

Stable isotope and hydrochemistry reveal source and quality of groundwater around Qinghai Lake, NE Qinghai-Tibet Plateau, China

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Abstract

The integrated use of isotopic and hydrochemical tracers is an effective approach for investigating complex hydrological processes of groundwater. Thorough understanding of recharge and quality of the groundwater is usually a prerequisite for effective groundwater management. This study investigated the water level, stable isotope and hydrochemistry of groundwater around the Qinghai Lake to reveal the recharge sources, hydrochemical evolution and water quality of groundwater. The relative altitudes of groundwater level ranged from -1.27 to 122.91 m with hydraulic gradient ranging from -6.20 to 43.14 the groundwater was flowing into the lake. Most of the groundwater points lay close to the local meteoric water line, and the slope of Local Evaporation Line of groundwater (LEL: $\delta^2\text{H} = 6.08 \delta^{18}\text{O} - 3.01$) was lower than the slopes of the LMWL, indicating that the groundwater were recharged primarily from precipitation at different altitude in the basin, though it had undergone varying degrees of evaporation. The hydrochemical analysis showed that the groundwater was mainly freshwater and its hydrochemical type was Ca-Mg-HCO₃. The groundwater chemistry was mainly controlled by carbonate dissolution around Qinghai Lake. Furthermore, high TDS and high concentrations of Na⁺, Mg²⁺, Cl⁻, or SO₄²⁻ in several groundwater were caused by the recharge source of lake water, the recharge source of fissure water, or by the dissolution of evaporite. The main sources of nitrate (NO₃⁻) in groundwater around Qinghai Lake were animal feces and sewage, suggesting that the pollution of groundwater should be paid more attention in animal husbandry areas on the Qinghai-Tibet Plateau, although the industrial and urbanization rates were relative low on the plateau. The scientific planning and engineering management of livestock manure and wastewater discharge in animal husbandry regions are very necessary to be carried out urgently, which could not only protect water resources for drinking, but also contribute to human health and sustainable development of the ecological environment of the Qinghai-Tibet Plateau.

Title page

Stable isotope and hydrochemistry reveal source and quality of groundwater around Qinghai Lake, NE Qinghai-Tibet Plateau, China

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Abstract: The integrated use of isotopic and hydrochemical tracers is an effective approach for investigating complex hydrological processes of groundwater. Thorough understanding of recharge and quality of the groundwater is usually a prerequisite for effective groundwater management. This study investigated the

water level, stable isotope and hydrochemistry of groundwater around the Qinghai Lake to reveal the recharge sources, hydrochemical evolution and water quality of groundwater. The relative altitudes of groundwater level ranged from -1.27 to 122.91 m (mean 25.70 m) with hydraulic gradient ranging from -6.20 to 43.14‰, indicating most of the groundwater was flowing into the lake. Most of the groundwater points lay close to the local meteoric water line (LMWL: $\delta^2\text{H} = 7.80 \delta^{18}\text{O} + 10.98$), and the slope of Local Evaporation Line of groundwater (LEL: $\delta^2\text{H} = 6.08 \delta^{18}\text{O} - 3.01$) was lower than the slopes of the LMWL, indicating that the groundwater were recharged primarily from precipitation at different altitude in the basin, though it had undergone varying degrees of evaporation. The hydrochemical analysis showed that the groundwater was mainly freshwater and its hydrochemical type was Ca-Mg- HCO_3 . The groundwater chemistry was mainly controlled by carbonate dissolution around Qinghai Lake. Furthermore, high TDS and high concentrations of Na^+ , Mg^{2+} , Cl^- , or SO_4^{2-} in several groundwater were caused by the recharge source of lake water (G29), the recharge source of fissure water (G1 and G6), or by the dissolution of evaporite (G4 and G25). The groundwater in location G4, G6, G11, G16, G24 and G25 were all currently exceed the drinking standards and not suitable for drinking. The main sources of nitrate (NO_3^-) in groundwater around Qinghai Lake were animal feces and sewage, suggesting that the pollution of groundwater should be paid more attention in animal husbandry areas on the Qinghai-Tibet Plateau, although the industrial and urbanization rates were relative low on the plateau. The scientific planning and engineering management of livestock manure and wastewater discharge in animal husbandry regions are very necessary to be carried out urgently, which could not only protect water resources for drinking, but also contribute to human health and sustainable development of the ecological environment of the Qinghai-Tibet Plateau.

Key words: Stable isotope; Hydrochemistry; Groundwater; Qinghai Lake; Qinghai-Tibet Plateau.

1. Introduction

Groundwater is a strategic and life-sustaining resource that is utilised for drinking water by 1.5 billion people around the world (Alley et al., 2002). Meanwhile, it plays significant roles in agriculture, the health of ecosystems, and the sustainable development of human societies and economies, especially in cold and semi-arid regions where surface water resources are relatively deficient (Giordano et al., 2009; Siebert et al., 2010; Qiu, 2010; Gleeson et al., 2012; Gleeson et al., 2016; Van Loon et al., 2016). In recent years, groundwater quality has been affected by the intensification of human activities as well as global climate change, which has attracted extensive attention worldwide (Li et al., 2013). Previous studies have found that groundwater levels have fallen at a phenomenal rate on both regional and global scales (Postel et al., 1996; Vorosmarty et al., 2000; Oki et al., 2006; Giordano et al., 2009; Rodell et al., 2009; Gleeson et al., 2012; Wada et al., 2012). Unsustainable depletion of groundwater would lead to a series of environmental problems, such as ground subsidence, aquifer unwatering, saltwater intrusion, and serious ecological degeneration (Matter et al., 2006; Edmunds, 2009; Liu et al., 2015; Goldin, 2016). Therefore, comprehensive studies of the spatial distribution, water quality, recharge source and hydrochemical evolution of regional groundwater are the foundation for the rational use of groundwater resources, which are also essential and contribute to the scientific management and sustainable development of regional water resources (Adams et al., 2001; Edmunds et al., 2006; Chang & Wang, 2010). The integrated use of isotopic and hydrochemical technology is an effective approach for investigating the complex hydrological processes of groundwater over a range of spatial and temporal scales (Clark & Frjtz, 1997; Gibson et al., 2005; Raghavendra et al., 2015; Wassenaar et al., 2011; Cui & Li, 2014). The recharge area and recharge elevation of groundwater could be determined based on the elevation effect of isotope in precipitation and the Local Meteoric Water Line, due to the isotope composition of groundwater mainly depends on the recharge source (Clark & Frjtz, 1997; Gu et al., 2011; Wang et al., 2015). Therefore, isotope and hydrochemical techniques are widely used to explore the recharge source and cyclic evolution of groundwater. For examples, Bicalho et al. (2019) developed a conceptual model for groundwater circulation by using isotopes and geochemical tracers. Younas et al. (2019) evaluated the recharge sources and geochemical identification in groundwater of the semi-arid alluvial aquifers of Pakistan based on stable isotopes and other major elemental data. Li et al. (2019) investigated the formation mechanism and mixing behaviour of Nanyang thermal spring based on isotopic and hydrochemistry techniques.

Qinghai Lake, the largest saltwater lake in China with an area of 4264 km², lies in the cold and semi-arid region of the north-eastern Tibetan Plateau. It is an important water body as well as an international wetland and China's national nature reserve for maintaining the ecological security of the north-eastern Tibetan Plateau (Tang et al., 1992; Cui & Li, 2015a). Meanwhile, it is a key area for social and economic development in Qinghai Province, such as ecological tourism and animal husbandry. Furthermore, the Qinghai Lake Basin is a closed drainage basin, it has become an ideal area for studying global climate change, environmental evolution and the uplift process of the Qinghai Tibetan Plateau, as well as the water cycle and eco-hydrological processes, because of its sensitivity to global climate change. In recent decades, a series of ecological and environmental problems have already arisen under the influence of climate change and human activities, such as grassland degradation, wetland reduction, and biodiversity decline, which have attracted attention from the local governments as well as the international community (Li et al., 2007; Xin, 2008; Cui et al., 2016). Previous studies, referring to geochemistry and water cycle of the Qinghai Lake Basin, were focus mainly on paleoclimate and environment change, lake evolution and its response to climate change, sources of precipitation, characteristics of river runoff, and so on (Chang et al., 2009; Cui & Li., 2015a; Cui & Li., 2015b; Fu et al., 2016; Tang et al., 2018). However, there are few studies having used the stable isotope and hydrochemical techniques to investigate the sources and water quality of the groundwater around Qinghai Lake.

Therefore, this study investigated water level, stable isotope and hydrochemistry of the groundwater around Qinghai Lake. The objectives are (1) to obtain the water level, stable isotope and hydrochemical characteristics of groundwater around Qinghai Lake; (2) to reveal and assess the water quality for drinking by analysing the ion concentrations (TDS, TH, Na⁺, Cl⁻, SO₄²⁻, and NO₃⁻); (3) to explore the possible causes of groundwater evolution and water quality. The results would contribute to knowledge about the hydrological and geochemical evolutions of groundwater around saltwater lakes in the Qinghai-Tibet Plateau, and inform water resource management in the Qinghai Lake Basin and Qinghai-Tibet Plateau.

2. Study area

The Qinghai Lake Basin (36°15'–38deg20'N, 97deg50'–101deg20'E), a closed basin with an area of 29661 km², lies in the cold and semiarid region of China's NE Qinghai-Tibet Plateau (Fig. 1). It also lies in a critical transitional zone where the Southeast Asian Monsoon (SEAM), the Westerly Circulation (WC) and the Qinghai-Tibet Plateau Monsoon meet (Cui & Li., 2015a; Li et al., 2018). The area and water surface altitude of Qinghai Lake were 4425 km² and 3195.82 m above sea level, respectively. The lake water has a salinity of 15.5 g/L and a pH of 9.06. Its water chemistry is characterised by ion proportions of Na⁺>Mg²⁺>K⁺>Ca²⁺ and Cl⁻>SO₄²⁻>CO₃²⁻>NO₃⁻ (Sun et al., 1991). Around the lake, the average annual air temperature is -0.1 °C, and the average annual precipitation is 357 mm (Cui & Li., 2015a). There are more than 50 rivers or streams flowing into Qinghai Lake (LZBCAS, 1994). The river system is unevenly distributed, being more developed in the west and north, and less in the east and south. River runoff is mainly sourced from the Buha, Shaliu, and Haergai Rivers, accounting for more than 75% of the total runoff into the lake.

The groundwater aquifers in the regions of late Palaeozoic marine limestone and sandstones, Silurian sandstone and schist, Triassic granite, and Quaternary deposits, are primarily carbonate aquifers, clastic rock aquifers, intrusive rock aquifers, and alluvial aquifers, respectively (Fig. 2; Cui & Li., 2014). The buried depth of groundwater around Qinghai Lake usually varies between 4 and 7 m. In the sparsely populated region, the buried depth is approximately 3 or 4 m, which is shallower than the water table in the densely populated region (Xiao et al., 2012).

3. Data source and methods

The precipitation samples were collected from every precipitation event during the period from January to December in 2018 at the meteorological bureau of Gangcha (3301.5 m a.s.l.), Qinghai Province, China. During the sampling period, a total of 104 samples, including 83 of rainwater and 21 of snow or sleet, were collected, filtered and stored in 30 ml high-density polyethylene square bottles for isotopic analyses.

Groundwater samples were collected from 34 sites in September 2018, which were evenly distributed around Qinghai Lake (Fig. 1). Location information of sampling sites was acquired using a global positioning system (GPS). All samples were filtered through 0.45 μm nylon filters. Water samples were stored in 30 ml high-density polyethylene square bottles for isotopic analyses and two 100 ml bottles for chemical analyses. Samples for cation testing were acidified with ultrapure HCl. The samples for anion and isotope testing were transported with ice bags and refrigerated at approximately 4 until laboratory analysis. The pH and electrical conductivity (EC) of groundwater was measured in situ using a handheld meter with a probe. The stable isotopes were analysed using the Los Gatos Research IWA-45-EP Isotopic Water Analyzer. The isotopic values were reported using the standard δ notation relative to the V-SMOW (Venna Standard Mean Ocean Water) standard; the precisions were ± 0.1 and ± 0.2 $\delta^{18}\text{O}$, respectively. The hydrochemical parameters of the groundwater samples were examined, including TDS (total dissolved solids), TH (total hardness), Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , and NO_3^- . The cations of the samples were determined using a Dionex-600 ion chromatograph, and the anions were measured using a Dionex-500 ion chromatograph. CO_3^{2-} and HCO_3^- were directly titrated in situ with phenolphthalein, methyl orange and sulfuric acid.

The Piper diagram (Piper, 1944) and the boomerang envelope model developed by Gibbs (Gibbs, 1970) were used to reveal the hydrochemical characteristics and evolution of groundwater. A Piper diagram generally used the major cations and anions of the water body to categorise the hydrogeochemical type of groundwater, river water and lake water, etc. (Piper, 1944; He et al., 2019). Gibbs (1970) analysed the chemical composition of surface water worldwide, and divided the factors controlling the composition of water into three endmembers, namely rock weathering, atmospheric precipitation, and evaporation/crystallisation (Machender et al., 2014). Meanwhile, the groundwater quality was assessed according to the Chinese State Standards for drinking water quality (Chinese Ministry of Health, 2006) and Chinese State Standards for groundwater water quality (Chinese General Administration of Quality Supervision, 2017). As shown in the standards, the highest acceptable limits of pH, TH, TDS and the concentrations of Na^+ , Cl^- , NO_3^- and SO_4^{2-} were 8.5, 450 mg/L, 1000 mg/L, 200 mg/L, 250 mg/L, 20 mg/L and 250 mg/L, respectively. In order to analyse the spatial characteristics of water level, isotope and hydrochemistry of groundwater around Qinghai Lake in more detail, the area around the lake was divided into four regions: east (G1-G11), south (G12-G20), west (G21-G29), and north (G30-G34) of Qinghai Lake.

4. Results and discussion

4.1 Isotope characteristic of precipitation

The $\delta^{18}\text{O}$ values of precipitation ranged from -30.54 to -0.76-222.63 to -0.33 ranges reported previously for global (-50 - +10 $\delta^{18}\text{O}$, -350 - +502001) and China (-35.5 - +2.5+24.0 Water Line (LMWL) was simulated by using the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ content of precipitation (Fig. 3): $\delta^2\text{H} = 7.80 \delta^{18}\text{O} + 10.98$ VSMOW ($n = 104$, $R = 0.985$). The slope of LMWL was similar to the slopes of meteoric water lines for Lasa (7.90; Tian et al., 2001), northwestern China (7.05; Liu et al., 2008) and western China (7.56; Ma et al., 2009). All slopes were less than 8, indicating that some non-equilibrium evaporation processes occurred as raindrops falling below the cloud base (Friedman et al., 1962; Dansgaard, 1964; Araguás-Araguás et al., 1998; Cui & Li, 2015a; Zhang & Wang, 2016). The LMWL was slightly above the GMWL due to the high d-excess value of precipitation in the Qinghai Lake Basin, suggesting that some continental moisture recycled to precipitation under low relative humidity conditions (Clark & Fritz, 1997; Pang et al., 2011; Kong et al., 2013; Pang et al., 2017).

4.2 Level variation of groundwater around Qinghai Lake

Due to some residents' wells being sealed, groundwater level was investigated in only 14 sites among the 34 sampling sites around Qinghai Lake (Table 2). The buried depth of the groundwater level ranged from 0.85 to 10.87 m (mean 3.97 m). The depth range was similar as that of previous study (0.9 m-8.2 m, mean 3.80 m; Xiao et al., 2013). However, the buried depth of groundwater level couldn't reflect the direction of groundwater due to the different elevation among the sampling sites. The relative altitude between the groundwater level and the water level of Qinghai Lake was calculated at each sampling site (Table 2). The

relative altitude of groundwater level ranged from -1.27 to 122.91 m (mean 25.70 m). The relative altitudes of most of the groundwater level, excluding G6 and G29, were positive values (Table 2), indicating the groundwater level were higher than the water level of Qinghai Lake, and most of the groundwater flowed into the lake, while the groundwater in location G6 and G29 would be recharged by the lake water. Based on the data of the positive altitude of groundwater level (Table 2), the average relative altitude was calculated for each region around the lake and were arranged: south > north > west > east, with altitude of 46.70 m, 38.32 m, 38.04 m, and 7.58 m, respectively.

The hydraulic gradient of each groundwater was calculated based on the relative altitude of groundwater level and the distance between sample site and Qinghai Lake (Table 2). The hydraulic gradient ranged from -6.20 to 43.14 gradient of each region around the lake was in the order: south > east > north > west, with value of 19.70 driving force of groundwater at the south of Qinghai Lake was stronger than other regions. According to the Fig. 2, fault escarpments and lacustrine sediment terraces had been developed extensively along the southern shore of Qinghai Lake, while the areas surrounding the lake and rivers were overlain by alluvial and lacustrine sediments whose age ranges from Quaternary to recent times (Fig. 2). The mountain runoff in the diluvial and alluvial plains recharged the groundwater via infiltration (Xiao et al. 2012). Therefore, the distribution and variation of groundwater level around Qinghai Lake would be mainly related to geomorphology, terrain, groundwater aquifers, fault, and so on (Jin et al., 2009; Xiao et al., 2012).

4.3 Stable isotopes of groundwater around Qinghai Lake

The $\delta^{18}\text{O}$ values of the groundwater around Qinghai Lake ranged from -10.41 to -5.86 $\delta^2\text{H}$ values ranged from -66.64 to -41.99 in the Qinghai Lake Basin (Fig. 3, Fig. 4). Comparing the groundwater samples with the local meteoric water line (LMWL) was useful for determining the water source in the investigation of the regional hydrology (Clark & Fritz, 1997). Most of the isotope data points lay close to the LMWL, and the slope of local evaporation line of groundwater (LEL: $\delta^2\text{H} = 6.08 \delta^{18}\text{O} - 3.01$) was lower than the slope of LMWL (7.80; Fig. 4). These all indicated that the groundwater around Qinghai Lake mainly came from the precipitation in the basin, which had undergone variable degrees of evaporation before infiltration (Friedman et al., 1962; Gremillion & Wanielist, 2000; Cui & Li., 2014).

According to the Fig. 5, the $\delta^{18}\text{O}$ values of the groundwater lying on the east, south, west and north of Qinghai Lake ranged from -10.41 to -7.78 and from -7.20 to -6.68 $\delta^{18}\text{O}$ values of -8.62 respectively, indicating that the groundwater around the lake were recharged by precipitation at different altitude, and the precipitation had undergone variable degree of evaporation before infiltration (Friedman et al., 1962; Gremillion & Wanielist, 2000; Cui & Li., 2014). The average $\delta^{18}\text{O}$ of the groundwater was in the order: $\delta^{18}\text{O}_{\text{North}} < \delta^{18}\text{O}_{\text{West}} < \delta^{18}\text{O}_{\text{South}} < \delta^{18}\text{O}_{\text{East}}$. There were two possible scenarios: One possibility was that the groundwater lying on the east of Qinghai Lake could have a relative higher recharge altitude than other regions around Qinghai Lake, the second possibility was that the groundwater lying on the north of Qinghai Lake could have undergone a stronger evaporation than other regions around the lake before infiltration. The LEL slope of groundwater lying on the east, south, west and north of Qinghai Lake was 7.25, 4.48, 4.22 and 3.94, respectively (Table 3; Fig. 4), indicating that evaporation degree of the groundwater before infiltration was in the order: North > West > South > East (Weyhenmeyer et al., 2002; Dogramaci et al., 2012), the result was agreed upon that of the second possible scenario. Comparing with the east and south regions, the north and west regions overlain by alluvial and lacustrine sediments had a relatively flat terrain with low hydraulic gradient (Fig. 1, Fig. 2, Table 2), leading the surface water flowed slowly and had long time to infiltrate (Gibson et al. 2005; Buda, 2013). The longer time surface water infiltrated into groundwater, the higher evaporation degree the groundwater was undergone before infiltration (Weyhenmeyer et al., 2002). These all suggested that evaporation degree of the groundwater in west and north regions was higher than that in south and east of Qinghai Lake.

In order to eliminate the influence of evaporation on the groundwater, the intersection between the LEL of groundwater in each region and the LMWL of precipitation was calculated (Table 3). The values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ on the intersection were the recharge (initial) isotope values from precipitation to the groundwater (Clark & Fritz, 1997; Cui & Li, 2014). The initial isotope value of the groundwater was in the order:

δ_{North} , δ_{West} , δ_{South} , δ_{East} , with value of -7.303). Due to altitude effect of $\delta^{18}\text{O}$ in precipitation, the average recharge altitude of the groundwater in four regions was in the order: East > South > West > North (Cui & Li, 2014).

According to the Fig. 5, the $\delta^{18}\text{O}$ value of G29 (-5.86‰) of lake water (average $\delta^{18}\text{O}$: 1.61‰) and the water level of G29 (relative altitude of -1.27m, hydraulic gradient of -6.20‰) (Table 2), suggesting that the groundwater in location G29 would be recharged by Qinghai Lake water. The water level of G6 (relative altitude of -0.12m) was also lower than the water level of Qinghai Lake (Table 2), but the $\delta^{18}\text{O}$ value of G6 (-9.03‰) was low (Fig. 5). There could be two reasons for the low water level and low $\delta^{18}\text{O}$ value in G6. One possibility was that the hydraulic connection between the G6 and lake water was not closely due to the slightly negative hydraulic gradient (-0.24‰) and the second possibility was that the G6 was recharged by fissure water with relative depleted isotopes, because G6 was located on the fault zone of the southern margin of Zhongqilian Massif (Fig. 2). Overall, the groundwater around the lake was mainly recharged by precipitation, and the $\delta^{18}\text{O}$ values of groundwater in different locations suggested that the altitude of the recharge areas varied.

4.4 Hydrochemistry groundwater around Qinghai Lake

The pH values of the groundwater around the lake ranged from 7.54 to 8.36 with a mean value of 8.04, indicating that the groundwater was slightly alkaline. The pH values were similar as those of the river waters (7.60-8.55) in the Qinghai Lake Basin (Jin et al., 2010). The electrical conductivity (EC) and total dissolved solids (TDS) values of most of groundwater samples, excluding G4, G6 and G29, ranged from 0.39 to 1.76 mS/cm and from 269 to 885 mg/L, respectively, with averages of 0.89 mS/cm and 523 mg/L, respectively. Compared with the river water (the average EC and TDS were 0.17 mS/cm and 341.79 mg/L, respectively) (Cui & Li, 2015b), the EC and TDS of the groundwater were relatively high, indicating that the interaction between water and rocks was stronger in the groundwater than that in the river water. The hydrochemical type of most of groundwater samples, excluding G1, G4, G6, G7, G10, G11, G23, G25, and G29, was Ca-Mg- HCO_3 (Fig. 6). The concentrations of Ca^{2+} and Mg^{2+} were relatively high, accounting for more than 60% of the cations. This finding indicated that the chemistry of groundwater would be mainly controlled by carbonate dissolution around Qinghai Lake.

For each index according to the Table 1, The TDS of groundwater at G4, G6 and G25 were more than 1000 mg/L; The Na^+ concentration of groundwater at G1, G4, G6, G25 and G29 were more than 170 mg/L; The Mg^{2+} concentration of groundwater at G4 were more than 110 mg/L; The Cl^- concentration of groundwater at G4 and G6 were more than 140 mg/L; The SO_4^{2-} concentration of groundwater at G1, G4 and G25 were more than 150 mg/L. And the hydrochemical types of G1, G4, G6, G25 and G29 were Na-Cl- SO_4 , Ca-Mg-Cl, Na-Cl- CO_3 , Na-Ca- HCO_3 , Na-Mg- HCO_3 , respectively (Fig. 6). There could be two reasons for the high TDS and high concentrations of Na^+ , Mg^{2+} , Cl^- , and SO_4^{2-} in the groundwater. One possibility was that the longer flow path increased the interaction time between water and rocks and raised the dissolved solids; the second possibility was that the groundwater was recharged by the lake water. The relative altitude of water level of G29 (-1.27 m) was lower than water level of Qinghai Lake; the location of G29 is very near from Qinghai Lake, with the distance of 0.20 km (Table 1, Fig. 1); and the $\delta^{18}\text{O}$ value of G29 (-5.86‰) was close to the lake water, indicating that there would have a significant hydraulic contact between G29 and the lake, and G29 would be recharged partly by the Qinghai Lake water (Cui et al., 2016). The $\delta^{18}\text{O}$ of G1 (-8.29‰) was lower than the lake water, indicating that the G1 and G6 were recharged partly by fissure water with relative depleted isotope. The relative altitudes of water level of G4 and G25 were higher than that of Qinghai Lake, and the $\delta^{18}\text{O}$ value of G4 (-7.85‰) was lower than the lake water, indicating that there would have a significant hydraulic contact between G4, G25 and the lake. High TDS and high concentrations would be dominated by heavy evaporation or dissolved solids (Xiao et al., 2012; Cui & Li, 2014). Meanwhile, G1, G4, G6, G25 and G29 were all located at east and west of Qinghai Lake (Fig. 1), suggesting that the sources of groundwater at east and west of Qinghai Lake were relative complex.

As shown in Fig. 7, all of the samples fell within the evolutionary path from “Rock dominance” to “Ocean” in the Gibbs boomerang envelope (Gibbs, 1970; Machender et al., 2014), suggesting that the chemical

composition of the groundwater around the lake was dominated by rock-weathering. The results were supported by that rock weathering, ion exchange and precipitation were the major geochemical processes responsible for the solutes in the groundwater within the Qinghai Lake Basin (Xiao et al. 2012; Cui & Li, 2014). Meanwhile, relative high concentrations of Na^+ and Cl^- in some groundwater were due to the evaporite dissolution in this area (Xu et al., 2010) or to the long migration path of groundwater with strong water-rock interaction (Cui & Li, 2014).

4.5 Evaluation of groundwater quality

In drinking water, high concentrations of some ions could cause great harm to human health, such as Na^+ , Cl^- , NO_3^- , SO_4^{2-} , and so on (Wasana et al., 2016; Nixdorf et al., 2017; Wasana et al., 2017). For example, high NO_3^- concentrations could result in birth defect, hypertension and high-Fe hemoglobin (Carpenter et al. 1998; Ho et al., 2011; Jones et al., 2016); high SO_4^{2-} concentrations could cause diarrhea, dehydration and weight loss (World Health Organization, 2008). According to the Chinese State Standards for drinking water quality (Chinese Ministry of Health, 2006) and Chinese State Standards for groundwater water quality (Chinese General Administration of Quality Supervision, 2017), the highest acceptable limits of pH, TDS, total hardness (TH) and the concentrations of Na^+ , Cl^- , SO_4^{2-} , and NO_3^- were 8.5, 1000 mg/L, 450 mg/L, 200 mg/L, 250 mg/L, 250 mg/L and 20 mg/L, respectively. As shown in Table 1 and Fig. 8, most of the groundwater was slightly and moderately hard freshwater, which fell within the standards for drinking water in all indices. However, the TDS of groundwater at location G4 (1520.05 mg/L), G6 (1092.44 mg/L) and G25 (1497.42 mg/L) was higher than the highest acceptable limits set by the standard (1000 mg/L) (Table 1); the Na^+ concentration of groundwater at G6 (371.34 mg/L) and G25 (308.21 mg/L) were higher than the standard of 200 mg/L; the Cl^- concentration of groundwater at G4 (294.79 mg/L) was higher than the standard of 250 mg/L; and the NO_3^- concentration of groundwater at G4 (100.88 mg/L), G11 (53.82 mg/L), G16 (74.46 mg/L), G24 (26.71 mg/L) and G25 (117.64 mg/L) were higher than the standard of 20 mg/L (Fig. 8). These all indicated that the groundwater in location G4, G6, G11, G16, G24 and G25 were all currently exceed the drinking standards and not suitable for drinking (Carpenter et al. 1998; Ho et al., 2011; Wasana et al., 2016; Wasana et al., 2017). According to the results of water level, isotope and hydrochemistry of groundwater around Qinghai Lake, high TDS and concentrations of groundwater in location G4 and G25 were dominated by heavy evaporation or dissolved solids (Xiao et al. 2012; Cui & Li, 2014). And high TDS and concentrations of groundwater in location G6 were dominated by recharging source of fissure water (Xu et al., 2010; Cui & Li, 2014). These all reflected the influences of natural factors on groundwater quality, such as geomorphology, terrain, groundwater aquifers, fault, and so on (Jin et al., 2009; Xiao et al., 2012).

In generally, the concentration of nitrate nitrogen in the water was higher than 3.0 mg/L, indicating that the water body was influenced by human activities (Babiker et al., 2004). As shown in Table 1, the concentration of NO_3^- in the groundwater were all higher than 4.60 mg/L, indicating that the groundwater around Qinghai Lake was affected by human activities, especially in location G4, G11, G16, G24 and G25 with high NO_3^- over the highest acceptable limits of NO_3^- (20 mg/L). Qinghai lake basin, lying in the Northeast Qinghai-Tibet Plateau, was a sparsely populated region with few mineral exploitation and large-scale factories (Li et al., 2018). Meanwhile, the region around the lake was a center of ecological tourism and animal husbandry for the Qinghai province (Tang et al., 1992). Therefore, the main sources of nitrate (NO_3^-) in groundwater around Qinghai Lake were animal feces and sewage. In order to further identify the source of nitrate in groundwater around the lake, the relationship between NO_3^- and Cl^- of groundwater was analysed (Fig. 9). Because the ratio analysis of major ions in groundwater, such as $\text{NO}_3^-/\text{Cl}^-$, $\text{SO}_4^{2-}/\text{Cl}^-$ and Cl^-/Br^- , could be used to determine the source of nitrate pollution and the migration process of pollutants (Liu et al., 2006; Chen et al., 2009; Murgulet et al., 2013). As shown in the Fig. 9, there was a positive correlation between NO_3^- and Cl^- ions in groundwater ($n=34$, $P<0.001$, $R=0.747$), further suggesting that the NO_3^- in groundwater was mainly originated from animal feces and sewage, which mainly came from the livestock breeding around Qinghai Lake.

Overall, the groundwater around Qinghai Lake came primarily from the atmospheric precipitation in the basin, the isotope and hydrochemistry of groundwater were mainly depended on the initial precipitation

and the dissolution of surrounding rocks in runoff process, which were controlled by groundwater aquifers, fault, terrain and geomorphology (Jin et al., 2009; Xiao et al., 2012; Cui & Li, 2014). But the impacts of livestock manure and waste water on groundwater quality could not be ignored around the lake, and even high concentrations of some ions in groundwater at east and west of Qinghai Lake had exceeded the highest acceptable limit values for drinking water. These suggested that the pollution of groundwater in animal husbandry areas on the Qinghai-Tibet Plateau should be paid more attention, although the industrial and urbanization rates were evenly relative low on the plateau (Wang et al, 2014). Hence, the scientific planning and engineering management of livestock manure and wastewater discharge in animal husbandry regions are very necessary to be carried out urgently, which could not only protect water resources for drinking, but also contribute to human health and sustainable development of the environment of the Qinghai-Tibet Plateau.

5. Conclusions

This study investigated the stable isotope of precipitation and water level, stable isotope and hydrochemistry of groundwater around Qinghai Lake. The LMWL was $\delta^2\text{H} = 7.80 \delta^{18}\text{O} + 10.98$, indicating that some non-equilibrium evaporation processes occurred as raindrops fell below the cloud base, and some continental moisture recycled to precipitation under low relative humidity conditions. Most of the groundwater points lay close to the LMWL, and the slope of LEL of groundwater was lower than the slope of LMWL, indicating that the groundwater around Qinghai Lake mainly came from the precipitation at different altitude in the basin, which had been undergone variable degrees of evaporation before infiltration. Most of the groundwater was slightly and moderately hard freshwater, and the hydrochemical type of groundwater was Ca-Mg- HCO_3 . The chemistry of groundwater would be mainly controlled by carbonate dissolution around Qinghai Lake. Meanwhile, the groundwater sources at east and west of Qinghai Lake were relative complex.

Most of the groundwater was slightly and moderately hard freshwater and fell within the standards for drinking water in all indices. However, the groundwater in location G4 (TDS, Cl^- , and NO_3^-), G6 (TDS and Na^+), G11 (NO_3^-), G16 (NO_3^-), G24 (NO_3^-) and G25 (TDS, Na^+ and NO_3^-) were all currently exceed the drinking standards and not suitable for drinking. Overall, the impacts of livestock manure and waste water on groundwater quality could not be ignored around the lake. Scientific planning and engineering management of livestock manure and wastewater discharge in animal husbandry regions are very necessary to be carried out urgently, which could not only protect water resources for drinking, but also contribute to human health and sustainable development of the environment of the Qinghai-Tibet Plateau.

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Data Availability Statement

Data available on request from the authors: The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Captions of Figures and Tables

Fig. 1. Location of the Qinghai Lake Basin and sites for sampling precipitation and groundwater

Fig.2. Geological map and elevation contours of the Qinghai Lake Basin

Φιγ. 3. Τη ρελατιονσηπ βετωεεν $\delta^2\text{H}$ ανδ $\delta^{18}\text{O}$ ιν πρεσιπιτατιον οφ τηε Χινγηαι Λακε Βασιν Φιγυρε

Fig. 4. Characteristics of the stable isotope of groundwater in four regions with the LMWL in the Qinghai Lake Basin

Φιγ. 5. $\delta^{18}\text{O}$ ιν γρουνδωατερ ιν διωφερεντ ρεγιον αρουνδ Χινγηαι Λακε

Fig. 6. Ternary plots of cations and anions of the groundwater around Qinghai Lake

Fig. 7. Plots of the major ions within the Gibbs boomerang model for groundwater around Qinghai Lake

Fig.8. Concentrations of Na^+ , Cl^- , SO_4^{2-} , and NO_3^- in groundwater around Qinghai Lake

Fig. 9. Relationship between NO_3^- and Cl^- in groundwater around Qinghai Lake

Table 1. Stable isotope and hydrochemical compositions of the groundwater around Qinghai Lake

Table 2. The water level information of 14 groundwater around Qinghai Lake

Table 3. The evaporation line of groundwater in different parts around Qinghai Lake

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