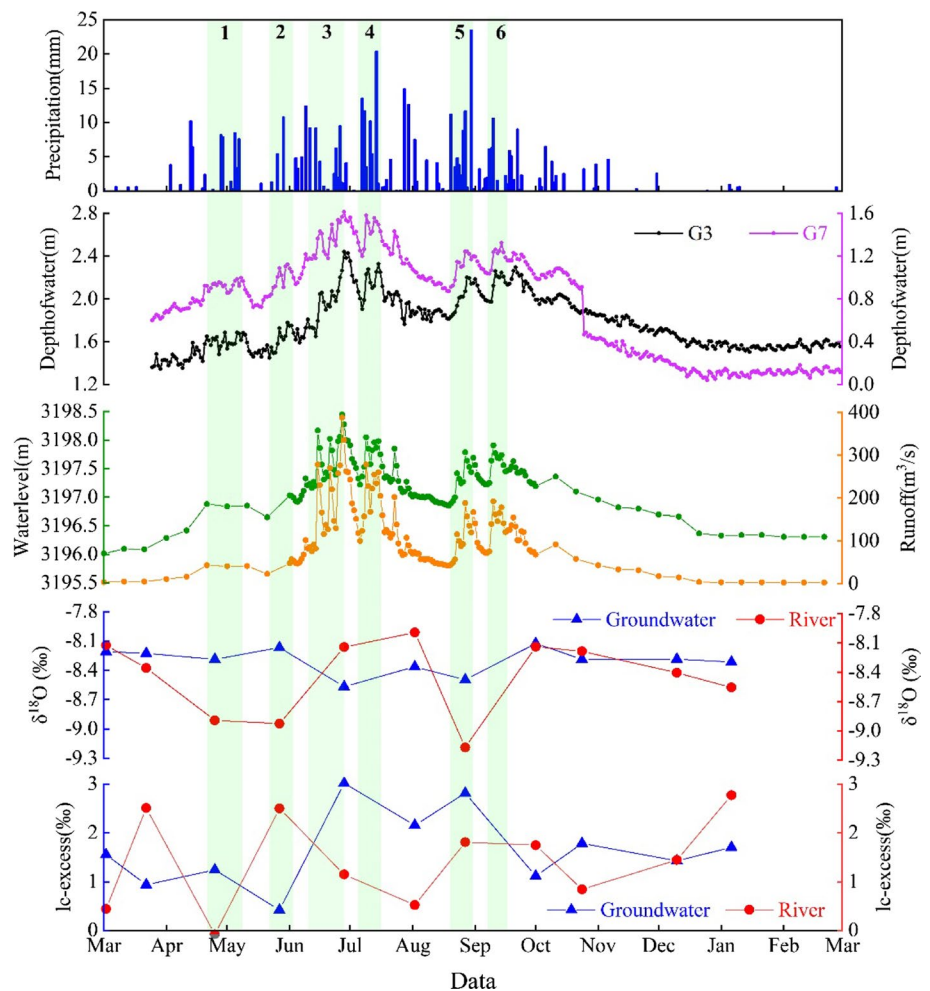
based on the major cations and anions in the Piper diagram (Piper 1944). Gibbs (1970) proposed that factors controlling the water composition could be divided into three end-members: rock weathering, atmospheric precipitation, and evaporation/crystallization, based on the chemical composition of surface water samples from across the globe. Landwehr and Coplen (2004) proposed line-conditioned excess ( $lc\text{-excess} = \delta^2H - a\delta^{18}O - b$ ) that represented the difference between the  $\delta^2H$  and a linear transform of the  $\delta^{18}O$  of a water sample. In the formula, a and b are the slope and intercept of the local meteoric water line.  $lc\text{-excess}$  was used to determine the fractionation of the hydrological processes (Dansgaard 1964; Evaristo et al. 2015). Water that undergoes fractionation by evaporation has a negative  $lc\text{-excess}$  (Landwehr et al. 2014; Sprenger 2016).

## Results

### Variation characteristics of water levels

The burial depth of the groundwater ranged from 2.4 to 6.1 m in the river valley. The depth of the groundwater at G3 and G7 ranged from 1.3 to 2.4 m (with an average of 1.8 m) and 0.1 to 1.6 m (with an average of 0.7 m), respectively (Fig. 2). The water level of the river ranged from 3196.0 to 3198.5 m a.s.l., and the runoff ranged from 2.8 to 388.0 m<sup>3</sup>/s (Fig. 2). The variation in the water level of the groundwater was consistent with that of the river (Fig. 2). The variation in the water level could be divided into two periods: the flood period (June to October) and the dry period (November to May of the following year) (Fig. 2). The flood period coincided with the rain period and the thawing period, indicating that temperature and precipitation influenced the hydrological process in the basin (Li et al. 2018a, b). The water levels of the groundwater and river water had three obvious peaks in May, July and September (Fig. 2). The maximum peak of the water level occurred in July. The variation in

**Fig. 2** Variations in the  $\delta^{18}O$  values,  $lc\text{-excess}$  values and water levels of groundwater and river water in response to precipitation

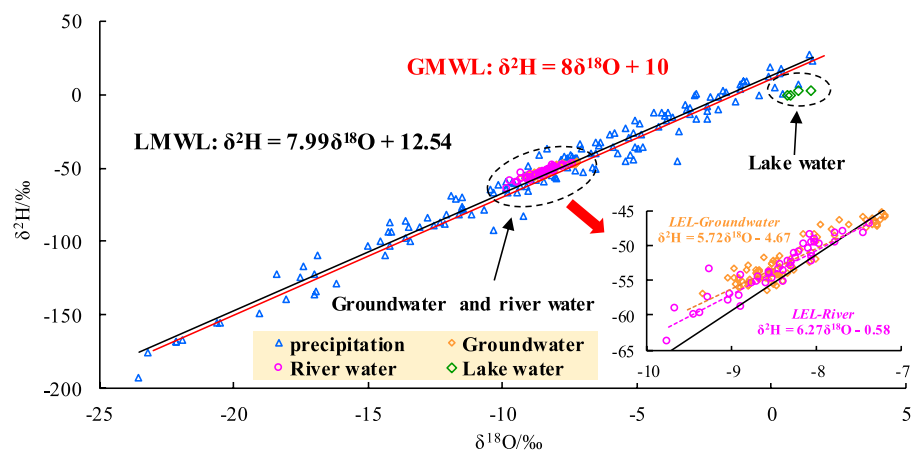


the upstream (G7) groundwater level was greater than that downstream (G3). Moreover, the changes in water levels mainly depended on precipitation, especially continuous precipitation and extreme precipitation events (Fig. 2).

### Composition of stable isotopes

The stable isotopes ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) in the precipitation, groundwater, river water and lake water are shown in Fig. 3. Precipitation had the maximum ranges of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , and the ranges in groundwater, river water and lake water were within the range of precipitation. The local meteoric water line (LMWL:  $\delta^2\text{H} = 7.99 \delta^{18}\text{O} + 12.54$ ) and local evaporation line of the groundwater and surface water (LEL-Groundwater:  $\delta^2\text{H} = 5.72 \delta^{18}\text{O} - 4.67$ ; LEL-River:  $\delta^2\text{H} = 6.27 \delta^{18}\text{O} - 0.58$ ; LEL-Lake:  $\delta^2\text{H} = 4.44 \delta^{18}\text{O} - 2.93$ ) were calculated by using the values of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  (Fig. 3). The slopes of the LEL of the groundwater (5.72) and river water (6.27) were lower than that of the LMWL (7.99) and higher than that of the LEL of lake water (4.44). The slope of the LEL of groundwater was lower than that of the LEL of river water due to the large runoff of the Buha River (Li et al. 2018a, b) and the strong evaporation of soil water (Liu et al. 2022). The samples of lake water were located below and near the enriched end of the LMWL because of the evaporation of lake water over many years (Echegoyen et al. 2022). The monthly averages of the  $\delta^{18}\text{O}$  and lc-excess values in the groundwater ranged from  $-8.57\text{‰}$  to  $-8.12\text{‰}$  and  $0.42\text{‰}$  to  $3.02\text{‰}$ , respectively (Fig. 2). The monthly averages of the  $\delta^{18}\text{O}$  and lc-excess values in the river water ranged from  $-9.17\text{‰}$  to  $-7.99\text{‰}$  and  $-0.08\text{‰}$  to  $2.77\text{‰}$ , respectively (Fig. 2). The variation in  $\delta^{18}\text{O}$  values of the groundwater was relatively small, and the variation in the  $\delta^{18}\text{O}$  values of the river water was relatively large (Fig. 2). The groundwater and river water had opposite changes in their  $\delta^{18}\text{O}$  and lc-excess values from March to July and the same changes in these values from July to February of the following year (Fig. 2).

**Fig. 3** The compositions of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in precipitation, groundwater, river water and lake water



### Geochemical characteristics

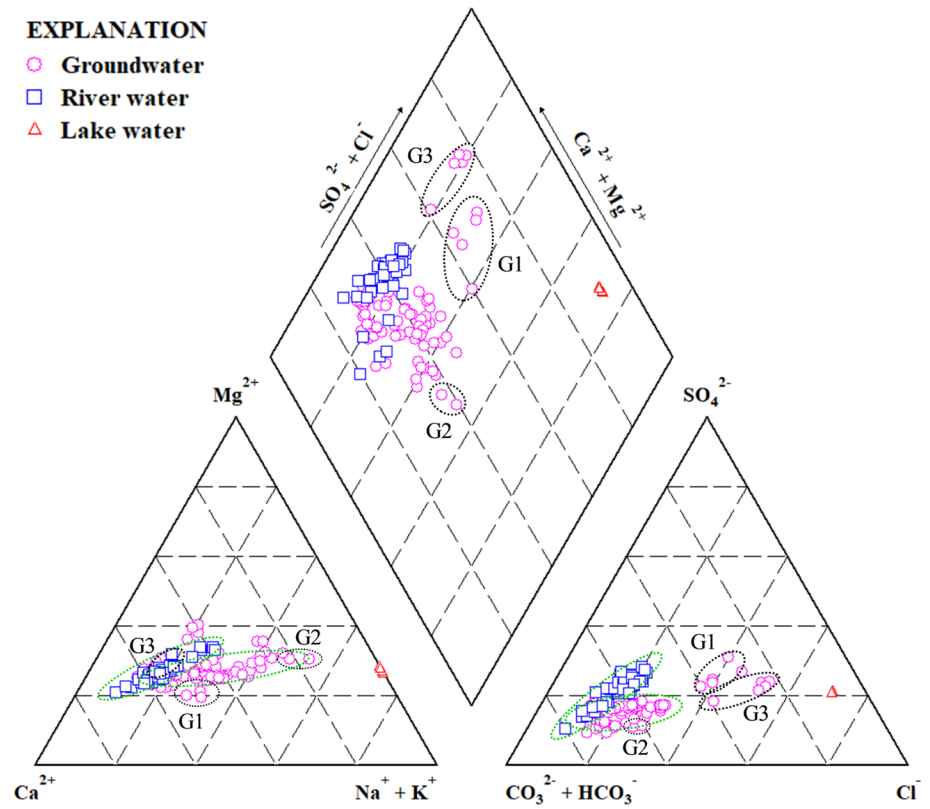
The pH values of groundwater, river water and lake water ranged from 7.4 to 8.9, 8.2 to 9.3 and 9.1 to 9.3, respectively. The average contents of TDS in groundwater, river water and lake water were 690 mg/L, 394 mg/L and 12,010 mg/L, respectively. These results indicated that the groundwater was slightly alkaline and that the lake water was alkaline. The mean values of total hardness (TH) in the groundwater and river water were 349 mg/L and 220 mg/L, respectively. The TDS and TH of groundwater were relatively high because of the intense interactions between rocks and water (Li et al. 2021). The hydrochemical types and the Gibbs boomerang model of the groundwater, river water and lake water are shown in Figs. 4 and 5. The hydrochemical types of most of the groundwater, river water and lake water samples were Ca–Mg–HCO<sub>3</sub>, Ca–Mg–HCO<sub>3</sub> and Na–Cl, respectively (Fig. 4). The hydrochemical types of some of the groundwater samples were Na–Mg–HCO<sub>3</sub> (e.g., site G2), Ca–Cl–HCO<sub>3</sub> (e.g., site G1) and Ca–Mg–Cl (e.g., site G3) (Fig. 4). The evolutionary paths of the groundwater, river water and lake water samples were from “Rock dominance” to “Ocean” (Fig. 5). Some of the groundwater samples had endmembers located between “Rock dominance” and “Ocean” (e.g., G1, G2 and G3) (Fig. 5).

### Discussion

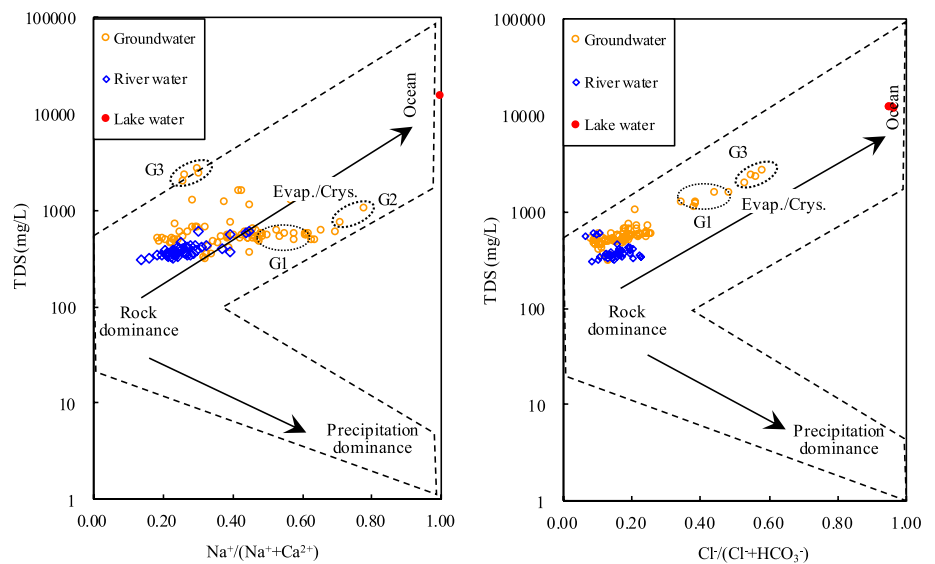
#### Factors affecting geochemical characteristics

All of the lake samples had “Ocean” endmembers (Fig. 5), indicating that the hydrochemical composition of lake water was primarily dominated by evaporation and crystallization (Gibbs 1970; Xiao et al. 2018). Most of the groundwater and river water samples had “Rock dominance” endmembers (Fig. 5), indicating that most groundwater and river water were primarily dominated by rock weathering (Cui and Li

**Fig. 4** Ternary plots of cations and anions in groundwater, river water and lake water



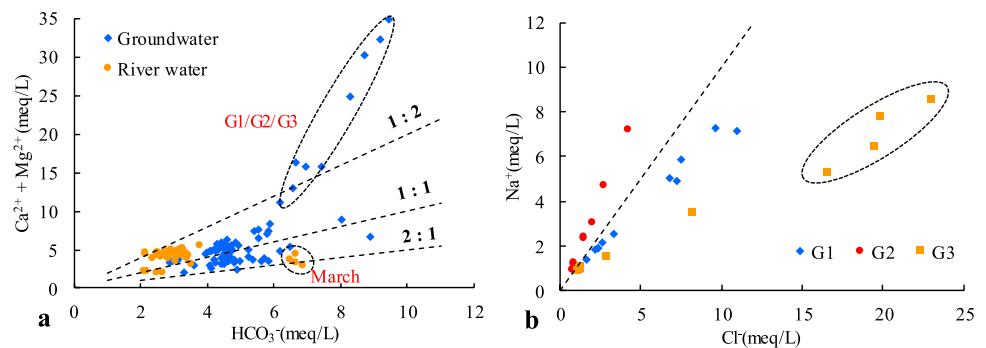
**Fig. 5** Plots of major ions within the Gibbs boomerang model for groundwater, river water and lake water



2014; Gibbs 1970; Yuan et al. 2020). The ionic ratios in water samples can identify origin of ions and anthropogenic effects in the water (Chen et al. 2018). Most of the river water had an  $\text{HCO}_3^- : (\text{Ca}^{2+} + \text{Mg}^{2+})$  ratio between 1:1 and 1:2 (Fig. 6a), indicating that calcite and gypsum were dissolved in the river runoff (Yuan et al. 2020). River water samples in March had an  $\text{HCO}_3^- : (\text{Ca}^{2+} + \text{Mg}^{2+})$  ratio close to 2:1 (Fig. 6a), and the TDS of the river water was relatively

high in March. These results indicated that dolomite dissolution was enhanced when the river runoff was low (Fig. 2). Most of the groundwater had an  $\text{HCO}_3^- : (\text{Ca}^{2+} + \text{Mg}^{2+})$  ratio between 1:1 and 2:1 (Fig. 6a), indicating that calcite and dolomite were dissolved in the groundwater runoff (Yuan et al. 2020). The ratios of  $\text{HCO}_3^- : (\text{Ca}^{2+} + \text{Mg}^{2+})$  in some groundwater samples (e.g., G1, G2 and G3) were greater than 1:2 (Fig. 6a), indicating an additional

**Fig. 6** Scatter diagram of the water samples, **a** molar ratios of ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ) vs.  $\text{HCO}_3^-$ , and **b** molar ratios of  $\text{Na}^+$  vs.  $\text{Cl}^-$



contribution of  $\text{Ca}^{2+}$  and/or  $\text{Mg}^{2+}$  from other sources and/or the deposition of carbon (Chen et al. 2020). The groundwater at G2 displayed an excess of  $\text{Na}^+$  over  $\text{Cl}^-$  (Fig. 6b), implicating the contribution of cation exchange (McNeil et al. 2005). The groundwater at G1 had a  $\text{Cl}^-$ :  $\text{Na}^+$  ratio close to 1:1 (Fig. 6b). By combining the results of Fig. 3 and Fig. 4, it was determined that the groundwater at G1 was affected by lake water (saltwater). The groundwater at G3 displayed an excess of  $\text{Cl}^-$  over  $\text{Na}^+$  (Fig. 6b), and the value of  $\text{NO}_3^-$  in that groundwater ranged from 5.0 to 275.9 mg/L (with an average of 88.06 mg/L). These results indicated that the groundwater at G3 was affected by human activity (Li et al. 2021). The cations of groundwater tended to change from  $\text{Ca}^{2+}$  to  $\text{Na}^+$ , and the cations of river water tended from  $\text{Ca}^{2+}$  to  $\text{Mg}^{2+}$  (Fig. 4). The anions of groundwater tended to change from  $\text{HCO}_3^-$  to  $\text{Cl}^-$ , and the anions of river water tended to change from  $\text{HCO}_3^-$  to  $\text{SO}_4^{2-}$  (Fig. 4). Therefore, the above results demonstrated that the intense evaporation of groundwater, cation exchange, saltwater intrusion and human activity affected the groundwater (Cui and Li 2014; Li et al. 2021; Xiao et al. 2012). This region has the same hydrochemical type, evolution process and geochemical control factors of groundwater as the closed basin in the Qinghai-Tibet Plateau and arid area of northwest China (Li et al. 2020; Tian et al. 2019; Xiao et al. 2018; Zhou et al. 2021). The anions of groundwater tended to change from  $\text{HCO}_3^-$  to  $\text{Cl}^-/\text{SO}_4^{2-}$ , and the cations tended to change from  $\text{Ca}^{2+}/\text{Mg}^{2+}$  to  $\text{Na}^+/\text{K}^+$ . Groundwater chemistry is controlled by mineral dissolution, cation exchange, evaporation and human activities (Li et al. 2020; Xiao et al. 2018).

### Characteristics of groundwater and river response to precipitation

Most of the groundwater and river water samples were located above the middle of the LMWL (Fig. 3). The  $\delta^{18}\text{O}$  value of the groundwater was depleted, and its lc-excess value was relatively high from June to October (Fig. 2). Substantial precipitation and rain occurred during this time (Fig. 2). These results indicated that groundwater and river water were recharged by precipitation at high altitudes or

large amounts of precipitation (Cui and Li 2014, 2015; Dotsika et al. 2010; Hughes and Crawford 2012). These results also indicated that the precipitation effect was more evident than the evaporation effect before infiltration into the ground and the evaporation of soil water and river water flows (Cui and Li 2014; Dotsika et al. 2010; Xiao et al. 2018). The  $\delta^{18}\text{O}$  value of the river water was enriched, and the lc-excess value of the river water was relatively low from June to October, indicating that the river water may be recharged by precipitation at low altitudes or evaporation of surface water, because the temperature was high from June to October in the study area (Li et al. 2018a, b; Hu et al. 2018). The obvious variations in the  $\delta^{18}\text{O}$  and lc-excess values in the groundwater and river water were closely related to the flood period and rain period (Fig. 2). According to previous studies, approximately 70–80% of the annual precipitation in the Qinghai Lake Basin occurs in summer and autumn (Hu et al. 2018). Therefore, the intensity-distribution of precipitation has significant control on the compositions of stable isotopes in groundwater and river water (Kalvans et al. 2020).

The water levels of the groundwater and rivers slightly increased in response to continuous precipitation (Green 1 in Fig. 2). The  $\delta^{18}\text{O}$  value of the groundwater was depleted and the lc-excess value increased. The  $\delta^{18}\text{O}$  value of the river water was depleted, and the lc-excess value of the groundwater decreased due to the recharge of the river water by meltwater. Because the  $\delta^{18}\text{O}$  value of the river ice was depleted upstream, it underwent intense evaporation during the freezing period. The water levels of the groundwater and rivers rapidly increased in response to the substantial amount of precipitation (Green 2 in Fig. 2). The  $\delta^{18}\text{O}$  value of the groundwater was enriched and the lc-excess value was decreased due to the groundwater recharge by soil meltwater. The  $\delta^{18}\text{O}$  value of river water was depleted, and the lc-excess value of the groundwater increased due to the recharge of the river water by precipitation at high altitudes. The groundwater and river water levels had large peaks in response to substantial and continuous precipitation (green bars 3, 4, 5 and 6 in Fig. 2). As the water level of the river rose, the pressure of the river on the groundwater increased on both sides of the river, the path of the groundwater increased. The  $\delta^{18}\text{O}$  value

of the groundwater was depleted and the  $lc$ -excess value increased. The  $\delta^{18}O$  value of the river water was enriched (green bars 3 and 4 in Fig. 2) or depleted (green bars 5 and 6 in Fig. 2). The  $lc$ -excess value of the river water decreased (green bars 3 and 4 in Fig. 2) or increased (green bars 5 and 6 in Fig. 2). Therefore, there could be four possible reasons for the different characteristics of isotopes in the groundwater and river water in response to precipitation: recharging by meltwater, precipitation altitude and intensity, soil water or the interaction between groundwater and surface water (Kalvans et al. 2020). The hydrological processes of groundwater in the plateau basin are similar due to the unique environmental settings and special groundwater system (Chang et al. 2018; Tan et al. 2021). For example, (1) the values of  $\delta^{18}O$  and  $\delta^2H$  in groundwater are closed to river water, (2) groundwater has an obvious response to precipitation and meltwater, and (3) groundwater has the characteristic of rapid regeneration. Meanwhile, the recharge of groundwater in this study area is consistent with that of closed basin in northwest arid area (Xiao et al. 2018).

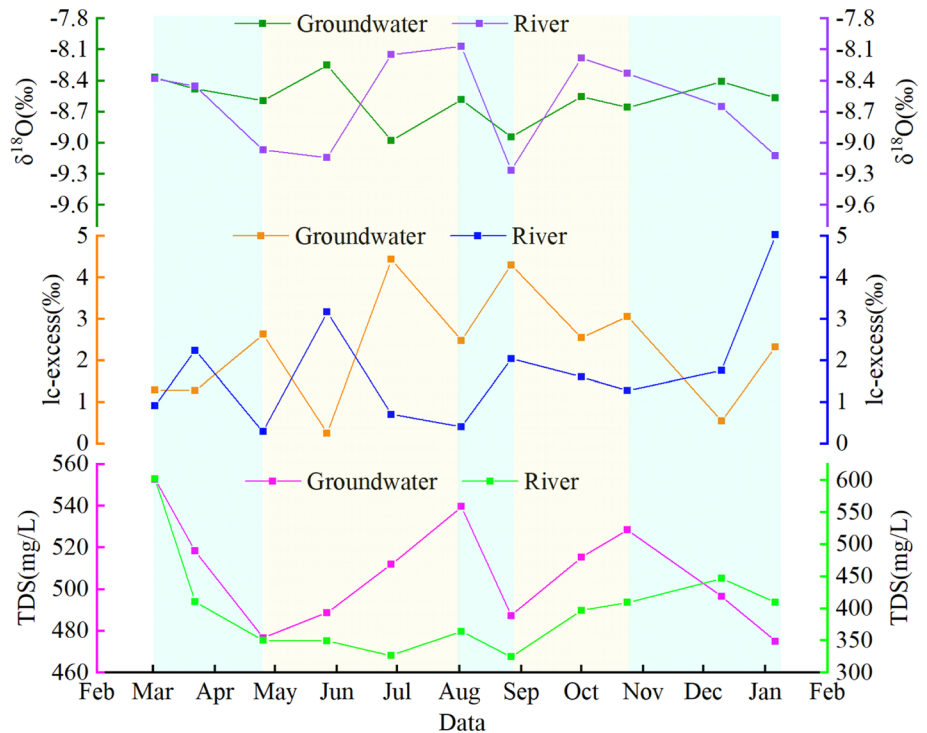
### Interaction between groundwater and surface water

The values of  $\delta^{18}O$  and  $\delta^2H$  in the groundwater and river water were not significantly different (Fig. 3), indicating that the recharge sources of the groundwater and river water were the same (both recharged from local precipitation and upstream river water). These results indicated a

strong hydrological connection between groundwater and river water in the river valley (Xu et al. 2017). Understanding the interaction between surface water and groundwater is crucial for clarifying the hydrological conditions in coupled water systems (Boyras and Kazezyilmaz-Alhan 2021; Sophocleous 2002; Yang et al. 2017). A continuous interaction between surface water and groundwater occurs near stream and lake areas and affects the total water budget of the hydrological system (Bertrand et al. 2014; Boyras and Kazezyilmaz-Alhan 2021; Winter et al. 1998).

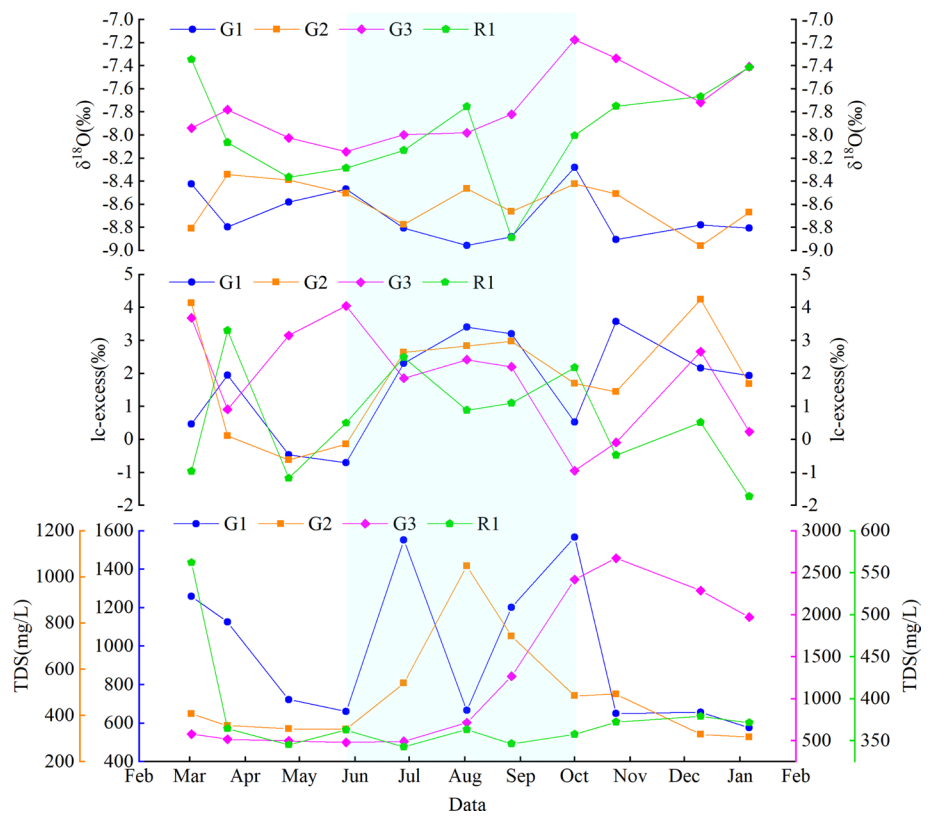
In this study, the interactions between groundwater and surface water were investigated in the main stream (Fig. 7) and river estuary (Fig. 8). According to the  $\delta^{18}O$ ,  $lc$ -excess and TDS values (Fig. 7), there can be two flow directions in the main stream: river flow to groundwater (from March to August) and groundwater flow to the river (from August to January in the next year). The  $\delta^{18}O$ ,  $lc$ -excess and TDS values of the groundwater and river water were different in the same flow direction due to the complexity of the recharge sources. As the temperature rose from March to May, the ice on the river began to melt. The TDS and  $\delta^{18}O$  values in the groundwater and river water rapidly decreased (Blue 1 in Fig. 7). As precipitation increased from May to August, the levels of the groundwater and river water increased (Fig. 2). The  $lc$ -excess and TDS values increased and the  $\delta^{18}O$  value decreased (Yellow 1 in Fig. 7). The groundwater path increased and the source of groundwater was recharged by precipitation at high altitudes due to the increasing pressure of the river on the groundwater. The  $\delta^{18}O$  and TDS

**Fig. 7** Characteristics of  $\delta^{18}O$ ,  $lc$ -excess and TDS values of groundwater (averaged from G5, G6 and G7) and river water (averaged from R2, R3 and R4) in the main stream





**Fig. 8** Characteristics of  $\delta^{18}\text{O}$ , lc-excess and TDS values of groundwater (G1, G2 and G3) and river water (R1) in the river estuary



values of the groundwater and river water rapidly decreased and their lc-excess values rapidly increased from August to September (Blue 2 in Fig. 7). Because the water levels of the groundwater and river declined (Fig. 2) and the flow direction changed as groundwater flowed to the river, the sources of groundwater and river water were recharged by precipitation or river water at high altitudes. The  $\delta^{18}\text{O}$  and TDS values of the groundwater and river water rapidly increased and their lc-excess values rapidly decreased from September to November (Yellow 2 in Fig. 7), indicating that more soil water flowed into the river through the groundwater. The water levels of the groundwater and river declined after November (Fig. 2), and soil water continuously flowed into the river through the groundwater. However, the groundwater and river water were recharged by water at high altitudes when the soil water was scarce (Blue 3 in Fig. 7).

The interaction between groundwater and surface water was more complex in this river estuary because of three interactions: groundwater and river, lake and river, and lake and groundwater. The influence of lake water on river water was not obvious (Figs. 4, 5 and 8) because the river water sampling sites were relatively far from the lake or because the river had a large amount of runoff (Fig. 1). The influence of lake water on groundwater (G1 and G2) was obvious (Figs. 4, 5, 6 and 8). The flow directions of the river estuary may be the same as those of the main stream: river flowing to groundwater (from March to August) and groundwater flowing to the river

(from August to January). However, the effect of lake water on groundwater was different from that of the main stream in the river estuary (Fig. 8). Although there was some flow from the groundwater to the river water in river estuaries, the groundwater was mainly recharged by groundwater runoff at high altitudes, and the river water was recharged by river water from upstream. Because the  $\delta^{18}\text{O}$  value in the groundwater was depleted compared with that in the river water, the TDS value in the groundwater was high compared with that in the river water (Fig. 8). The  $\delta^{18}\text{O}$  values of in the groundwater (G1 and G2) decreased, and the lc-excess and TDS values increased during the flood period (green in Fig. 8). The  $\delta^{18}\text{O}$  and TDS values of the groundwater (G2) increased in August (Fig. 8), and the level of groundwater declined in August (Fig. 2), indicating that the groundwater (G2) was affected by lake water. The  $\delta^{18}\text{O}$  and lc-excess values of the groundwater at G1 were similar to those of the groundwater at G2, but the TDS of the groundwater at G1 was higher than that of the groundwater at G2, indicating that the groundwater at G1 was largely affected by lake water. This may be because the groundwater at G1 was close to the lake, and the depth below the surface was shallow (Fig. 1). The variation level of the groundwater at G3 was similar to that of the groundwater at G7 (Fig. 2), but the  $\delta^{18}\text{O}$ , lc-excess and TDS values were different from those of other groundwater samples (Fig. 8) because the groundwater at G3 was affected by human activity (Figs. 4, 5, 6 and 8). The effect of human activities on groundwater-surface water interactions

has been previously confirmed (Hancock 2002; Liu et al. 2015; Yang et al. 2017).

### Changes in the water quality during the interaction between groundwater and surface water

Water is a necessary resource for human survival and development, and changes in water quality directly affect human health, so research on environmental quality impacts on water has attracted much attention (Lapworth et al. 2022; Ma et al. 2020; Ondrasek et al. 2021; Winter 2001). In this study, the interaction between surface water and groundwater had a certain impact on the water environment (Figs. 7 and 8). The TDS value of the river water increased after groundwater flowed into the river (Fig. 7), indicating that the water quality of the river water was degraded. Studies have found that high concentrations of dissolved organic carbon (DIC) occurred when DIC-enriched groundwater dominated river discharge (Stewart et al. 2022). The TDS value of the groundwater increased when the water levels of the river and groundwater increased (Figs. 2, 7 and 8). The groundwater path increased and the duration of the interaction between rocks and water increased. Therefore, the increasing pressure of the river on the groundwater will cause the deterioration of groundwater quality. The TDS value in the groundwater was higher than 1000 mg/L in the river estuary (Fig. 8), so the water quality of the groundwater should be focused because it had exceeded the national health standard (Chinese General Administration of Quality Supervision 2017). Moreover, the TDS value in the groundwater was higher in the river estuary than in the main stream, indicating that the quality of the groundwater was affected by the high ion concentrations and TDS content of the lake water. The phenomenon of water quality deterioration caused by saltwater intrusion is often reported in inland saltwater lakes and coastal zones (Akshitha et al. 2021; Li et al. 2016a, b). According to this study (Figs. 4, 5, 6 and 8) and previous studies (Li et al. 2021; Xiao et al. 2012), the quality of groundwater is affected by human activity. The contents of TDS of groundwater and river water increased from upstream to downstream in closed lake basins and mountain areas (Li et al. 2020; Xiao et al. 2018). The increases of TDS and  $\text{NO}_3^-$  are particularly prominent in the areas of intense natural variability (Chiogna et al. 2018; Li et al. 2018a, b; Longyang 2019) and human activity (Rose 2007; Zhang et al. 2017). In conclusion, the influence factors of water quality should be taken seriously.

### Conclusions

This study investigated the compositions of stable isotopes, hydrochemical characteristics and water levels of different water bodies, and revealed the responses of groundwater and rivers to precipitation and the interaction between surface

water and groundwater, and explored the influence of the interaction between groundwater and surface water on water quality. The LMWL ( $\delta^2\text{H}=7.99 \delta^{18}\text{O}+12.54$ ) and LEL of the groundwater and surface water (LEL-Groundwater:  $\delta^2\text{H}=5.72 \delta^{18}\text{O}-4.67$ ; LEL-River:  $\delta^2\text{H}=6.27 \delta^{18}\text{O}-0.58$ ; LEL-Lake:  $\delta^2\text{H}=4.44 \delta^{18}\text{O}-2.93$ ) were calculated by using the values of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in different water bodies. The hydrochemical types of most of the groundwater, river water and lake water samples were Ca–Mg– $\text{HCO}_3$ , Ca–Mg– $\text{HCO}_3$  and Na–Cl, respectively. The groundwater was slightly alkaline and the lake water was alkaline. The variation in the water level of the groundwater was consistent with that of the river, and the variation in the water level could be divided into two different periods: the flood period (June to October) and the dry period (November to May). There could be four possible reasons for the different characteristics of isotopes in the groundwater and river water in response to precipitation: recharging by meltwater, precipitation altitude and intensity, soil water or the interaction between groundwater and surface water. Our results also indicated that the water quality of the river water was degraded when the groundwater flowed into the river. The quality of the groundwater and river water was affected by the high ion concentrations and TDS content of the lake water. The increasing pressure of the river on the groundwater will cause the deterioration of groundwater quality. The quality of the groundwater was also affected by saltwater intrusion and human activity.

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**Data availability** The data used in this study are available from the corresponding author upon reasonable request.

### Declarations

**Conflict of interest** The authors declare that they have no competing interests.

**Ethical approval** The authors confirm that the work has been done according to ethical standards of scientific research.

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