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RESEARCH ARTICLE - HYDROLOGY

Hydrochemical characteristics and water quality assessment of groundwater in the Yishu River basin

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Abstract

Groundwater is the primary source of water for human development in the Yishu River basin, and therefore characterizing groundwater quality is essential for sustainable development of groundwater resources in the region. This study aimed to determine the hydrochemical characteristics and water quality of groundwater in the Yishu River basin by sampling 45 wells in October 2016 and May 2017. Hydrochemical characteristics of groundwater were determined using integrated hydrochemical analysis and the groundwater quality was evaluated based on the water quality index (WQI). Groundwater of the Yishu River basin was characterized as weak alkaline hard water with mean concentrations of total hardness and total dissolved solids of less than 500 mg L^{-1} and 1000 mg L^{-1}, respectively, and the principal chemical components of groundwater were higher in 2016 than in 2017. A Piper diagram showed that 64.4% of the water samples contained Ca–HCO_3 type water and 27% contained mixed water (27%). The dominant processes driving the chemical composition of groundwater were found to be dissolution of silicate and carbonate minerals and cation exchange. The saturation index indicated that carbonate minerals were supersaturated, whereas gypsum, fluorite, and halite were unsaturated. The WQI indicated good groundwater quality in the Yishu River basin, with only one water sample classified as having "poor" water quality in 2016 and 2017, respectively. However, these samples contained high nitrate concentrations (> 200 mg L^{-1}), which may be the result of domestic sewage discharge and/or the use of agricultural fertilizers.

Keywords Groundwater · Hydrochemical characteristics · Water quality assessment · Yishu River basin

Introduction

Groundwater resources are a valuable component of freshwater resources and the hydrological cycle and have direct importance for sustaining natural ecosystems and human development (Bouderbala et al. 2016; Liu et al. 2019a; Yetiş et al. 2019). Under natural conditions, groundwater is characterized by good and stable water quality, and therefore can act as an ideal drinking water source (Moore et al. 2006). However, increased human development has resulted in the pollution of the groundwater environment to varying degrees, in particular, domestic sewage and wastewater discharged by industrial and mining enterprises has infiltrated into the groundwater system in many regions, thereby posing a serious threat to groundwater quality (Gnanachandrasamy et al. 2018; Liu et al. 2018). The quality of regional groundwater can be evaluated scientifically through the analysis of groundwater hydrochemical data. These data provide the necessary basis for the prevention and control of groundwater pollution and facilitate sustainable development of groundwater resources (Yang et al. 2016; Tiwari et al. 2017).

There have been many studies on the hydrochemistry of groundwater in recent years. These studies have used various integrated geochemical methods to assess groundwater quality, including statistical analysis, Piper diagrams, Gibbs diagrams, ion ratio scatter diagrams, and the saturation index (SI). Statistical analysis can reflect the basic characteristics of groundwater chemistry, whereas the Piper diagram can facilitate an understanding of the chemical types of groundwater. Gibbs diagrams and the major ions ratio reveal the

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underlying processes responsible for the chemical components in groundwater, and SI reflects the dissolution and precipitation of minerals (Piper 1944; Gibbs 1970; Yang et al. 2016; Liu et al. 2019a; Li et al. 2020). The water quality index (WQI) is an accessible and widely used method for assessing groundwater quality, and is a mathematical tool which considers the impact of various water quality indicators by assigning weights to the various water quality variables, thereby transforming a large number of water quality variables into a dimensionless single value representing the overall water quality (Şener et al. 2017; Hamlat and Guidoum 2018; Wagh et al. 2019).

Groundwater is the dominant source of water for industrial, agricultural and domestic use in the Yishu River basin. Therefore, the characterization of groundwater hydrochemical characteristics and water quality is essential for sustainable development of groundwater resources in the Yishu River basin. However, the groundwater hydrochemistry and water quality of the study area remains poorly studied. The present study conducted sampling of groundwater during both the dry and wet seasons, and aimed to characterize the groundwater hydro-chemical characteristics and its underlying processes using integrated hydrochemical methods such as Piper diagrams, Gibbs diagrams, the ionic ratio coefficient, and SI. In addition, the WQI was used to evaluate and compare the water quality over the dry and wet seasons. The results of the present study can further understanding of the geochemical characteristics of groundwater of the Yishu River basin and can serve as the basis for sustainable development of groundwater resources in this region. This study can also act as a reference for hydrochemistry research and water quality evaluation of groundwater in other areas.

Study area

The study area of the present study is the Yishu River basin, which contains the Yi and Shu rivers comprising two large-scale mountain torrent channels running through the Yimeng Mountains, from north to south. The Yishu River basin (Fig. 1) is located in the southern part of Shandong Province in the area bounded by latitude 34°17′–36°23′ north and longitude 117°25′–119°11′ east. The basin falls within a warm temperate continental monsoon climate zone with four distinct seasons, abundant sunshine and abundant rainfall. The annual mean precipitation measured over 2003–2015 is 880.6 mm, with the rainy season extending over May–August. The basin contains three main mountain ranges from north to south, namely the Yi Mountains, Meng Mountains and Ni Mountains, extending northwest to southeast. The terrain of the basin is high in the northwest and low in the southeast, with hilly areas accounting for more than 70% of the total area and forming part of the low hilly area of southeastern Shandong. The northwest part of the basin contains bedrock mountainous area, whereas the middle part contains hilly area and the lower reaches of the Yishu River basin in the south contains alluvial-proluvial plain. The Yishu River basin forms part of the Huai River basin, and the overall river flow direction within the basin is from north to south. The Yi River originates in the Lu Mountain and flows into Jiangsu Province in Tancheng City with a maximum runoff of 1.54×10^4 m^3 s^{-1}, whereas the Shu River originates in Yi Mountain and eventually discharges into the Yellow Sea through Jiangsu, with a total length of 260 km and a maximum runoff of 7.290×10^3 m^3 s^{-1}.

The study area contains well-developed faults and experiences frequent geotectonic activities (Fig. 1). The Yishu fault zone (Tanlu fault zone) consists of four main faults which cover the entire area, namely Changyi-Dadian, Anqiu-Juxian, Yishui-Tangtou and Tanqin-Gegou. The lithology of the Yishu River basin is relatively complex, including Neogene purple-red sandstone and glutenite, Cretaceous volcanic rocks and Jurassic sandstone and shale, Carboniferous and Permian coal measured strata, Ordovician and Cambrian limestone, Archaean complex and igneous rocks of various periods.

Groundwater can be categorized into four types according to groundwater storage conditions, the hydrological properties of rocks and the hydraulic characteristics of groundwater (Wang et al. 2014). The pore water of loose rocks is mainly distributed within the plain areas and along the banks of the Yi and Shu rivers and their tributaries, and the aquifer consists of medium-fine sand, coarse sand and gravel. The pore water of loose rocks is also distributed in the valleys and the margins of valleys of low mountains and hills in the central and northern parts of the study area. The pore-fissure water of clastic rocks is stored in Permian, Carboniferous, Jurassic, Cretaceous, Neogene and Carboniferous strata. The fracture-karst water in carbonate rocks occurs in the Cambrian and Ordovician limestone with fissure karst development and also in the Sinian and Cambrian limestone-shale, sandstone and marl. The fissure water of bedrock is mainly distributed in weathering fissures and structural fissures of magmatic rocks in different stages, and the depth and water quality of groundwater show obvious seasonal changes. The recharge of groundwater in the Yishu River basin is mainly through precipitation infiltration, followed by irrigation infiltration, valley undercurrent recharge, lateral inflow recharge and river lateral recharge.

Materials and methods

Sampling and analysis

In this study, 45 wells in Yishu River basin were investigated and sampled. Groundwater samples were sampled twice in

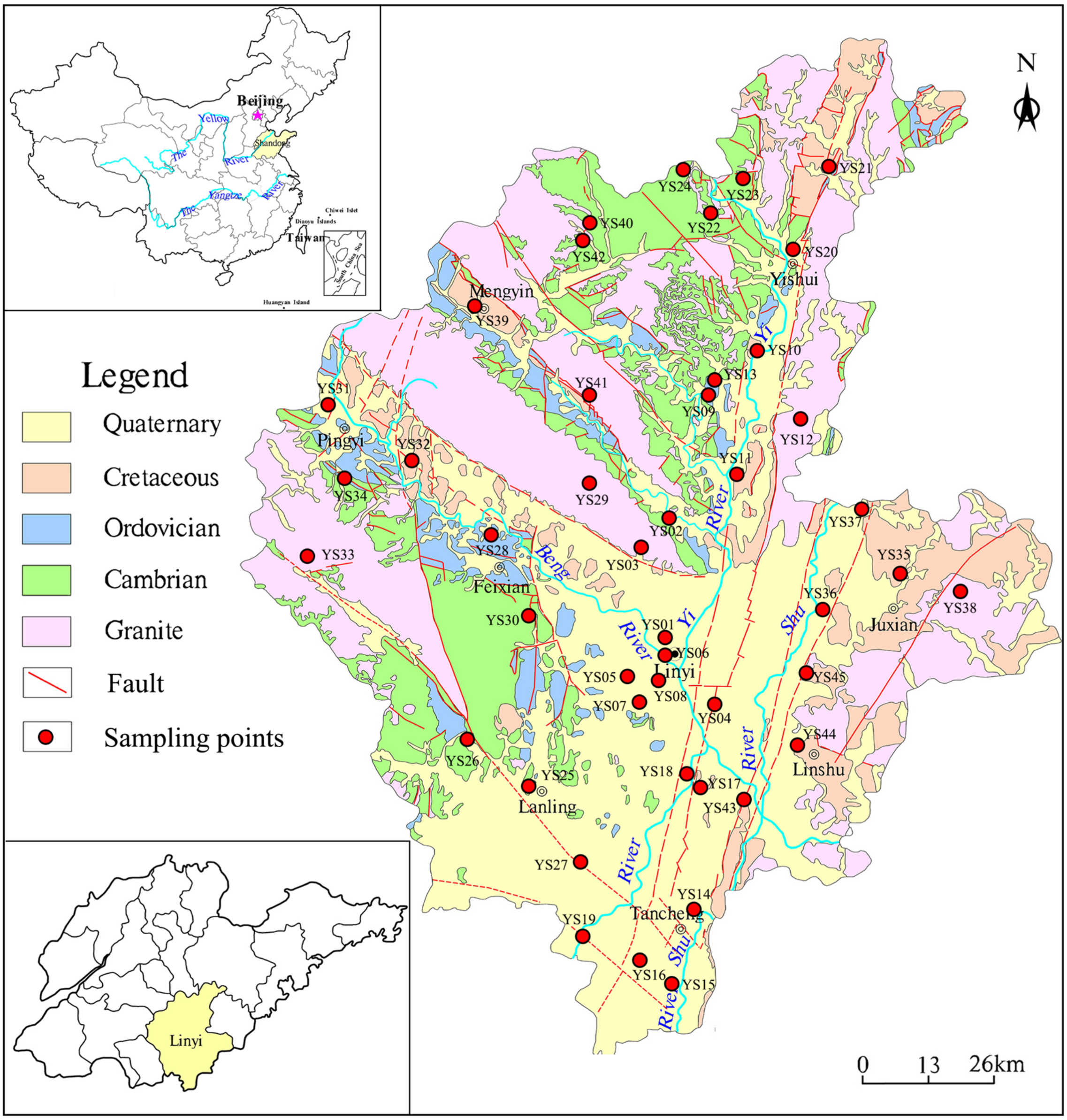

Fig. 1 Location of the Yishu River basin and distribution of groundwater samples

October 2016 and May 2017, respectively. All samples were collected from pumping wells most of which are less than 30 m in depth. The sampling position is shown in Fig. 1. Samples were taken from plastic bottles cleaned (2–3 times) by water samples to be sampled. After sampling, the sampling bottle was sealed with a sealing film to prevent the leakage of water samples, and refrigerated (4 °C) until laboratory analysis.

The pH value of groundwater samples was determined in the laboratory by pH acidity meter (PHS-3C). Total dissolved solids (TDS), K^+, Na^+, Ca^{2+}, Mg^{2+} and total hardness (TH) were analyzed by inductively coupled plasma-optical emission spectrometer (optima7000DV). SO_4^{2-}, Cl^-, NO_3^-, F^- were measured by using ion chromatography (ICS-600). HCO_3^- and chemical oxygen demand (COD) were determined by titration. In addition, the normalized inorganic charge balance (NICB) was calculated as follows:

$$\mathrm{NICB} = 100 \times (\mathrm{TZ}^+ - \mathrm{TZ}^-)/\mathrm{TZ}^+ \quad (1)$$

where TZ^+ is the cationic charge ($TZ^+ = [Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}]$, meq/L) and TZ^- is the anionic charge ($TZ^- = [Cl^-] + [HCO_3^-] + [SO_4^{2-}] + [NO_3^-] + [F^-]$, meq/L). In this study, the absolute values of the NICB in all samples were less than 9, with a mean value of 4.84, suggesting the accuracy of the water quality data.

Analytical methods

In this study, the basic characteristics of groundwater hydrochemistry are analyzed by using the descriptive statistics technique. Based on the traditional classical hydrochemical methods such as Piper diagram (Piper 1944), Gibbs model (Gibbs 1970), ion ratios and saturation indexes (SI), the hydrochemical characteristics, and formation mechanism of groundwater are determined. The saturation indexes (SI) values were calculated using PHREEQC software.

$$SI = \log \frac{IAP}{K} \tag{2}$$

where IAP indicates the ion activity product and K stands the mineral dissolution equilibrium constant. $SI > 0$, $SI = 0$ and $SI < 0$, respectively, represent the three states of the mineral in the supersaturated state, the equilibrium state and the unsaturated state.

Water quality index (WQI), which can reflect the comprehensive impact of multiple parameters on water quality, is a simple, effective and popular technique (Adimalla 2019; Deepa and Venkateswaran 2018; Şener et al. 2017). Based on the relative importance of different chemical components in water quality evaluation, different weight (w_i) values were set to calculate WQI values. The calculation process was shown in Fig. 2. In this study, the groundwater quality of Yishu River basin in 2016 and 2017 was evaluated by WQI with WHO (WHO 2008) standard as the limits. In addition, in order to further understand the spatial distribution of groundwater quality in the study area, the WQI spatial distribution map was obtained by the universal kriging method.

Results and discussion

Hydrochemical characteristics of groundwater

In order to understand the hydrochemical characteristics of groundwater in Yishu River basin, 90 groundwater samples were collected from 45 sites in 2016 and 2017, and the

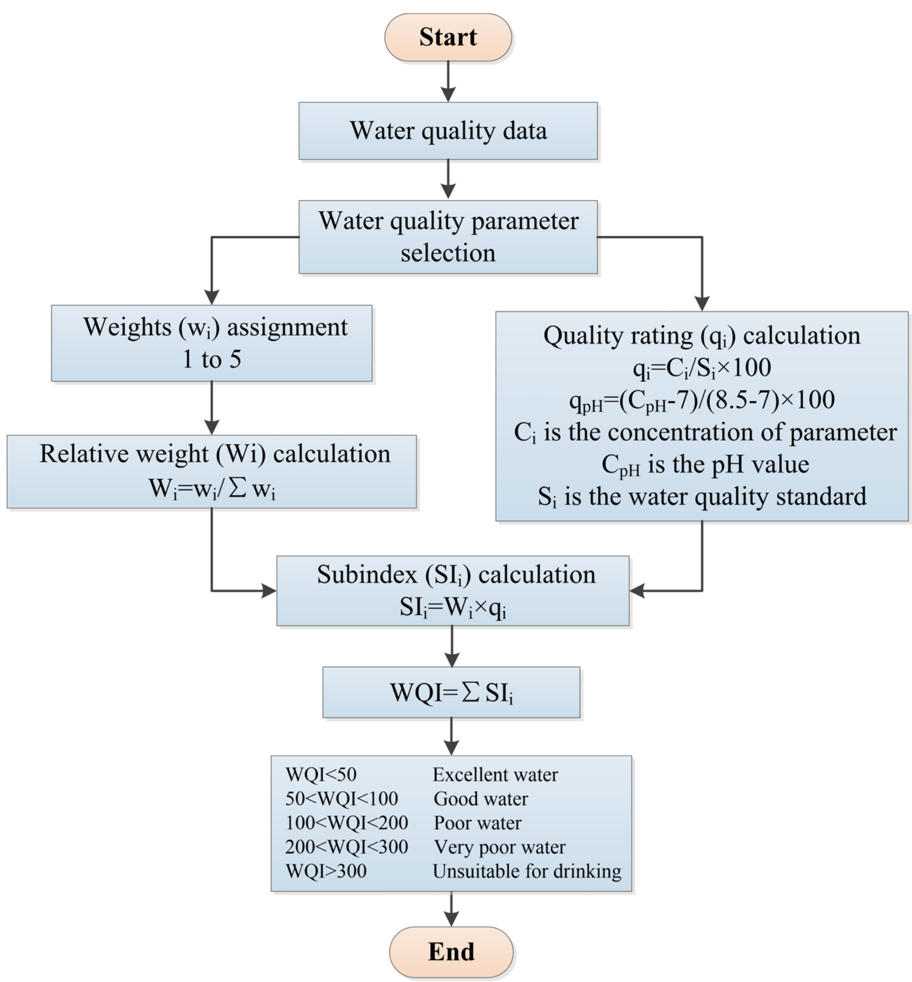

Fig. 2 Flow-process diagram of WQI calculation

descriptive statistical results are shown in Table 1, including Max(maximum), Min(minimum), Mean, SD(standard deviation) and CV(coefficient of variation). TDS and TH are two important parameters reflecting the quality of groundwater. In this study, the groundwater of Yishu River basin has a concentration of TDS ranging from 234.00 to 1311.00 mg/L in 2016 and 286.00 to 1144.00 mg/L in 2017, respectively. The concentration of TH is between 176.09 and 860.89 mg/L^{-1} in 2016 and from 176.49 mg L^{-1} to 845.70 mg L^{-1} in 2017. These results indicate that groundwater of the Yishu River basin can be classified as hard water (Fig. 3), although the mean concentrations of both TDS and TH were within the permissible limits of the WHO (2008) standards, indicating that groundwater in the study area can on the whole be classified as good. The pH values of groundwater samples were between 7.32–8.31 in 2016 and 7.05–8.25 in 2017, within the WHO drinking water standard of 6.5–8.5.

Ca^{2+} and Na^+ were found to be the dominant cations in groundwater of the Yishu River basin, with the order of the cationic content being $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ (Fig. 4). Concentrations of Ca^{2+} and Na^+ ranged from 37.61 to 313.43 mg L^{-1} and from 6.50 to 185.00 mg L^{-1} in 2016, respectively, with a means of 131.78 mg L^{-1} and 47.15 mg L^{-1}, respectively, whereas they ranged from 33.86 to 256.22 mg L^{-1} and from 4.47 to 104.88 mg L^{-1} in 2017, respectively, with means of 92.70 mg L^{-1} and 34.28 mg L^{-1}, respectively. The order of mean ion content of the groundwater samples was $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^- > F^-$ in 2016 and $HCO_3^- > Cl^- > NO_3^- > SO_4^{2-} > F^-$ in 2017. The concentrations of HCO_3^- in 2016 and 2017 varied from 94.48 to 434.60 mg L^{-1} and from 91.29 to 381.25 mg L^{-1}, respectively, with means of 276.85 mg L^{-1} and 257.78 mg L^{-1}, respectively. The concentrations of Cl^-, SO_4^{2-} and NO_3^- in 2016 ranged from 18.32 to 271.14 mg L^{-1}, 2.82 to

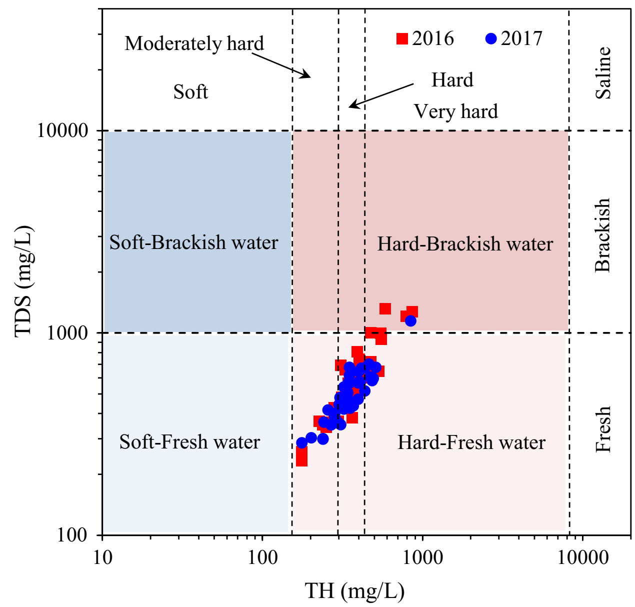

Fig. 3 Plot of total dissolved solids (TDS) versus total hardness (TH) for groundwater samples collected from the Yishu River basin in 2016 and 2017

Table 1 Statistical summary of hydrochemical variables within the groundwater samples collected from the Yishu River basin in 2016 and 2017

Parameters	2016					2017				
	Max	Min	Mean	SD	CV	Max	Min	Mean	SD	CV
pH	8.31	7.32	7.84	0.25	3.16	8.25	7.05	7.85	0.32	4.13
TH (mg/L)	860.89	176.09	398.62	133.16	33.41	845.70	176.49	354.83	106.90	30.13
TDS (mg/L)	1311.00	234.00	623.53	244.81	39.26	1144.00	286.00	497.13	151.34	30.44
Ca^{2+} (mg/L)	313.43	37.61	131.78	52.94	40.17	256.22	33.86	92.70	36.55	39.43
Mg^{2+} (mg/L)	56.08	0.60	17.06	11.75	68.86	87.52	4.47	30.26	14.52	47.97
K^+ (mg/L)	38.93	0.43	5.00	8.45	168.98	14.72	0.34	2.40	2.95	122.92
Na^+ (mg/L)	185.00	6.50	47.15	36.92	78.31	104.88	4.70	34.28	20.82	60.74
Cl^- (mg/L)	271.14	18.32	78.74	47.06	59.77	177.19	28.18	73.25	33.59	45.86
SO_4^{2-} (mg/L)	513.73	2.82	139.84	103.85	74.27	211.75	3.52	64.34	46.69	72.57
HCO_3^- (mg/L)	434.60	94.48	276.85	81.85	29.56	381.25	91.29	257.78	64.73	25.11
NO_3^- (mg/L)	221.16	3.27	62.82	50.81	80.87	372.09	2.63	70.46	60.99	86.56
F^- (mg/L)	1.80	0.02	0.28	0.31	111.35	2.04	0.01	0.27	0.36	132.12
COD (mg/L)	4.37	0.60	1.27	0.72	57.01	1.73	0.00	0.61	0.35	57.57
$SI_{Calcite}$	1.51	0.20	0.86	0.27	31.72	1.23	− 0.76	0.72	0.38	53.07
$SI_{Dolomite}$	2.71	− 0.32	1.06	0.65	61.33	2.21	− 1.43	1.29	0.78	60.48
$SI_{Fluorite}$	− 0.07	− 4.17	− 2.32	0.75	− 32.38	− 0.27	− 5.13	− 2.58	0.91	− 35.29
SI_{Gypsum}	− 0.56	− 3.13	− 1.48	0.45	− 30.38	− 1.10	− 3.00	− 1.94	0.44	− 22.77
SI_{Halite}	− 5.92	− 8.48	− 7.20	0.54	− 7.44	− 6.45	− 8.44	− 7.32	0.44	− 6.05

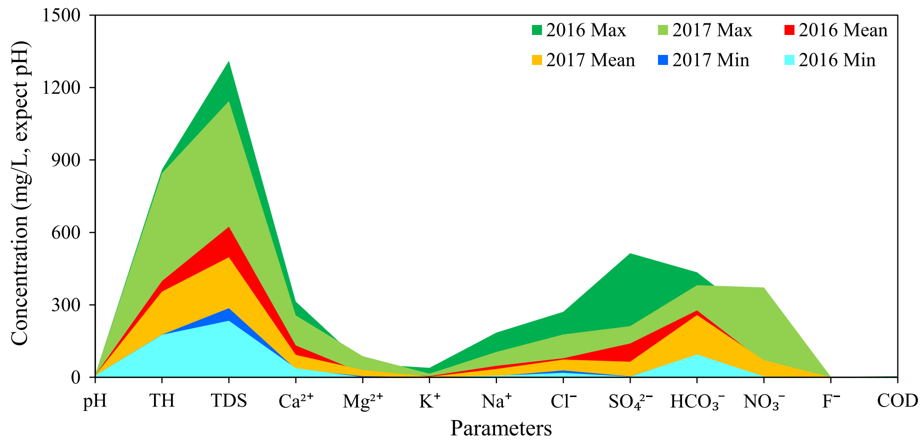

Fig. 4 Statistical summary of water quality variables of groundwater samples collected from the Yishu River basin in 2016 and 2017

513.73 mg L^{-1} and 3.27 to 221.16 mg L^{-1}, respectively, with means of 78.74 mg L^{-1}, 139.84 mg L^{-1} and 62.82 mg L^{-1}, respectively, whereas they ranged from 28.18 to 177.19 mg L^{-1}, 3.52 to 211.75 mg L^{-1} and 2.63 to 372.09 mg L^{-1} in 2017, respectively, with means of 73.25 mg L^{-1}, 64.34 mg L^{-1} and 70.46 mg L^{-1}, respectively. The highest Cl^-, SO_4^{2-} and NO_3^- concentrations in 2016 were observed at locations YS30 (271.14 mg L^{-1}), YS04 (513.73 mg L^{-1}) and YS09 (214.24 mg L^{-1}), whereas they were observed at positions YS06 (177.19 mg L^{-1}), YS13 (211.75 mg L^{-1}) and YS23 (205.42 mg L^{-1}) in 2017, respectively.

The analysis showed that the mean and maximum values of water quality variables were higher in 2016 compared to 2017 (Fig. 5). However, the maximum values of NO_3^- and F^- were higher in 2017, which may be related to sampling being conducted over October in 2016 and in May in 2017.

Hydrochemical type

The Piper diagram is an accessible and widely used technique for hydrochemical analysis (Liu et al. 2018) which can be used to demonstrate the general chemical characteristics

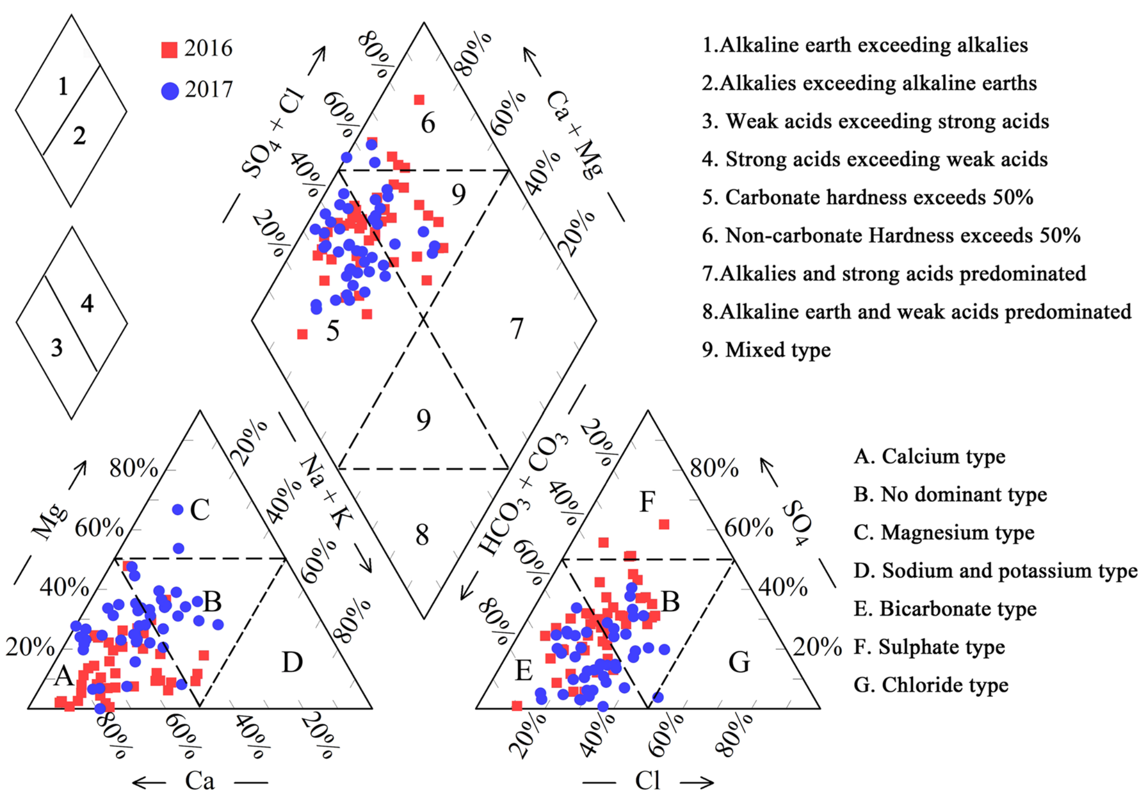

Fig. 5 Piper diagram for groundwater samples collected from the Yishu River basin in 2016 and 2017

of water samples and the relative contents of various ions. In addition, by combining Piper diagrams with geological and hydrogeological information for the study area, the evolution of the chemical composition of groundwater can be analyzed.

A Piper diagram was used to plot the 90 groundwater samples collected from the Yishu River basin (Fig. 5). As shown in the two triangles Fig. 5, most samples (75.6%) fell within the calcium type zone (zone A) whereas 57.8% fell in the bicarbonate type zone (zone E). The diamond shown in Piper diagram indicates that most of the groundwater samples can be categorized into the Ca–HCO_3 (64.4%) and mixed (26.7%) types. This may indicate that the dissolution of carbonate minerals, which can release large amounts of Ca^{2+} and HCO_3^-, is an important hydrogeochemical process occurring in groundwater of the study area.

Underlying mechanisms responsible for the hydrochemistry of the groundwater samples

Gibbs diagram

Although Gibbs model diagram (Gibbs 1970) does not reflect the influences of human activities on hydrochemical components, it is widely used within the analysis of natural processes driving hydrochemistry in water (Li et al. 2016). The Gibbs model map contains three regions representing the three important processes responsible for hydrochemistry of water, namely precipitation, evaporation and rock weathering. A Gibbs diagram was used to plot the 90 groundwater samples (Fig. 6). The analysis showed that rock weathering was the dominant process driving hydrochemistry of all water samples, which indicates that rock weathering is the dominant process controlling the hydrochemistry of groundwater of the Yishu River basin.

Ratio graphs of ions

Ion ratio analysis can be applied to further determine the types of rock involved within the rock weathering processes driving hydrochemistry of water (Yang et al. 2016; Thirumurugan et al. 2018; Gao et al. 2019; Liu et al. 2019b). The relationships between molar ratios of ions such as Ca^{2+}/Na^+, Mg^{2+}/Na^+, and HCO_3^-/Na^+ can be used to determine the effects of carbonate, silicate, or evaporite rocks on controlling the hydrochemical composition of water (Gaillardet et al. 1999; Qu et al. 2019).

The molar ratios of Ca^{2+}/Na^+, Mg^{2+}/Na^+, and HCO_3^-/Na^+ in the groundwater samples ranged between 0.52–12.67, 0.01–5.11 and 0.83–22.81, respectively. These results indicate that the weathering of silicates and carbonates dominated the hydrochemistry of the water samples, which indicates that the dissolution of silicate and carbonate minerals is the main driver of groundwater chemical composition in the Yishu Basin (Fig. 7).

The relationship between Na^+ and Cl^- shown in Fig. 8a indicates that the groundwater samples mainly fell to the left of the line of $Na^+/Cl^- = 1$, showing that Cl^- content of groundwater is higher than that of Na^+. This may be due to cation exchange (Li et al. 2015). In addition, the water samples located on the $Na^+/Cl^- = 1$ line indicate that they were derived from the dissolution of halite (Eq. 3). It can be seen in Fig. 8b that most of the water samples fell to the right of the $Ca^{2+}/SO_4^{2-} = 1$ line, indicating that the concentration of Ca^{2+} is significantly higher than that of SO_4^{2-} and that the dissolution of gypsum (Eq. 4) is not the main source of Ca^{2+}

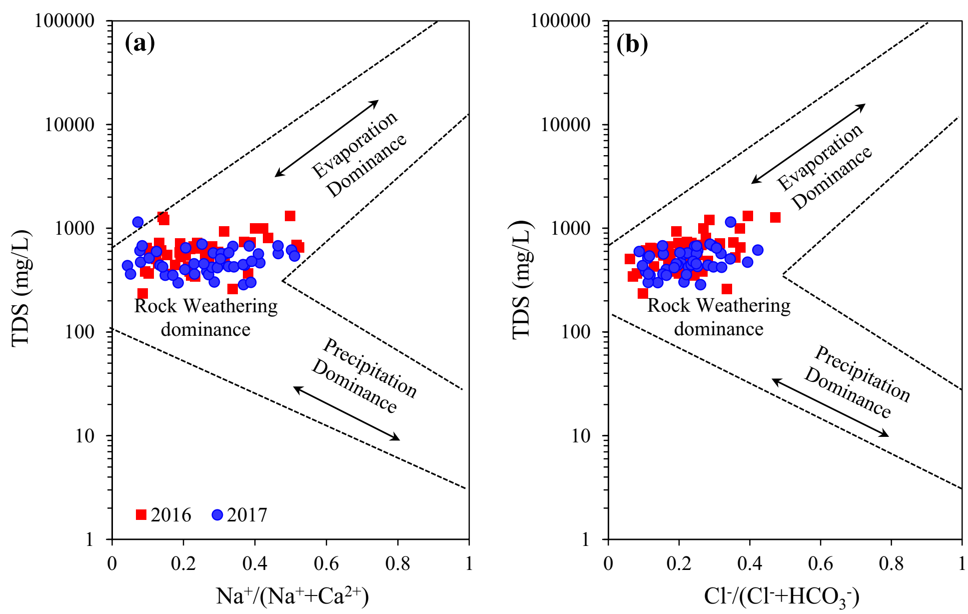

Fig. 6 Gibbs diagram for groundwater samples collected from the Yishu River basin in 2016 and 2017

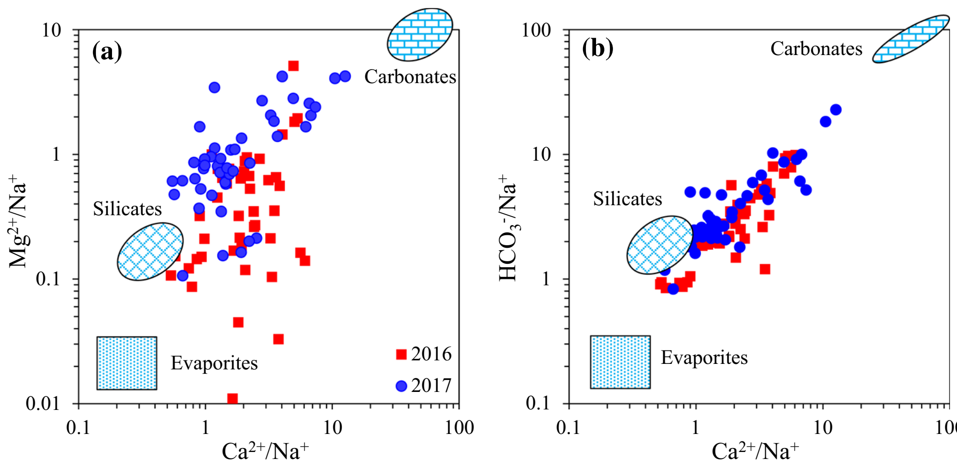

Fig. 7 An end-member diagram of ionic ratios for groundwater samples collected from the Yishu River basin in 2016 and 2017

and SO_4^{2-} in groundwater. The relationship between Ca^{2+}, $Ca^{2+}+Mg^{2+}$, and HCO_3^- can reflect the dissolution process of carbonate minerals such as calcite and dolomite (Eqs. 5, 6). It can be seen in Fig. 8c that most groundwater samples were located between the $Ca^{2+}/HCO_3^- = 1$ line and $Ca^{2+}/HCO_3^- = 0.5$ line and closer to the 1:2 line, whereas Fig. 8d shows that water samples were mainly distributed between the $Ca^{2+}+Mg^{2+}/HCO_3^- = 1$ line and the $Ca^{2+}+Mg^{2+}/HCO_3^- = 0.5$ line, indicating that groundwater contents of Ca^{2+}, Mg^{2+} and HCO_3^- are mainly derived from the dissolution of calcite, followed by dolomite. The relationship between ($Ca^{2+}+Mg^{2+}$) and ($HCO_3^- + SO_4^{2-}$) shows that most of the water samples were located near the 1:1 line and close to the right side (Fig. 8e), which indicates that the dissolution of silicate and carbonate minerals is an important factor affecting the hydrochemical composition of groundwater. In addition, the position of water sample points above the $(Ca^{2+}+Mg^{2+})/(HCO_3^- + SO_4^{2-}) = 1$ line indicates the presence of the cation exchange process (Eq. 7), whereas the water samples located below the 1:1 line represents the presence of the reverse cation exchange process (Eq. 8). The relationship between $Na^+ + K^+ - Cl^-$ and $SO_4^{2-} + HCO_3^- - Ca^{2+} - Mg^{2+}$ is usually used to identify cation exchange processes in groundwater (Yang et al. 2016). A value of $Na^+ + K^+ - Cl^-/SO_4^{2-} + HCO_3^- - Ca^{2+} + Mg^{2+} = 1$ indicates that cation exchange is the main mechanism driving the composition of hydrochemistry (Fig. 8f). In the present study, water sample points were distributed along the 1:1 line, indicating that cation exchange played an important role in determining the hydrochemistry of the samples.

$$NaCl \rightarrow Na^+ + Cl^- \tag{3}$$

$$CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \tag{4}$$

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \tag{5}$$

$$CaMg(CO_3)_2 + 2H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^- \tag{6}$$

$$2NaX + Ca^{2+} \rightarrow 2Na^+ + CaX_2 (\text{Ion exchange}) \tag{7}$$

$$CaX_2 + 2Na^+ \rightarrow Ca^{2+} + 2NaX\ (\text{Reverse Ion exchange}) \tag{8}$$

Saturation index

The saturation index (SI) is often used to reflect the dissolution and precipitation of related minerals in aqueous solutions (Wang et al. 2017; Liu et al. 2019b), with SI > 0, SI = 0 and SI < 0 representing states of supersaturated, equilibrium and unsaturated minerals, respectively. Table 1 and Fig. 9 show the calculated SI values.

The values of $SI_{Calcite}$ and $SI_{Dolomite}$ ranged from 0.20 to 1.51 and from − 0.32 to 2.71, respectively, with mean values of 0.86 and 1.06, respectively. In addition, SI values of most water samples (98%) were greater than 0, suggesting that the carbonate minerals in the groundwater samples tend to precipitate out of solution. $SI_{Fluorite}$, SI_{Gypsum}, and SI_{Halite} values of all groundwater samples were less than 0, varying from − 5.13 to − 0.07, − 3.13 to − 0.56 and − 8.48 to − 5.92, respectively, with mean values of − 2.45, − 1.71 and − 7.26, respectively. The calculated SI values for fluorite, gypsum and halite were all negative, indicating that these minerals were unsaturated.

Groundwater quality assessment

A comprehensive assessment of the quality of groundwater in the study area was conducted by incorporating 13 water

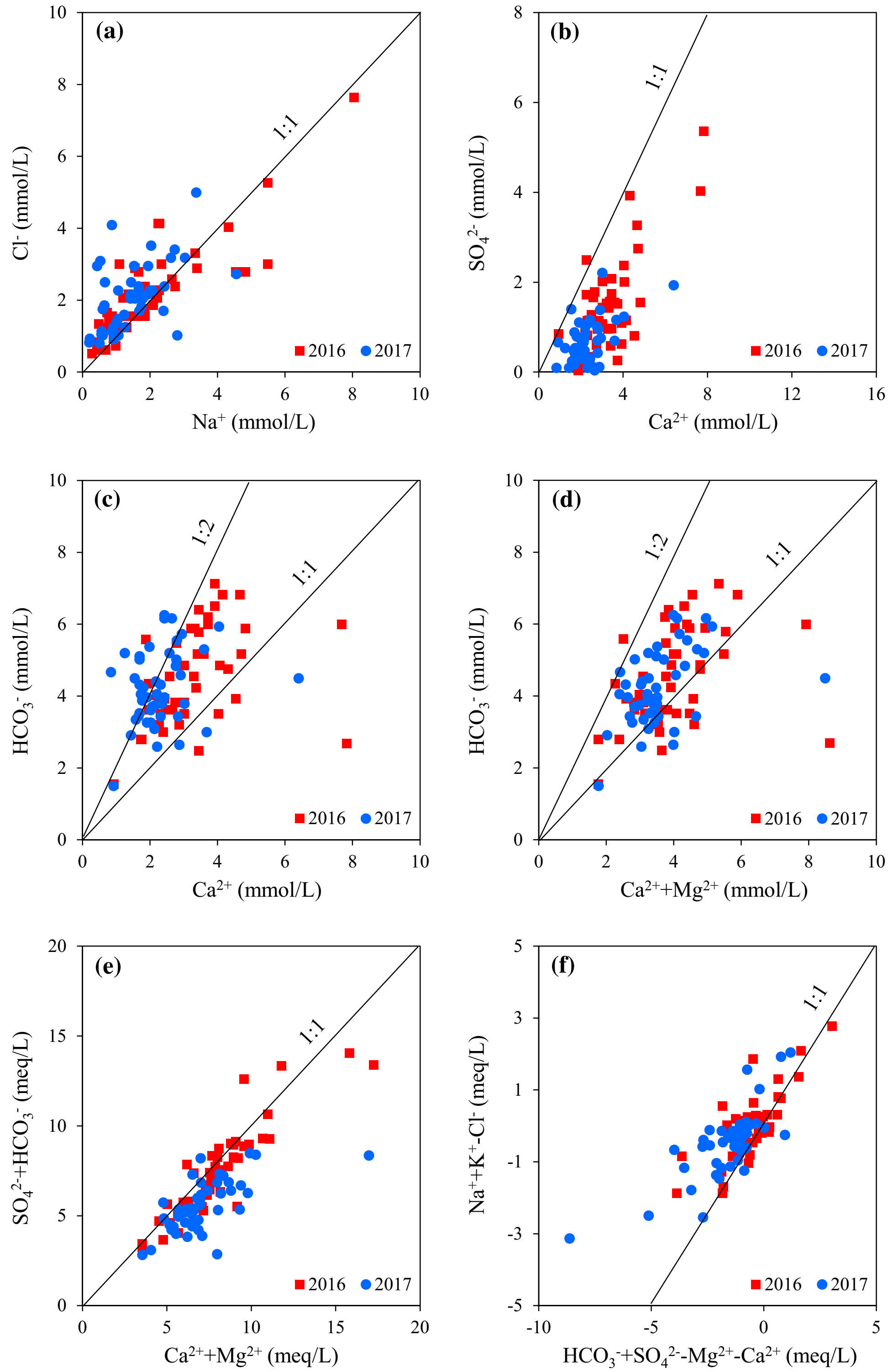

Fig. 8 Relationships between major ions of groundwater samples collected from the Yishu River basin in 2016 and 2017

quality variables within the WQI method (Ramos et al. 2016; Şener et al. 2017) (Fig. 2). Weightings are assigned to the various water quality variables incorporated into the WQI according to their relative importance in water quality assessment (Table 2). The highest weight (5) was assigned to NO_3^- and F^-, whereas the lowest weight (2) was assigned to Ca^{2+}, Mg^{2+}, HCO_3^- and K^+.

Table 3 shows the calculated WQI values for the 90 groundwater samples, whereas Fig. 10 shows the spatial distribution of WQI in 2016 and 2017. The computed WQI

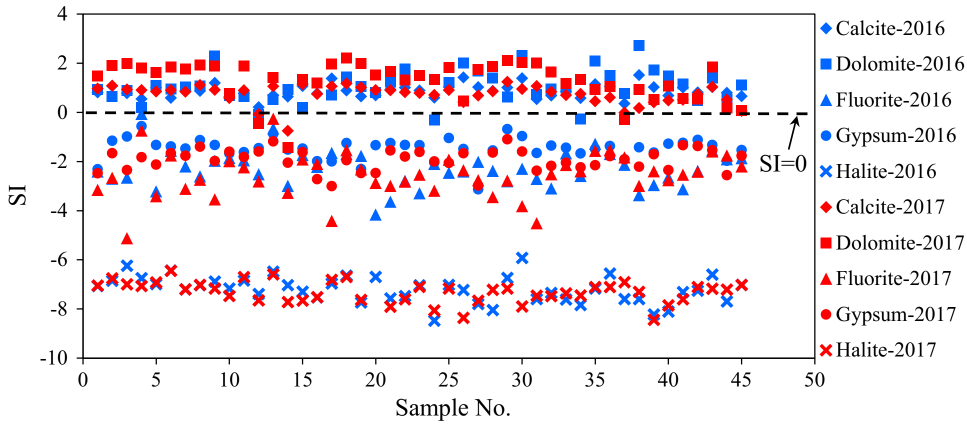

Fig. 9 Calculated SI values for calcite, dolomite, fluorite, gypsum and halite for groundwater samples collected from the Yishu River basin in 2016 and 2017

Table 2 Relative weights assigned to hydrochemical variables for the construction of the water quality index (WQI) for groundwater samples collected from the Yishu River basin in 2016 and 2017

Parameters	WHO standards (2008)	Weight (w_i)	Relative weight (W_i)
K^+ (mg/L)	12	2	0.0476
Na^+ (mg/L)	200	3	0.0714
Ca^{2+} (mg/L)	300	2	0.0476
HCO_3^- (mg/L)	–	2	0.0476
Mg^{2+} (mg/L)	30	2	0.0476
Cl^- (mg/L)	250	4	0.0952
SO_4^{2-} (mg/L)	250	4	0.0952
F^- (mg/L)	1.5	5	0.1190
NO_3^- (mg/L)	50	5	0.1190
TH (mg/L)	500	3	0.0714
COD (mg/L)	10	4	0.0952
TDS (mg/L)	1000	3	0.0714
pH	6.5–8.5	3	0.0714
		$\sum w_i = 42$	$\sum W_i = 1$

values for 2016 and 2017 ranged from 18.63 to 105.24 and from 25.53 to146.67, respectively, with means of 52.51 and 47.81, respectively. The results of the WQI assessment indicated that the groundwater quality of the Yishu River basin can be classed as “excellent” to “poor” for both 2016 and 2017. The highest WQI values obtained for 2016 and 2017 were for location YS09 () and YS29 (), respectively. Among the water quality samples, 57.8% and 69.9% fell within the "excellent" category in 2016 and 2017, respectively, whereas 40.0% and 28.9% fell within the "good" water quality category, respectively. The results showed that in general, the groundwater quality of the Yishu River basin over 2016 and 2017 was excellent and suitable for domestic use. The WQI spatial distribution map shows that groundwater samples of "poor" water quality occurred in Yinan County (YS09) in the upper reaches of Yishu River basin in 2016, whereas they appeared in the southwest of Yinan County (YS29) in 2017. YS09 in 2016 and YS29 in 2017 had higher NO_3^- concentrations of 221.16 mg L^{-1} and 372.09 mg L^{-1}, respectively. It is speculated that the poor water quality at these two locations may be related to the discharge of domestic sewage and the use of agricultural fertilizers.

Figure 10 shows a clear difference in the spatial distributions of the WQI for 2016 and 2017, indicating temporal variability of the groundwater quality in the study area. In addition, Table 1 shows that the concentrations of the water quality variables within groundwater were higher in 2016 than in 2017. This result may be due to samples being collected over different months between the two sampling years, with samples collected during October in 2016, which falls in the rainy season, and during May in 2017, which falls in the dry season. Since precipitation is the main source of groundwater recharge in the study area, surface pollutants may infiltrate the groundwater as precipitation during the wet season. Therefore, it can be expected that the levels of water quality variables will be higher in the rainy season compared with the dry season.

Groundwater is the main source of water for human development in the Yishu River basin. The acceleration of urbanization in recent decades has resulted in a significant increase in the impact of human activities on the groundwater environment. Therefore, the spatial and temporal resolutions of groundwater monitoring should be increased to facilitate the sustainable development of groundwater resources.

Conclusions

Hydrochemical data collected through the analysis of 90 groundwater samples taken from the Yishu River basin in 2016 and 2017 allowed the hydrochemical characterization of groundwater in the region through traditional hydrochemical analysis methods. In addition, the WQI was used to assess the water quality of groundwater in the region. The

Table 3 Water quality index (WQI) values and water types of groundwater samples collected from the Yishu River basin in 2016 and 2017

Sample No	2016		2017		Sample no	2016		2017	
	WQI	Water type	WQI	Water type		WQI	Water type	WQI	Water type
YS01	30.89	Excellent	35.25	Excellent	YS24	18.63	Excellent	35.90	Excellent
YS02	39.93	Excellent	52.60	Good	YS25	47.30	Excellent	41.73	Excellent
YS03	64.43	Good	43.41	Excellent	YS26	68.11	Good	31.82	Excellent
YS04	99.27	Good	71.32	Good	YS27	23.95	Excellent	25.53	Excellent
YS05	38.14	Excellent	38.48	Excellent	YS28	39.80	Excellent	49.15	Excellent
YS06	54.94	Good	52.74	Good	YS29	83.70	Good	146.66	Poor
YS07	38.19	Excellent	38.88	Excellent	YS30	99.61	Good	51.91	Good
YS08	53.93	Good	48.11	Excellent	YS31	36.66	Excellent	30.65	Excellent
YS09	105.24	Poor	40.98	Excellent	YS32	39.73	Excellent	53.90	Good
YS10	39.26	Excellent	43.93	Excellent	YS33	41.57	Excellent	36.65	Excellent
YS11	49.27	Excellent	47.23	Excellent	YS34	23.98	Excellent	49.58	Excellent
YS12	57.54	Good	46.79	Excellent	YS35	67.39	Good	51.51	Good
YS13	78.59	Good	65.18	Good	YS36	62.32	Good	40.95	Excellent
YS14	39.07	Excellent	30.23	Excellent	YS37	28.89	Excellent	34.05	Excellent
YS15	85.52	Good	26.61	Excellent	YS38	45.23	Excellent	67.12	Good
YS16	35.83	Excellent	31.91	Excellent	YS39	31.69	Excellent	28.95	Excellent
YS17	40.64	Excellent	40.39	Excellent	YS40	61.40	Good	44.98	Excellent
YS18	68.54	Good	66.38	Good	YS 41	37.84	Excellent	54.66	Good
YS19	56.40	Good	35.22	Excellent	YS42	37.07	Excellent	68.89	Good
YS20	59.44	Good	61.53	Good	YS43	94.11	Good water	36.10	Excellent
YS21	35.52	Excellent	46.92	Excellent	YS44	29.24	Excellent	36.93	Excellent
YS22	68.04	Good	37.33	Excellent	YS45	51.01	Excellent	44.73	Excellent
YS23	55.18	Excellent	87.73	Good					

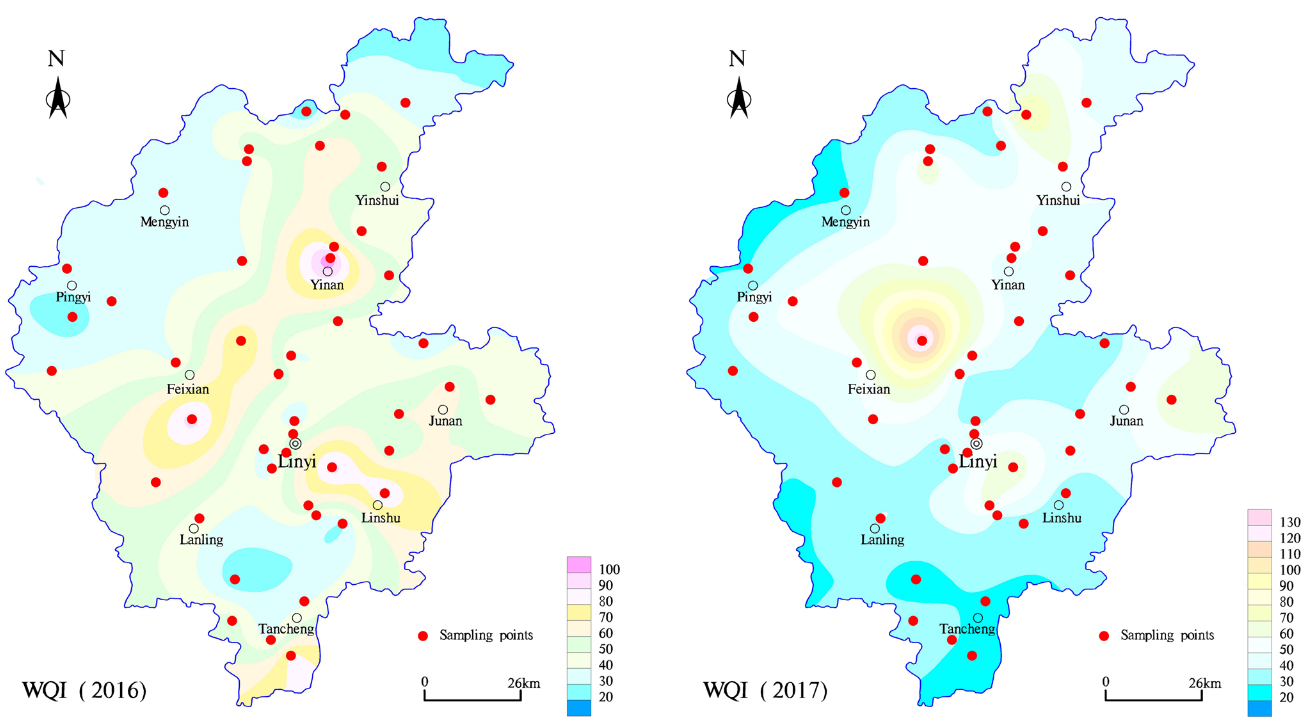

Fig. 10 Map showing the distribution of water quality index (WQI) values for groundwater samples collected from the Yishu River basin in 2016 and 2017

following main conclusions can be drawn from the present study:

1. The mean concentrations of TDS and TH in the groundwater of the Yishu River basin are less than 1000 mg L^{-1} and 500 mg L^{-1} respectively, whereas pH falls between 7.05 and 8.31. These results indicate that the groundwater can be classified as weak alkaline hard water. Overall, the mean concentrations of major water quality variables were higher in 2016 than in 2017.
2. The main processes driving the hydrochemistry of groundwater in the study region are the dissolution of silicate and carbonate minerals and cation exchange, which results in the dominance of HCO_3^- and Ca^{2+} within groundwater of the Yishu River basin. The dominant hydrochemical types of the samples were found to be the Ca–HCO_3 and mixed types. The calculated SI values showed that carbonate minerals in groundwater were saturated (SI > 0) whereas gypsum, fluorite and salt rock were unsaturated (SI < 0).
3. The calculated WQI values for most water samples were less than 100, which indicates that the groundwater quality of the Yishu River basin can generally be categorized as "good". Only one water sample from each year, 2016 and 2017, was shown to have poor water quality, possibly due to domestic sewage discharge and agricultural activities. Increased spatial and temporal scales of groundwater monitoring are needed for the sustainable development of groundwater resources under increased pressure by accelerating urbanization and increasing population.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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